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27th International Chugaev Conference on Coordination Chemistry

and

4th Young Conference School “Physicochemical Methods in the Chemistry of Coordination Compounds”

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The Conference celebrates the 80th birthday
of Academician Gleb A. Abakumov

BOOK OF ABSTRACTS

Nizhny Novgorod

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Сборник содержит материалы пленарных, секционных и стендовых докладов, представленных на **XXVII Международной Чугаевской конференции по координационной химии** и **IV Молодежной школе-конференции «Физико-химические методы в химии координационных соединений»** (2–6 октября 2017 года, Нижний Новгород).

Professor Lev Alexandrovich Chugaev

(1873-1922)

XXVII Международная Чугаевская конференция по координационной химии приурочена к 80-летию академика Глеба Арсентьевича Абакумова

Всемирно известный ученый и организатор науки

Блестящий ученый, умелый администратор, действительный член Российской академии наук, профессор, доктор химических наук, лауреат государственной премии СССР, научный руководитель Института металлоорганической химии им. Г.А. Разуваева Российской академии наук, профессор Нижегородского государственного университета им. Н.И. Лобачевского Глеб Арсентьевич Абакумов встречает свой 80-летний юбилей в полном расцвете творческих сил, успешно развивая, углубляя и открывая новые направления в области химии свободных радикалов и металлоорганических соедениней.

Более чем за полвека он прошел яркий путь от младшего научного сотрудника до директора института, а затем научного руководителя, воспитав и собрав за это время вокруг себя неординарных и талантливых исследователей, составляющих в настоящее время его научную школу.

Под руководством Г.А. Абакумова получены результаты мирового уровня: обнаружен факт образования комплексов стабильных нитроксильных радикалов с галогенидами металлов III группы; открыты реакции окислительного расщепления арилзамещенных N-окситриазенов с синхронной генерацией «in situ» свободных арильных радикалов и нитрозосоединений, на основе которых была создана модификация метода «спиновых ловушек» для изучения короткоживущих свободных радикалов в растворах методом ЭПР; открыты реакции пространственно-затрудненных о-хинонов с льюисовыми кислотами – галогенидами металлов III группы, приводящие к металлокомплексам стабильных анион-радикалов о-семихинонов.

В 1981 году Г.А. Абакумовым с соавторами был открыт уникальный фото-(термо)механический эффект, проявляющийся в том, что тонкие игольчатые кристаллы о-семихинонового родий-дикарбонильного комплекса обратимо меняли свою форму (изгибались) под действием светового излучения видимого и инфракрасного диапазонов. Суть этого явления связана с обратимым переносом электрона с металла на лиганд под действием внешнего возбуждения.

Другим значительным достижением является создание и развитие концепции «спиновых меток» путем использование «спинмеченных» лигандов для изучения строения и свойств комплексов металлов с диамагнитными ионами.

К настоящему времени получены очень важные результаты в области химии непереходных металлов. На примере комплексов сурьмы, алюминия и галлия с редокс-активными катехолатными, амидофенолятными и диамидными лигандами впервые было показано, что непереходные элементы в сочетании с редокс-активными лигандами проявляют свойства, считавшиеся ранее характерными только для переходных элементов: обратимое присоединение и активация малых молекул и непредельных соединений.

Наряду с фундаментальными исследованиями, школа академика Г.А. Абакумова отличается прикладным аспектом своей деятельности. Наиболее значительным результатом, полученным в последнее время, является синтез пористых инновационных полимерных материалов, которые находят применение в медицине, в частности, для создания искусственных протезов.

Другой чрезвычайно важной сферой деятельности академика Г.А. Абакумова являлось руководство Институтом металлоорганической химии им. Г.А. Разуваева Российской академии наук. Получив в 1988 году «благословение» своего учителя академика Григория Алексеевича Разуваева, Глеб Арсентьевич 27 лет был бессменно директором ИМХ РАН. Пережив тяжелейшие девяностые годы, коллектив института под руководством Г.А. Абакумова устоял, продолжил свое развитие, обогатив отечественную и мировую науку уникальными результатами. Продуманная кадровая политика позволила значительно омолодить кадровый состав научного подразделения. В настоящее время 80% научных сотрудников института находятся в возрасте до 39 лет. Показателем успешной работы института является избрание трех сотрудников ИМХ РАН членами-корреспондентами Российской академии наук; три сотрудника стали стипендиатами международного фонда Александра фон Гумбольдта (Германия); к настоящему времени получено 10 грантов Российского научного фонда, 35 грантов Российского фонда фундаментальных исследований. ИМХ РАН регулярно проводит на высоком научном уровне международные конференции на теплоходе, пользующиеся большой популярностью и известностью в России и зарубежом.

Г.А. Абакумов автор более 700 научных работ, большинство из которых опубликованы в высокорейтинговых журналах.

Свое восьмидесятилетие Г.А. Абакумов встречает с большими научными достижениями в окружении многочисленных учеников. При этом сочетание опыта и традиций старшего поколения с энтузиазмом и энергией научной молодежи служат надежным залогом будущего развития научной школы академика Г.А. Абакумова.

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Plenary lectures

NOVEL COPPER(I) AND GOLD(I) COMPLEXES OF 1,5-DIAZA-3,7-DIPHOSPHACYCLOOCTANES WITH “SNIMULI-RESPONSIVE LUMINESCENCE.

A. A. Karasik, I. D. Strelnik, E. I. Musina, O. G. Sinyashin

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The rich photophysical and coordination properties of the gold(I) and copper(I) compounds, caused from the metalophilic interactions, made a strong impact to the complexes design. In this regard, the copper and gold complexes construction becomes a promising area in the aim of the search of the “stimuli-responsive” or OLED materials. Within last few decades a chemistry of heterocyclic aminomethylphoshines containing two or four phosphorus atoms incorporated into the cyclic skeleton has been developed in our research group. Recently we synthesised gold(I) and copper(I) complexes based on the diazadiphosphacyclooctanes, containing pyridyl moieties at the phosphorus atoms. A strong “stimuli-responsive” luminescence of the gold(I) complexes, resulted from the conformational changes in the aminomethylphosphine cycle, was found.

Diazadiphosphacyclooctanes are classified as a P,P-chelate ligands. Despite of this, unpredicted formation of the P,P-bridge coordination mode of the diazadiphosphacyclooctane moiety towards copper(I) iodide was discovered. We obtained the original copper-iodide core, which was unknown earlier. We found promising intensive blue, green and white luminescence of the di- and hexanuclear copper(I) complexes. [1,2,3,4]

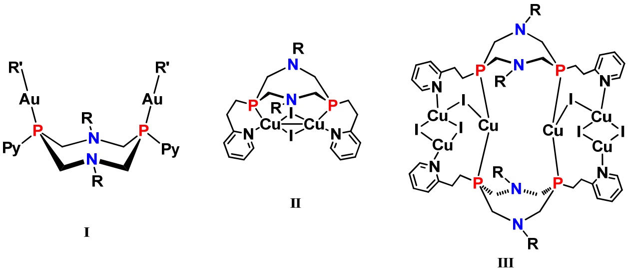

Figure 1 *Structure of di- and hexanuclear gold(I) and copper(I) complexes*

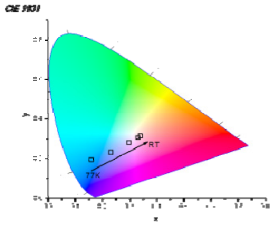

Figure 2 *CIE diagram of hexanuclear copper(I) iodide complex*

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THE STRUCTURE AND CHEMICAL THERMODYNAMICS OF URANIUM AND THORIUM COORDINATION COMPOUNDS

A.V. Knyazev, N.G. Chernorukov, N.N. Smirnova, M.E. Komshina,
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In the near future uranium and thorium will keep the importance as nuclear fuel for atomic power engineering. The modern science has a specific range of unsolved problems at various stages of a nuclear power complex from the extraction of uranium and thorium mineral from raw material to the processing of spent nuclear fuel. The synthesis of the coordination compounds was carried out by three various methods: (1) solid state reactions and reactions in melt; (2) reactions under hydrothermal conditions; and (3) precipitation reactions from solutions. The techniques, developed by us, allowed obtaining in total of more than 300 compounds and more than half of them were prepared and identified for the first time. Realized crystal chemistry systematization of studied compounds allows concluding that the element with the highest oxidation number (in our case uranium and thorium) determines the forming structure, as usual for majority others complex compounds. We could sort all the compounds into three types according to structural features, that is, compounds with frame; layer and isle structures. The temperature dependences of heat capacities at constant pressure for about 50 compounds in a temperature interval from 7 to 350 K were studied in an adiabatic vacuum calorimeter. The obtained data allowed describing possible phase transitions and calculating absolute entropies of formation of the compounds. It is significant to note that heat capacities at constant pressure of the majority uranyl compounds monotonously grow with rising temperature without any visible anomalies. On the contrary, the physical transitions are observed in uranylvanadous acid, uranylcarbonates and uranylsulfates. The description of transitions was made by means of McCallaf–Vestrum classification of physical transitions. The most widespread type of transitions in the given layered compounds is isothermal (I) transitions connected with polymorphic transitions in the crystal. The polymorphism is caused by possible shifts or rotations of layers relatively to each other in the crystalline structure. Isothermal transitions are seen as "peaks" on the curve of heat capacity; the area of "peaks" is numerically equal to the enthalpy of phase transition. The physical transitions, which are more rarely met with, are H-transitions and they are observed as "humps" on the curve of heat capacity. According to physical point of view the given anomaly may be connected with "defreezing" of rotations around metal – water bond in structures of the appropriate crystallohydrates. The sole compound which shows the third kind of physical transitions, i.e., G-type (glass-like) one, is tetrasodium uranyltricarbonate. The nature of this anomaly is, probably, related to the presence of cation–cation interactions in the structure of this compound that is confirmed by us using Voronoi–Dirihle calculations of polyhedra with program complex TOPOS.

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COMPLEX BISMUTH IODIDES AND POLYIODIDES: FROM STRUCTURAL DIVERSITY TO LIGHT-HARVESTING MATERIALS FOR PHOTOVOLTAICS

A. V. Shevelkov[a]

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Recent discovery [1] of prominent photovoltaic properties of inorganic and hybrid iodoplumbates with the perovskite crystals structure has led to major progress in the field of light-harvesting materials for solar cells and caused a transition from the classical Grätzel solar cells to so-called all-solid or perovskite ones. Various iodoplumbates have already displayed an appreciable level of photovoltaic efficiency exceeding 20% [2] responding to the improved methods of preparation as well as compositional optimization and doping. However, these wonderful compounds contain toxic lead, which is readily bio-available owing to the instant solubility of compounds in water [3], thus hindering their widespread uses as light-harvesting materials. In response to this issue, other iodometallates have become increasingly attractive, in particular, those of bismuth.

In this paper, we present and discuss our recent discoveries in the field of chemistry of iodobismuthates. We consider complex bismuth iodides and polyiodides formed with different cations ranging from those of alkali-metals to singly or doubly charged organic ammonium cations. The following structural issues will be considered: (i) dimensionality of iodobismuthate substructures, (ii) their assembling through hydrogen bonds into 3D frameworks, and (iii) introduction of polyiodide moieties and their diverse role in structure formation. Discussed will be details of their electronic structures; in particular, we will show that the structure near the Fermi level and hence optical absorption properties are insensitive to the nature of a cation, and the optical absorption is primarily associated with the charge transfer from the I 5p orbitals at the top of the valence band to the Bi 6p orbitals at the bottom of the conduction band. The electronic structure will be discussed along with the experimental data on optical absorption. We will to show that structural features of compounds in question govern the band width that ranges from 1.2 to 1.9 eV. Finally, we will provide insights on the potential of complex bismuth iodides and polyiodides as light-harvesting materials.

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HOMO– AND HETEROMETALLIC CARBOXYLATE CADMIUM COMPLEXES

A.A. Sidorov, N.V. Gogoleva, M.A. Shmelev, I.L. Eremenko

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The purpose of the investigation that we began was to complete the chemical knowledge of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} carboxylate complexes with the information of the chemistry of Cd^{II} compounds. This work is the consistent continuation of our previous studies of the chemistry of homo- and heterometallic Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} complexes. The chemistry of cadmium and listed 3d-metals carboxylate complexes has many common features. The data, received through synthesis and investigation of properties of cadmium carboxylates, will be useful for setting new tasks, connected with the chemistry of 3d-metals carboxylate compounds.

The appreciable inactivity of cadmium complexes allowed us to obtain a row of stable intermediate compounds, which were not traced in similar reactions of 3d-metals complexes. The stability of cadmium complexes to hydrolysis permitted us to distinguish a variety of unusual products from aqueous solutions. The synthesis and the study of the reaction output of cadmium carboxylates with ligands having bulky substituents provided us additional information about sterically hindered carboxylates. These results proved to be useful for the structural analysis of 3d-metals complexes that were obtained earlier.

We are solving problems of choosing anions of monocarboxylic acids to receive more full information about the chemistry of cadmium carboxylates. A big attention is given to features of the structure of cadmium carboxylate complexes, which are connected with the bigger than six coordination number of the cadmium ion. We found conditions of additional coordination of ligands on stable heterometallic fragments also typical for 3d-elements. This showed us new opportunities of using cadmium compounds in solving different practical problems. Heterometallic complexes where cadmium atoms combine with alkaline, alkaline-earth and rare-earth elements are most important objects of out investigations so far as forming stable metal fragments can persist in many reactions of ligands substitution and may be used for the synthesis of new wireframe coordination polymers.

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COMPLEXES OF „SUPERPODAL“ LIGANDS – REACTIVITY AND FUNCTION

Andreas Grohmann

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We have been exploring claw-like pentadentate ligands (“superpodal” ligands), and how their transition metal complexes can bring about unusual small-molecule reactivity. The talk concentrates on iron and copper, and ligands with donor sets N5, NP4 and NN2O2. A nitrite reductase model and oxoferryl complexes of tuned coordinative strain will be discussed, as will be a set of copper complexes that put a new, process-engineering spin on catechol oxidase modelling. The talk will conclude on a materials chemistry note: Can the bulk spin-crossover behaviour displayed by certain iron(II) complexes be conserved – and possibly harnessed – in ordered arrays on surfaces?

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REDOX ACTIVITY OF CARBENE LIGANDS; CONVERGENT AND DIVERGENT RADICAL-TYPE PATHWAYS OF 'CARBENE RADICALS'

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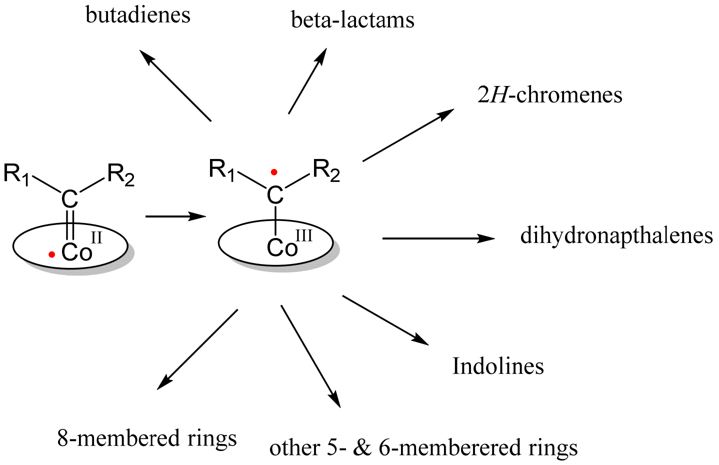
Radicals are intrinsically reactive, and were long believed to be "too reactive to be selective". However, in the coordination sphere of transition metals highly selective radical-type processes are certainly possible. In fact, radical-type reactions are tremendously important in several bio-synthetic pathways mediated by metallo-enzymes. Nature solves its most difficult and most interesting bio-synthetic problems with radical-reactivity. Yet, despite their radical-nature, these reactions proceed with ultrahigh precision and selectivity.

Inspired by such intriguing catalytic radical-type transformations mediated by metallo-enzymes, we are investigating new catalytic radical-type transformations mediated by synthetic (open-shell) organometallic catalysts.[1]



This presentation is focussed on the diverse radical-type reactivity of cobalt-carbene (and nitrene) complexes, in which the transient reactive moieties act as redox active ligands producing discrete carbene (and nitrene) radicals.[2] Such species provide unique opportunities in developing new catalytic ring-closure protocols.[3] Here we report on their diverse radical-type pathways, revealing both convergent pathways and unique divergent routes to a variety of desirable organic ring products.

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NEW LANTHANIDE (II) AND (III) COMPLEXES. SYNTHESIS, STRUCTURE, SELECTIVE C-H BOND ACTIVATION AND CATALYTIX APPLICATIONS

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Lanthanide alkyl complexes deserve particular interest as highly active species that exhibit unique reactivity and ability to promote activation and derivatization of unsaturated and saturated hydrocarbons.

New families of thermally stable homoleptic Ln(II) and Ln(III) alkyl complexes containing bulky and polyidentate ligands were synthesized and characterized. The synthesis, structures and reactivity of new heteroleptic Ln(II) and Ln(III) alkyl species supported by various ligands will be considered as well.

New alkyl complexes proved to be highly efficient and selective catalysts for intermolecular olefin hydrophosphination, hydrothiolation, hydrobenzylation and hydroarylation reactions.

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SYNTHESIS AND REACTIONS OF $[B(CN)_3]^{2-}$, CONTAINING NUCLEOPHILIC BORON ATOM.

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Boron compounds have been traditionally regarded as ‘‘Lewis acids’’ preferring to accept electrons rather than donate them [1]. Species containing nucleophilic boron are well investigated for boron in metal borides (e.g., MgB_2) [2] and clusters (e.g., $[B_{11}H_{13}]^{2-}$) [3], but in the remaining boron chemistry they are unusual [1, 4-6].

In 2011, we have reported the synthesis, structural and spectroscopic properties of the new species with nucleophilic boron, $[B(CN)_3]^{2-}$, starting from $[B(CN)_4]^-$ [7, 8]. The starting compound, $[B(CN)_4]^-$ [9-11], is of great importance for the synthesis of the ionic liquids [11]. Tetracyanoborate serves also as a starting compound for the synthesis of $[B(CF_3)_4]^-$ [12], $[B(CNMe)_4]^{3+}$ [13], $[B(CO_2H)_4]^-$ [13], $[B_2(CN)_6]^{2-}$ [14] and other compounds.

The syntheses of compounds with $[B(CN)_3]^{2-}$ were carried out by reacting $M[B(CN)_4]$ either with M (M = Li, Na, K) in liquid ammonia at -30/-40 °C or with BuLi in THF at room temperature [7]. $M_2[B(CN)_3]$, (M = Na, K) and $Li_2[B(CN)_3]\cdot THF$ are yellow solids. They readily react with water or another proton-donors to salts containing the $[BH(CN)_3]^-$ anion [8]. $K_2[B(CN)_3]$ is thermally stable up to 230 °C, whereas $Li_2[B(CN)_3]*THF$ decompose at 120 °C to $Li_2[B(CN)_3(CH_2)_4O]$. $Na_2[B(CN)_3]$ react slowly with NH_3 at 0 to 10 °C to $Na_2[BH(CN)_2\{C(NH)_2\}]$ [7, 8]. The reaction of $M_2[B(CN)_3]$ (M = Li, K) with $HgCl_2$ in THF suspension yield a mixture of different compounds, of which the $[Hg(B(CN)_3)_2]^{2-}$ dianion is the main product [15].

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MOLECULAR BORROMEAN RINGS BASED ON HALF-SANDWICH METAL FRAGMENTS

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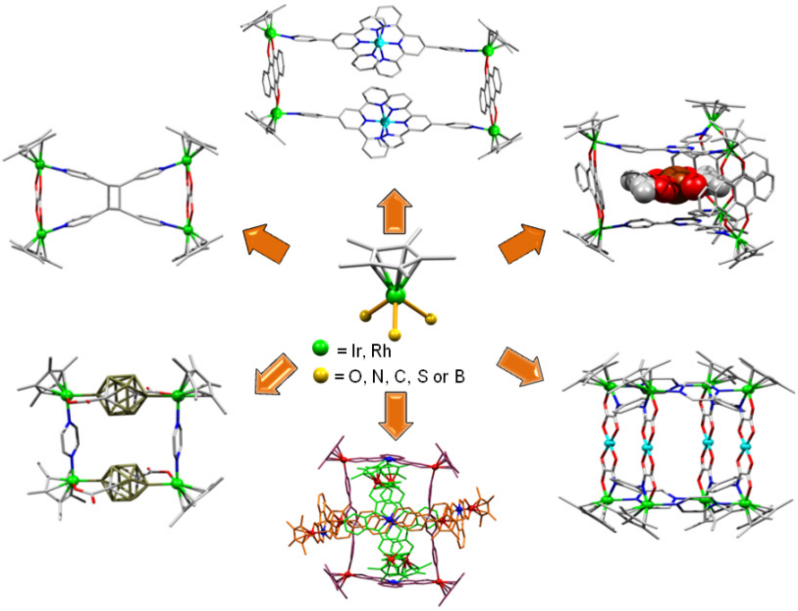
The construction of new inorganic and organometallic macrocycles and cages with interesting structural features and technologically useful functions have been topics of intense study with considerable potential.[1] One of the chief motivating factors to growth in this field is the development of new, functional and tunable donor building blocks that can bridge transition metals. Ideal building blocks should be easily accessible, exhibit high affinities toward transition metals, and possess facial coordination sites can undergo exchange reactions with various ligands. Half-sandwich transition metal complexes (Cp*M, Cp* = η^5-C_5Me_5) are useful model compounds in which one hemisphere of the coordination shell is blocked by the voluminous Cp* rings. In the protected space below the Cp* ligands, various bidentate or tridentate ligands can be accommodated.



Motivated by interest in supramolecular chemistry with organometallic half-sandwich complexes, we have initiated a new approach for preparing organometallic macrocycles via C-H and B-H activations with Terephthalate and dicarboxylate carborane.[2] We report herein an efficient method for synthesizing molecular macrocycles of half-sandwich iridium and rhodium complexes via C-H and B-H activation directed muticomponent self-assembly under mild condition. [3]

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AMINATION AND SMALL MOLECULE ACTIVATION

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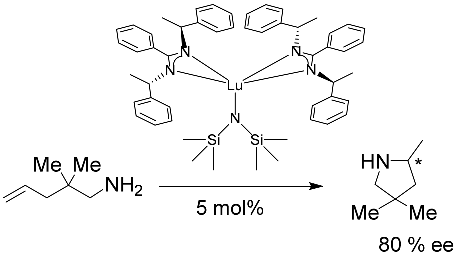
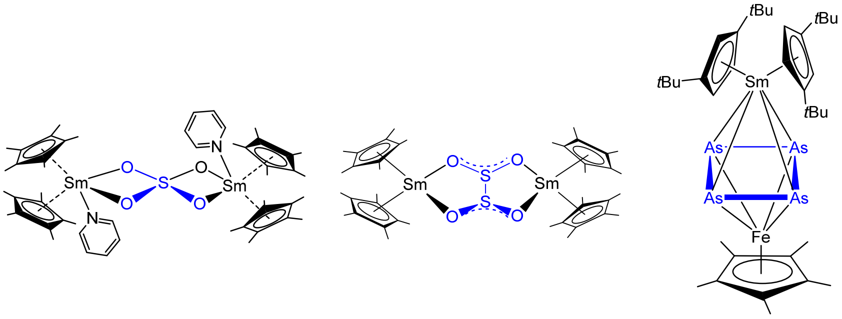
Two new approaches to catalytic amine synthesis will be discussed in the first part. Platinum(II)-crosslinked single-chain nanoparticles, which were obtained by adding [Pt(1,5-cyclooctadiene)Cl_2] to polymers featuring triarylphosphine ligand moieties, were used as recyclable homogeneous catalysts for the amination of allyl alcohols.[1] Then, the synthesis of the first enantiomerically pure amidinate rare earth metal complexes is shown. Some of these compounds are suitable catalysts for the asymmetric intramolecular hydroamination. Good activity and enantiomeric excess values have been observed (Scheme 1).[2]



Scheme 1. Enantioselective hydroamination catalyzed by amidinate rare earth metal complexes

In the second part of the lecture, reaction of white phosphorous,[3] sulfur dioxide,[4] and other small molecules[5] with di- and trivalent lanthanide complexes will be discussed. Neither a discrete molecular SO_2 complex nor a polyphosphide of the *f*-block elements was known before we started our investigations.



Scheme 2. Examples of products resulting from the reaction of samarocene with small molecules.

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METAL COMPLEXES WITH DUAL PHYSIOLOGICAL MODE OF ACTION – CANDIDATES FOR SELECTIVE ANTICANCER AGENTS

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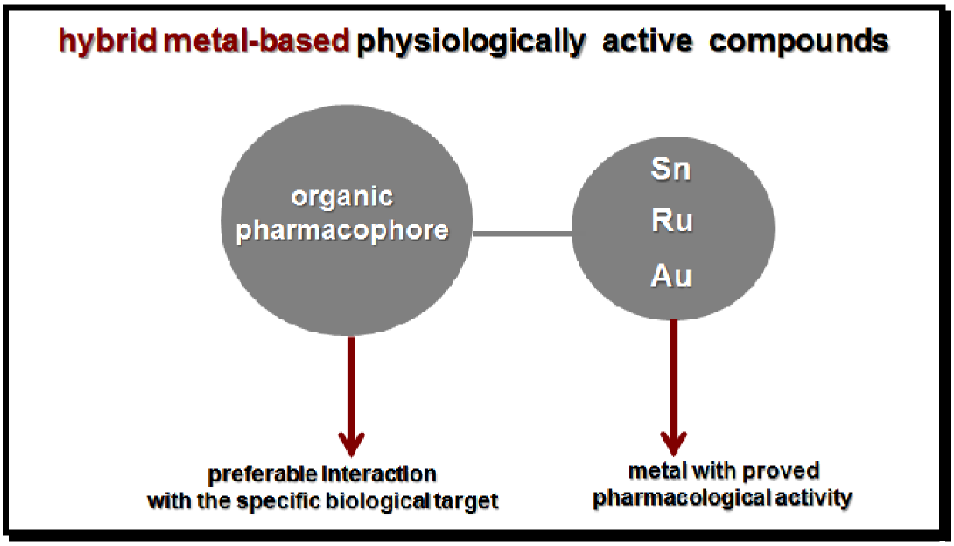
This study is focused on a novel approach to design hybrid metal-based physiollogically active compounds with dual modes of action – prooxidative/cytotoxic activity of metal and protective antioxidative activity of 2,6-dialkylphenol group. The synthesis and anti/prooxidant activity and cytotoxicity studies of novel organometallic/coordination compounds are presented and discussed.



The biological activity has been studied in *in vitro, ex vivo, in vivo* experiments in lipid peroxidation and mitochondria-associated processes, by using neurons, liver homogenates and in enzymatic reactions (*xanthine oxidase*, *lipoxygenase, gluthathione reductase, thioredoxine reductase*). A detailed screening of the antitumor potency of optimized lead compounds on a panel of human tumor cell lines and non-malignant counterparts, as well as testing of acute toxicity and antitumor efficacy in animal tumor model will be presented.

Thus, we can conclude that the combination of two physiologically active moieties in a complex molecule is a promising approach to find the novel hybrid selective therapeutic agents with opposed biological mode of action.

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MACROCYCLIC COPPER(I) AND SILVER(I) PYRAZOLATES: PRINCIPLES OF SUPRAMOLECULAR ASSEMBLIES WITH LEWIS BASES

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Macrocyclic copper(I) and silver(I) pyrazolates represent an important class of coordination compounds used in numerous fundamental areas, such as acid-base chemistry, metallophilic bonding, supramolecular assemblies [1]. In this lecture we discuss the host-guest complexes of the macrocyclic copper(I) and silver(I) pyrazolates and wide range of organic and organometallic bases possessing hydride, halide, carbonyl, phospine and π-electronic fragments [2-5]. The purpose of this lecture is to show the relationship between the solution and solid state chemistry of the target complexes using our approach. The study in solution focuses on the competition between different basic sites within the guest and on the selectivity to certain basic centers. It allows determining the complexes compositions and their thermodynamic parameters (formation constants, ΔH°, ΔS°) and predicting the solid state supramolecular architecture. Peculiar features of crystal packing depending on the base type, complexation strength and the presence of secondary basic center will be summarized and analyzed (Figure 1). The influence of complexes formation and their crystal packing on photo-physical properties of the host macrocycles will be discussed. The perspective of using these complexes for creating new light-emitting materials will be discussed

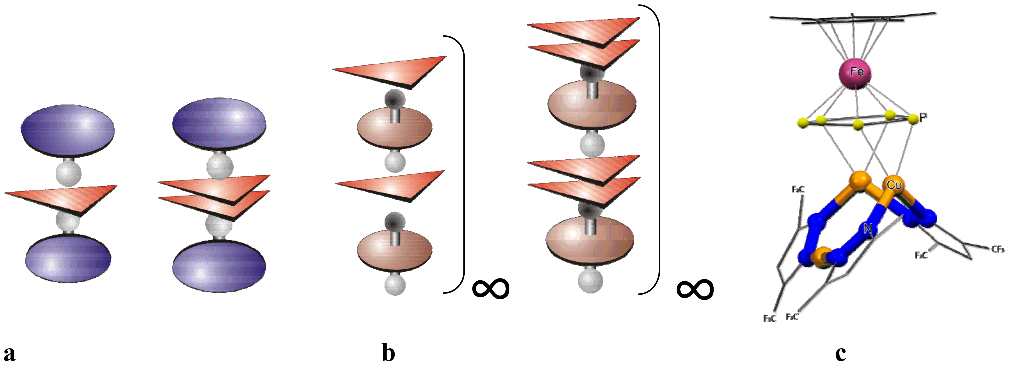

Figure 1. Types of complexes formed by trinuclear macrocycles (depicted as triangles) with monodentate bases (a), polydentate bases (b) and [Cp*Fe(η^5-P_5)] (c).

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COORDINATION CHEMISTRY OF MACROCYCLIC LIGANDS AND NEW FUNCTIONAL MATERIALS ON THEIR BASIS

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Functional properties of such macrocyclic ligands as porphyrins and their derivatives are widely exploited in natural and artificial systems. The molecular structure of free base porphyrins and their complexes can be precisely adapted to the target function and the operating environment by varying the substituents on the macrocycle. Another tool widely used by nature to increase the functional performance of tetrapyrroles is the coordination and supramolecular chemistry approaches. Such approaches lead to wide range of application of synthetic porphyrins and their analogues including such important field as photodynamic therapy of cancer (PDT). In this report the recent results of our group concerning coordination and supramolecular chemistry of porphyrins and phthalocyanines is discussed in the context of its application for development of new materials including hybrid ones [1-8].

Special attention will be paid to porphyrin derivatives as attractive photosensitizers in PDT. One of the main requirements for efficient photosensitizer is ability for selective accumulation in tumors. A big challenge for the application of Pcs is limited accumulation in the malignant tissues, which severely reduces their PDT efficacy. Nano delivery systems can overcome this disadvantage and at the same time increase the solubility and efficiency of Pcs for PDT application. This aspect will also be discussed in this report.

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EXCITING NEW CHEMISTRY OF ALUMINUM AND SILICON

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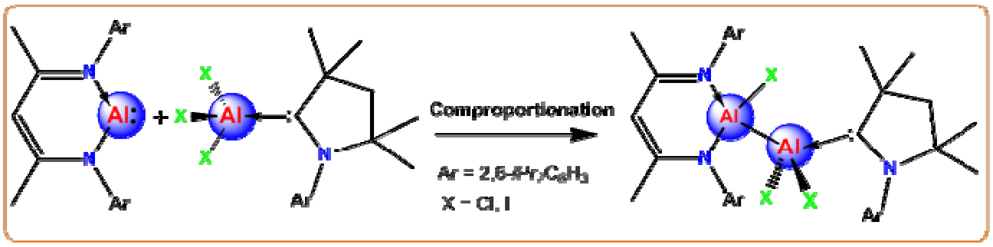
Aluminum and silicon are the most abundant solid elements in the earths' crust. They are ubiquitous available and are ideal elements for the development of sustainable chemistry. The interstellar space is the biggest "laboratory" in the universe and a guide to new chemistry. A few compounds have been characterized by spectroscopic tools. In previous years chemists have used noble gas conditions and low temperatures to prepare such species which are extremely sensitive and do not exist at room temperature. Our method of isolating is different. We are using NHC (N-heterocyclic carbenes) or cAAC (cyclicalkylamino carbenes) as Lewis bases to stabilize the prepared intermediates and recrystallize them at room temperature: such as Si, Si_2, Si_3, HSiSiH and others.

Some time ago we prepared the first stable carbene analogue of aluminum(I).Its reaction with aluminum(III)trichloride resulted in the asymmetric Al-Al with aluminum of oxidation state II by comproportionation.



Another highlight of aluminum was the prepation of the first stable mono molecular radical of aluminum.

The catalytic properties of various transformations such as hydrogenation, cyanation, deprotonation and activation reaction will be demonstrated using aluminum compounds.

Moreover, the preparation and characterization of the first silylene-phosphinidene of composition RSi(:)-P(cAAC) will be reported and other interconnected P-Si compounds with low coordinate elements are discussed.

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CATION-ANION PALLADIUM COMPLEXES: THE EFFECT OF THE HYDROGEN BOND CHARACTER ON THEIR STABILITY AND BIOLOGICAL ACTIVITY

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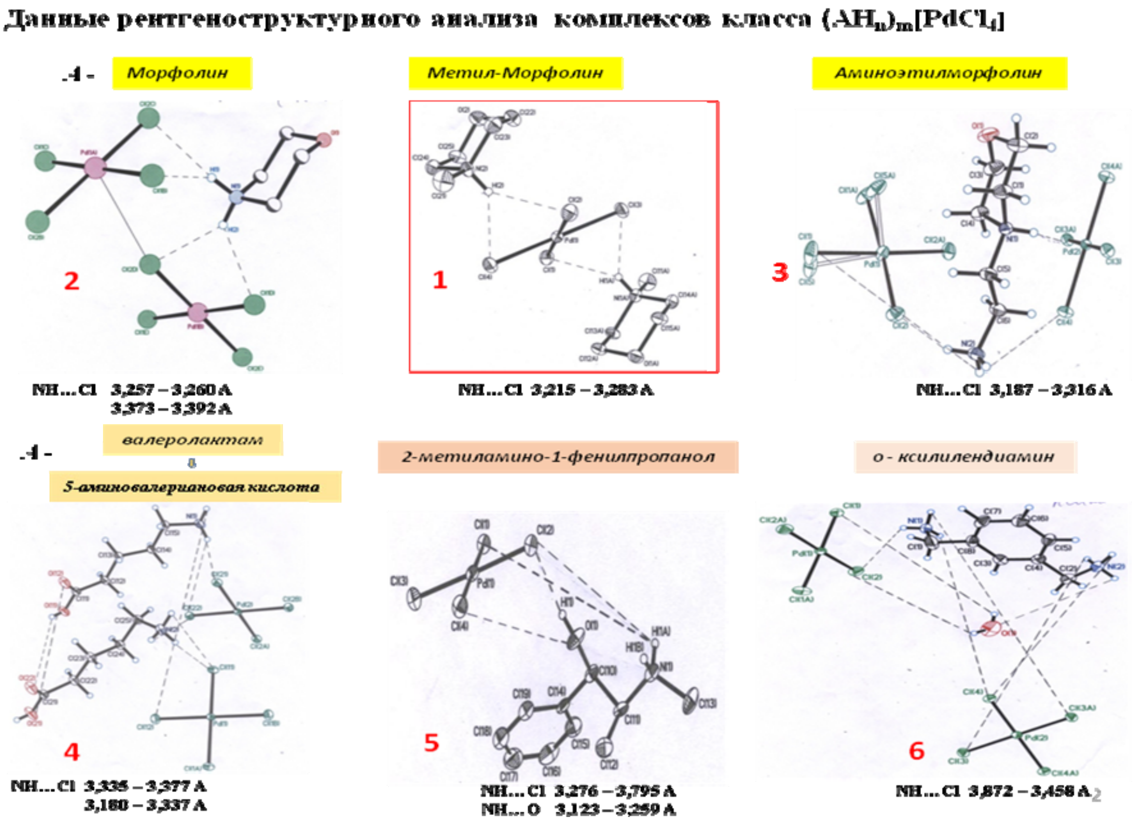
Long-term investigation of different types of palladium compounds allowed to determine a new class biologically active palladium complexes $(AH_n)_m[PdCl_4]$ as a results of systematical research of composition – structure – biological activity for palladium complexes with different types of nitrogen containing ligands. Cation-anionic complexes $(AH_n)_m[PdCl_4]$, have a supramolecular structure with strong intra- and intermolecular hydrogen bonds between Cl –ions and protonated nitrogen atoms or hydroxyl groups (if present) of ligands. These data were obtained from X-ray diffraction analysis of series of the cation-anoinic palladium complexes. [1, 2]

The first tetraacido-complexes $(AmH_2)_2[Pd(RCO_2)_4]$, when R – $CHCl_2$, CCl_3, CF_3 with cation - protonated morpholine – were synthesized. The structure of $(AmH_2)_2[Pd(CF_3CO_2)_4]$ was set from X-ray diffraction analysis. The possibility of formation palladium tetrahalocarboxylates of morpholonium depends on parity of acid – base properties of RCOOH and amine.



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27th International Chugaev Conference on Coordination Chemistry
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LOWER RIM THIACALIX[4]ARENES DERIVATIVES: SYNTHESIS AND COORDINATION PROPERTIES

I. Antipin[a,b], S. Solovieva[a,b], A. Konovalov[a,b]

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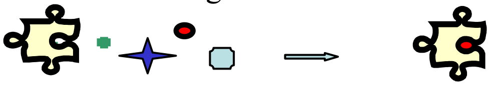
Lower rim thiacalix[4]arenes derivatives in *cone* and *1,3-alternate* conformations have many advantages to create a wide range of precursors for the design of very sophisticated supramolecular architectures.

Main approaches to the stereo and chemoselective functionalization of calix[4]arene platforms that allows to change significantly hydrophilic-lipophilic properties of macrocycles and to raise efficiency and selectivity of the interaction with substrates will be presented. The regularities of aggregation and complexation of calixarenes with substrates of different nature: non-electrolytes, cations, anions will also be examined. Particular attention will be paid to the application of calixarene derivatives for the construction of various supramolecular and nanosystems, devices and "smart" materials: nanoparticles, metal-coordinated networks, Langmuir-Blodgett nanolayers, molecular magnets etc.

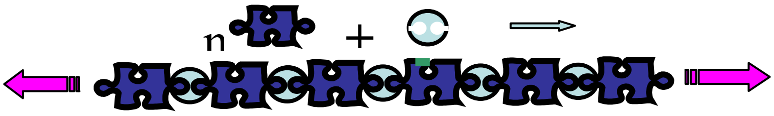
Main topics:

1. Synthesis and structure of thiacalix[4]arenes derivatives

2. Molecular recognition



3. Noncovalent assembly «bottom – up»



Acknowledgements - The authors gratefully acknowledge of the RSF grants (14-13-01151 for the support of the part of receptor for organic compounds and self-assembly on interfaces and 15-13-30006 for support of the MOFs part). Authors also thank the RFBR (grant 16-03-00920) for the financial support of the clusters magnetic properties investigation.

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PROTON-COMPLEXING AGENTS: EXPERIMENTS WITH DIETHANOLAMINE

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Salt solutions $Cu(OTf)_2$ and $Fe(OTf)_3$ in DEA (OTf – triflate anion $CF_3SO_3^-$, DEA – diethanolamine $HN(CH_2CH_2OH)_2$) were named "ionic liquids" in papers [1-2] and their indicated structure $[M(DEA)_6](OTf)_n$ corresponded to coordination compounds. Later the same group of authors has established [3] the structure of crystals, isolated from the mixture $Cu(OTf)_2$+DEA. Composition and structure of the complex compound were very different from previously proposed for ionic liquid containing copper, namely: [Cu(DEA)(DEA-H)]OTf, where DEA-H is DEA molecule with a deprotonated alcohol group. Both ligands DEA are chelate one.

Systems $Cu(OTf)_2$+6DEA and $Fe(OTf)_3$+6DEA were studied [4] by methods EXAFS и DTA-MS. We have shown that CN of copper atom in solution does not exceed 4, but it is equal to 6 in the case of iron atom. In this regard, it was concluded that system $Cu(OTf)_2$+DEA consists of the copper complex [Cu(DEA)(DEA-H)]OTf and solvent DEA_4HOTf. System $Fe(OTf)_3$+6DEA is presumably solution of complex compound $[Fe(DEA)_3]$ $(OTf)_3$ with chelate ligands DEA in excess of DEA. In order to study the solvent DEA_4HOTf we investigated mixtures with molar ratios DEA/HOTf and DEA/HNO_3 = 9/1, 4/1, 3/1, 3/2, 1/1, 1/2, 1/3 and pure DEA by methods ^1H-NMR and DSC. It was found out that the chemical shift value of the combined (due to fast exchange of protons) signal of amine and alcohol groups in ^1H-NMR spectra grows when the composition changes from pure DEA to the ratio DEA/HOTf and DEA/HNO_3 = 4/1and after that point remains constant, what may indicate the existence of a compound of formula DEA_4HOTf, which decomposes at elevated temperatures without DEA evaporation while DEA is volatile in the system $Fe(OTf)_3$+6DEA. The difference between systems DEA+HOTf and DEA+HNO_3 consists only in the fact that with the ratio DEA/acid=1/1 signals of amine and alcohol groups exist separately (rapid exchange of protons is interrupted) in the former system but the combined signal is stored in the later. To find out the reasons for the differences a salt DEA.HNO_3 was studied by X-ray crystal structure analysis and ^1H-MAS NMR.

In connection with the discovery of a concert mechanism for the exchange of protons in alcohols [5, 6] the role of protons in the systems under study is discussed as unique complexing agents.

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SPIN CROSSOVER IN HOMO- AND HETEROLIGAND IRON(II) COORDINATION COMPOUNDS WITH TRIS(PYRAZOL-1-YL)METHANES

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Iron(II) coordination compounds with polynitrogen containing heterocyclic ligands in octahedral ligand environment draw much attention due to their spin crossover (SCO) behaviour. The reversible transfer from the low spin (LS) to high spin (HS) state could be induced by means of an external impact, such as temperature, pressure or light irradiation [1,2]. The complexes those exhibit change in color under SCO, attract the most enhanced attention due to their particular importance for practical application. We have synthesized and investigated a representative number of iron(II) complexes with polynitrogen containing ligands, in particular, 1,2,4-triazole, *tris*(pyrazol-1-yl)methane and their derivatives, those exhibit spin crossover $^1A_1 \Leftrightarrow {}^5T_2$ [3]. This transition is accompanied by thermochromism.

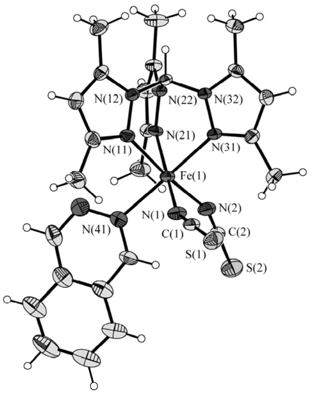

Fig. 1. Structure of molecular complex $[Fe(HC(3,5\text{-}Me_2Pz)_3)(phz)(NCS)_2]$.

Recently we have obtained a number of novel homo- and heteroligand iron(II) complexes with *tris*(pyrazol-1-yl)methanes and different anions. Alongside with *tris*(pyrazol-1-yl)methane or *tris*(3,5-dimethylpyrazol-1-yl)methane, in the inner area of the heteroligand complexes, there occur other nitrogen containing heterocycles such as pyrazole and its derivatives, tetrazole, phthalazine. In addition, we have synthesized iron(II) complexes with *tris*(pyrazol-1-yl)methane, in whose outer sphere there are cluster anions present, in particular, *closo*-borates, carboranes, as well as $[Mo_6Hal_{14}]^{2-}$ (Hal = Cl^-, Br^-) and $[Re_6S_8(CN)_6]^{4-}$. The compounds have been studied using methods of XRD phase and structural analysis, static magnetic susceptibility, as well as electron, infrared and Mossbauer spectroscopy techniques. Most of the complexes under investigation exhibit spin crossover $^1A_1 \Leftrightarrow {}^5T_2$, accompanied by thermochromism, with a pink (purple) ⇔ white color change.

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INTERRELATION OF STRUCTURE AND PROPERTIES OF BORON COMPLEXES WITH DIPYRROMETHENE

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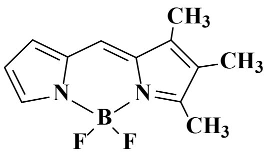
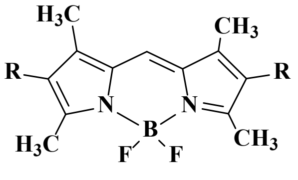
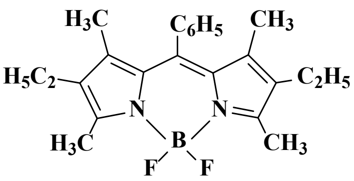
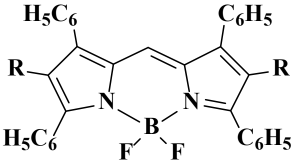
Synthesis of new coordination compounds with intensive chromophore-fluorescent properties in visible area of a spectrum is a subject of scientists special interest. The priority of researches in the field of fluorescence chemistry of coordination compounds is to study of ways of changing of absorption wavelengths, emission, time of a life and a quantum yield of fluorescence of organic molecules for specific practical and theoretical problems. The listed parameters can be configured properly by means of a ligands environment variation and properties of solvent in case of Bodipy.





R=H, C$_1$-C$_7$, Hal





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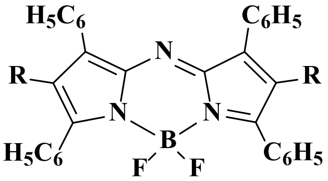

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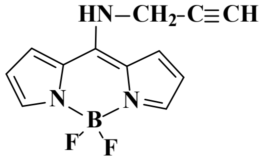

The structure of molecule, the electronic interference of functional substituents and the heterocyclic ligand chromophore were determined the contribution to the change in the spectral-luminescent characteristics of the difluorobolymethenes difluoroborates. However, systematic researches in this field of knowledge are rather not numerous.

In the report results of researches solvation interactions of boron complexes with structurally-various dipyrromethenes in a series of organic solvents are discussed.

In particular, the influence of the symmetry of alkyl substitution in a complex molecule, the amount, extent and nature of the substituents (alkyl-, aril-, halogen-), and the replacement the methine *meso*-bridge for the *aza*-group are considered.

The results of calorimetric and spectral studies, as well as thermoanalysis in oxygen air or argon atmosphere are analyzed.

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HETEROMETALLIC COMPLEXES AS INDIVIDUAL MOLECULAR COMPOUNDS AND PRECURSORS FOR POLYMERS

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The properties of materials formed from molecular compounds (organic molecules or coordination compounds) are determined by their composition, structure and crystalline packing. The presence of functional organic groups, the nature of the metal ion(s) determine the electronic structure of the molecules of their properties at the molecular level. In addition, packaging effects can weaken or intensify physicochemical characteristics, such as, effects of luminescence or magnetism. Molecular coordination compounds can play a role of precursors for the synthesis of complex functional compounds, for example, under the crystallization with other molecules, forming supramolecular architectures, or under the chemical reactions with the metal containing agents resulting in the formation of coordination polymers having high dimensionality. Heteronuclear molecular complexes, *s*-3*d*, 3*d*-3*d*, 3*d*-4*f*, etc., are very perspective building blocks for the development of chemistry of new type heteronuclear coordination compounds and molecular materials exhibiting unusual chemical and physical properties. Among them it is worthwhile to single out large polynuclear molecules, porous heteronuclear coordination polymers as well as metal organic frameworks (MOFs) developing magnetic, luminescence and sorption properties and can be constructed by varying the composition of metal core, bridged ligands (for example, carboxylates) and the electronic nature of metal ions.

In the presented report we demonstrate a new series of molecular and polymer metal-organic carboxylate {Li-3*d*, 3*d*-4*f*} architectures synthesized by traditional and new methods, as well as their chemical and physical characteristics, which depend not only on the composition of new molecules, but also on their structure and crystalline packaging.

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POLYNIOBATES: EMERGING LIGANDS. A WALK THROUGH THE PERIODIC SYSTEM

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Chemistry of polyoxoniobates is scarcely studied and was restricted for a long time to alkali metal salts with hexanuclear anions of the Lindqvist type $[Nb_6O_{19}]^{8-}$. The reason is that polyniobates exist only in medium and strongly alkaline media and mostly form amorphous jellylike precipitates upon the addition of transition metal salts. In our recent cycle of works, new methods were developed for the inclusion of heterometals into the polyoxoniobate structures, including those with the formation of novel structural types. It turns out that the Lindqvist-based hexaniobate $[Nb_6O_{19}]^{8-}$ anions can act as robust ligands towards various inorganic and organometallic cationic species containing noble metals (coordination to Pt, Rh, Ir, Ru will be discussed) which are active catalysts in electrochemical oxidation of water and methanol. The organometallic fragments like $\{C_6H_6Ru\}^{2+}$ or $(Cp^*Rh\}^{2+}$ are convenient markers for studying polyoxoniobates and tantalates in solutions by the NMR method. The scope of this chemistry can be expanded by substitution of one of the terminal $\{Nb{=}O\}^{3+}$ groups in $[Nb_6O_{19}]^{8-}$ by another fragment with similar coordination preferences, such as $\{Te\text{-}OH\}^{5+}$. Even though $[Nb_6O_{19}]^{8-}$ are robust under ordinary conditions, there hydrothermal reactions in the presence of tetrahedral building blocks (VO_4^{3-}, CO_3^{2-}, SiO_4^{4-}) produces a rich chemistry which involves high-nuclearity polyniobates of nanoscopic size, such as $[Si_4Nb_{16}O_{56}]^{16-}$, $[VNb_{14}O_{42}(CO_3)_2]^{13-}$, $[V_4Nb_{24}O_{76}]^{12-}$. Their coordination chemistry will also be discussed. Supramolecular aggregation of $[Nb_6O_{19}]^{8-}$ templated by metal cations gives giant aggregates such as series of mixed-valent Cu(II)-Cu(III)-polyniobates or Co(III) polyniobates [1,2].

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METALOCOMPLEXES OF MACROHETEROCYCLIC COMPOUNDS AS A BASIS FOR CREATING NEW FUNCTIONAL MATERIALS

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Metal complexes of synthetic macroheterocyclic compounds, like the chlorophyll and heme, have a wide variety of properties. Stability, redox and photo activity, the ability to self-assemble into complex supramolecular ensembles makes these compounds perspective for synthetized of new functional materials. Unique properties of metal complex of synthetic macroheterocyclic compounds open wide perspectives for a variety of applications.

Methodical approaches to the synthesis of metal complexes of macroheterocyclic compounds: porphyrins, phthalocyanines, porphyrazines, and the creation of new functional materials on their basis are report. Physic-chemical characteristics of metalcomplexes and their relation to applied properties are considered.

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COORDINATION PEROXOCOMPOUNDS OF P-BLOCK ELEMENTS. NEW APPLICATIONS.

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Peroxocomplexes of Ge, Sn and Te were isolated from aqueous hydrogen peroxide solutions and characterized by single crystal and powder X-ray diffraction studies, FTIR, Raman spectroscopy and thermal analysis [1-3]. The crystal structure of peroxogermanates and hydroperoxostannates consists of centrosymmetric hexanuclear peroxogermanate $[Ge_6(\mu\text{-}OO)_6(\mu\text{-}O)_6(OH)_6]^{6-}$ and homoleptic hexahydroperoxostannate $[Sn(OOH)_6]^{2-}$ anions, respectively [1,2]. Peroxotellurate anions in both isolated ammonium peroxotellurates contain a binuclear $Te_2(\mu\text{-}OO)_2(\mu\text{-}O)$ fragment with one μ-oxo- and two μ-peroxo bridging groups [3]. Hydrogen peroxide interacts with germanium, tin and other p-block elements only under basic conditions and then peroxo- or hydroperoxo complexes are formed. Additionally, since hydrogen peroxide is acidic it induces the polycondensation and sol formation by oxo or peroxo bridging mechanism. However hydrogen peroxide acts also as a capping agent and the hydroperoxo coordination prevents gelation and stabilizes the sol state which can be used to form thin films on particulates [4-6]. Peroxogermanate, peroxostannate and other p-block element peroxocomplexes are used as precursors to coat clays, graphene oxide (GO) and other particulates and then can be transformed to corresponding oxide and sulfide films [4-9].
P-block element oxides and sulfides - reduced GO composites synthesized via peroxide method demonstrate good electrochemical properties as anodes for Li, Na and K ion batteries. It is proposed to expand the application of p-block elements peroxocomplexes for synthesis of new composite nanomaterials for solar cells, supercapacitors, etc.

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COORDINATION nd-nf COMPLEXES FOR CREATING SINGLE ION AND SINGLE MOLECULE MAGNETS. THE PRESENT STATE, PROSPECTS, AND TRENDS OF DESIGN

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In this review, we briefly discuss some new trends in the design of single molecule magnets based on transition (3d, 4d, 5d) and rare-earth (4f) metal ions. Within this broad theme, the emphasis of the present review is placed on the molecules which exhibit strong magnetic anisotropy originating from the unquenched orbital angular momenta in the ground orbitally degenerate (or quasi-degenerate) states. Along with the general concepts, we consider selected examples of the systems comprising orbitally-degenerate metal ions, and demonstrate how one can benefit from strong single-ion anisotropy arising from the first-order orbital angular momentum. The role of crystal fields, spin-orbit coupling, and structural factors is discussed. Some observation stemming from the analysis of the isotropic exchange interactions, magnetic anisotropy, and strongly anisotropic orbitally-dependent superexchange are summarized as guiding rules for the controlled design of single molecule magnets exhibiting high barriers for magnetization reversal and, consequently, high blocking temperatures.

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SUPRAMOLECULAR DEVICES AND MACHINES THAT USE LIGHT AS AN ENERGY SOURCE

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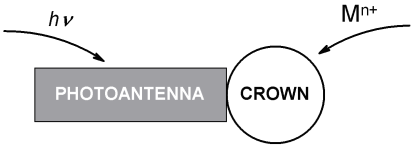
[b]*Institute of Problems of Chemical Physics of RAS, Chernogolovka, RUSSIA.*

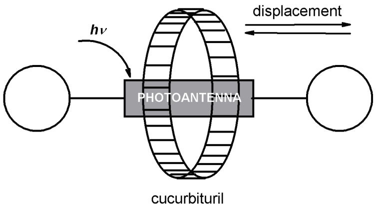
Currently a new trend is formed in nanotechnology “bottom-up”: supramolecular engineering of supramolecular devices and machines for various purposes. The most convenient means for controlling supramolecular devices and machines is light, which can be easily adjusted both in the wavelength and in the amount.

We propose a new unique class of polyfunctional photoactive compounds: unsaturated (polymethine) dyes functioning as photochromes, fluorophores and ionophores [1]. A large body of research has been performed for their synthesis, determination of their spatial structures, study of self-assembly features to give supramolecular systems, and also study of fluorescent, photochemical and complexing properties.

Resulting from the research, we elaborated for the first time universal supramolecular meccano, allowing one to accomplish building-up, with using a limited number of complementary compounds with participation of metal cations and hydrogen bonds, photoactive supramolecular systems of varied architecture with adjusted properties [2]. Within the same class of compounds one can construct in solution, solid and at the air-water interface new types of photoswitchable supramolecular devices, photocontrolled supramolecular machines, photoactive monolayers and monocrystals susceptible to all of the key photoprocesses.



supramolecular devices



supramolecular machines

The high practical value of these studies deserves attention. They provide a new strategy for the design of materials for supramolecular and nanophotonics, which was demonstrated, first of all, by the creation of practically important sensor [3] and photochromic materials [4, 5].

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LANTHANIDE HOMO- AND HETEROMETALLIC CHALCOGENIDE COMPLEXES

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Solid phases based on or containing chalcogenides (Q = S, Se, Te) of rare-earth metals (Ln) are well-known as widespread versatile inorganic materials revealing unique luminescent, magnetic, thermoelectric, etc. properties. The solid state chemistry of Ln chalcogenides is quite well developed. In contrast to that the molecular chalcogenide complexes of Ln are far less common and are often considered as 'unconventional' compounds because of the combination of highly ionic metals and highly covalent ligands. Interest to the Ln chalcogenide complexes mainly caused by a possibility to use them as molecular precursors of functional solids with unusual compositions and structural motifs. In this respect, the compounds of more variable compositions, namely homo- and heterometallic polychalcogenide complexes, are of particular interest.

The report is based on our recent results in the field of synthetic chemistry of the compounds with Ln–Q bonds: functionalized chalcogenolates, homometallic Ln polychalcogenides, and mixed *d*-*f*-metal chalcogenides (some examples are shown in Fig. 1.). The major approaches used for the synthesis of such compounds are: (1) salt metathesis; (2) reduction of Q-containing substrates either by the Ln(II) complexes or the Ln(III) complexes containing redox-active ligands. Details of the chemistry and structural features of the novel Ln–Q compounds as well as their chemical and physical properties are the matter of the discussion.

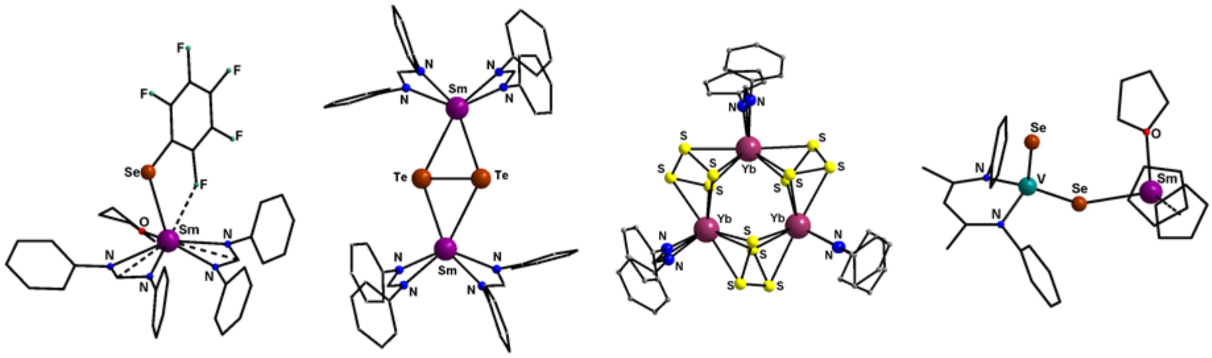

Fig. 1. Molecular structures of the chalcogenide complexes (from left to right): [(Fiso)$_2$Sm(SeC$_6$F$_5$)], [(Fiso)$_4$Sm$_2$(μ-η^2-Te$_2$)], [{(Fiso)Sm}$_3$(μ-η^3,η^3-S$_4$)$_3$] and [(^{Me}nacnac^{Dipp})V(=Se)(μ-Se)Sm(thf)Cp*$_2$]. All alkyl substituents and H atoms are omitted for clarity.

Acknowledgements - This work is supported by Russian Science Foundation (16-13-10294)

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DOUBLE COMPLEX SALTS AS SINGLE SOURCE PRECURSORS FOR ONE-RUN SYNTHESIS GOLD-CONTAINING NANOALLOYS

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Design of nanosized polymetallic systems is a necessary part of modern machinery construction, microelectronics, chemical industry and catalysis. The development of this direction makes possible to create materials possessing predefined properties. Synthesis of compounds combining several different metals is of long-term interest as a possible route to novel starting objects for preparation of modern functional materials. Double complex salts (DCS) comprising partly charged coordination entities are very convenient for preparation of such precursors. Intrinsically intimate location of transition metal ions in the crystal structure of such compounds allows one to obtain metal- and metal-containing systems on their thermal decomposition. The successful development of this direction demands for fundamental information on the structure and properties of the precursor compounds.

The recent "boom" of gold catalysis strongly inspired our interest to gold-containing DCS. The report presents the data for 32 new DCS containing the cations ($[AuEn_2]^{3+}$ and $[AuDienCl]^{2+}$) in the cationic part of the complex, or the anionic part contains complex anions $[AuCl_4]^-$ and $[AuBr_4]^-$, charge balance being achieved with complex ions of other noble metals. All compounds were studied with powder and single crystal diffraction, IR-spectroscopy, thermal behavior of the DCS was studied in different atmospheres. The stereochemistry of the coordination cores was studied, some interesting binuclear complexes of gold and palladium, gold and platinum were found. The obtained information on isostructurality of some series of the obtained DSC makes possible to prepare solid solutions containing three or more metals in the predefined stoichiometry.

Acknowledgements. The work has been supported by grant of Russian Science Foundation (project №16-13-10192).

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FLUORINATED 2-ETHOXYMETHYLIDENE-3-OXO ESTERS IN SYNTHESIS OF LIGANDS AND METALOCOMPLEXES

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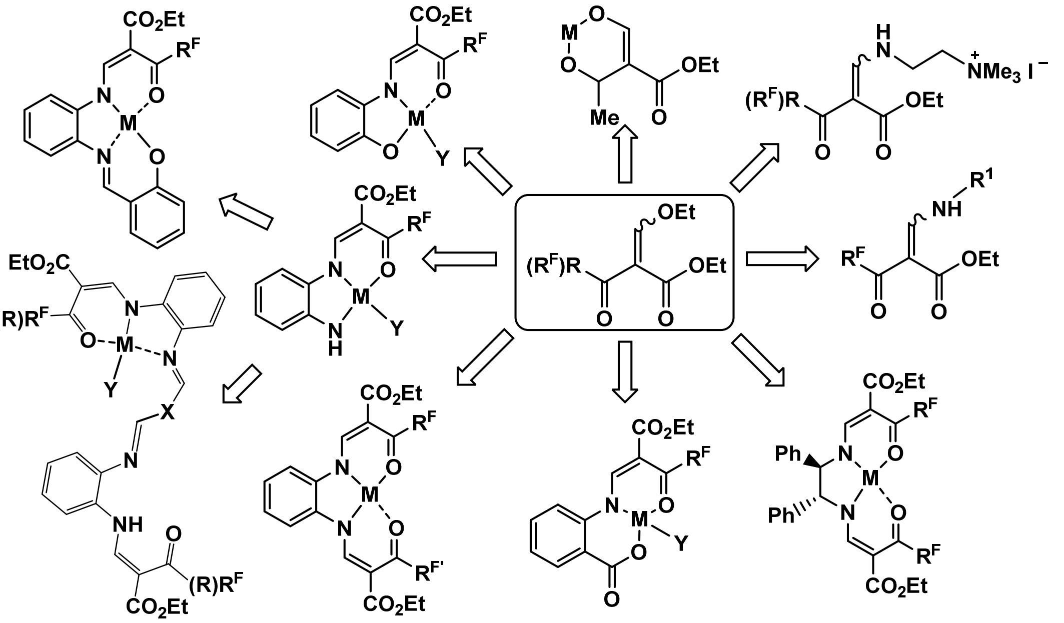
1,3-Dicarbonyl compounds are the popular building blocks that allow to perform various synthetic tasks, including targeted production of practically important molecules. The promising reagents are also their 2-ethoxymethylidene derivatives. The high reactivity of these compounds in reactions with different nucleophiles provides convenient approaches for the construction of various open-chain frameworks. It allows to design on their basis a variety of ligands. Their application as chemical reagents for metal complexes synthesis is reported.



Acknowledgements - This work was supported by the Presidium of the Ural Branch of the Russian Academy of Sciences (project no. 15-21-3-7) and the State Program for Supporting of Leading Scientific Schools of the Russian Federation (grant no. NSh-8922.2016.3).

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STABILITY AND REACTIONS OF IODIDE-SULFIDE-NITRIDE CLUSTERS OF NEODYMIUM AND DYSPROSIUM

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Thermal stability and some reactions of recently obtained unusual three-nuclear iodide-sulfide-nitride clusters of neodymium(III) and dysprosium(III) of general formulae of $Ln_3I_5(S_2)(S_2N_2)(THF)_{10}$ are provided. Possible pathways of transformations are discussed.

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RHODIUM COMPLEXES WITH CARBORANYL LIGANDS OF DIFFERENT TYPES IN ONE MOLECULE

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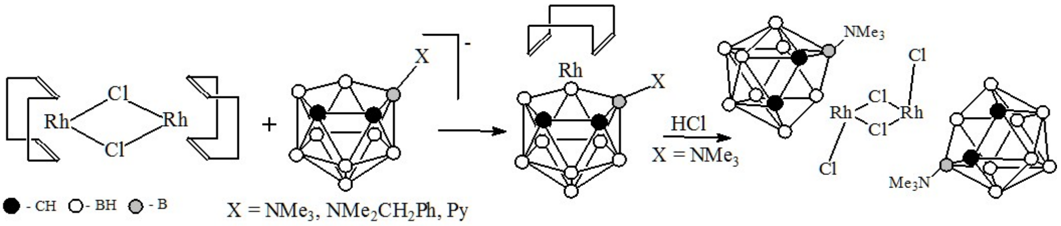
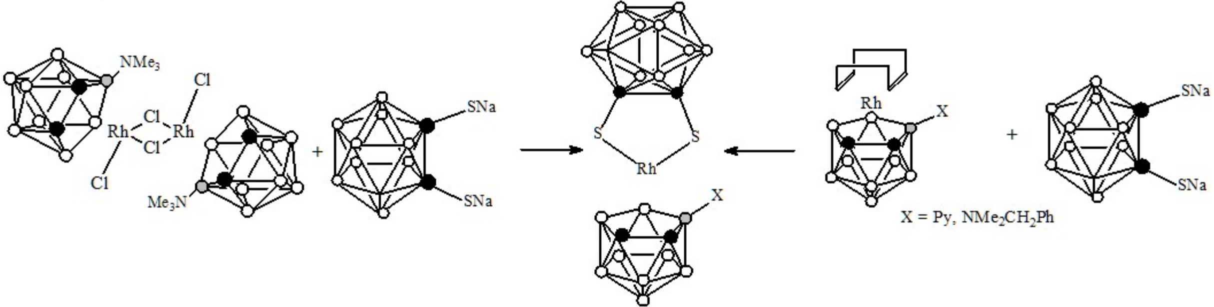
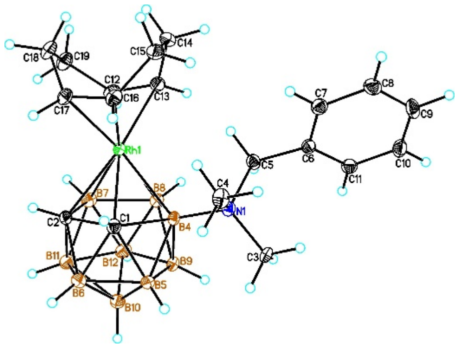
The first rhodacarboranes containing σ- and π-carboranyl ligands in one molecule were synthesized. At the first step rhodium(I) complexes 3-(η^2:η^2-1,5-COD)-4-L-3,1,2-$RhC_2B_9H_{10}$ (X = NMe_3, NMe_2CH_2Ph, Py) were obtained by the reactions of dimeric complex [(1,5-COD)RhCl]$_2$ with sodium or lithium derivatives of the corresponding charge-compensated dicarbollides. Contrary to another two, NMe_3-derivative was unstable and without purification was transformed into dimeric complex [μ-3-Cl-3-Cl-4-NMe_3-3,1,2-$RhC_2B_9H_{10}$]$_2$ via reaction with aq. HCl.

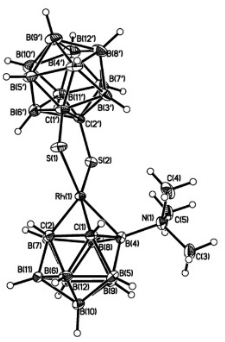


At the next step, the reaction of obtained complexes with disodium *ortho*-carboranyl-1,2-dithiolate 1,2-$(NaS)_2$-1,2-$C_2B_{10}H_{10}$ gave deep green complexes 3-(κ(S,S)-1',2'-$C_2B_{10}H_{10}$-1',2'-S_2)-4-X-3,1,2-$RhC_2B_9H_{10}$.



Structures of 3-(η^2:η^2-1,5-COD)-4-Me_2NCH_2Ph-3,1,2-$RhC_2B_9H_{10}$ and 3-(κ(S,S)-1',2'-$C_2B_{10}H_{10}$-1',2'-S_2)-4-Me_3N-3,1,2-$RhC_2B_9H_{10}$ were determined by single crystal X-ray diffraction.





Acknowledgements - This work was partially supported by Russian Foundation for Basic Research (grants 16-03-00724 and 16-53-53079).

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POROUS COORDINATION POLYMERS: FROM SYNTHESIS AND STRUCTURE TO FUNCTIONAL PROPERTIES

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Last decade witnessed an exploding development of porous coordination polymers (PCP)/metal-organic frameworks (MOF) research area. Metal-organic frameworks are an important class of modern porous materials and represent a particular structural and functional variety. They are built from metal centers of different geometries and polytopic organic ligands. MOF materials have high specific surface area in comparison to other inorganic and organic porous solids. The synergy of metallic and organic blocks in MOFs leads to interesting catalytic, magnetic and luminescent activity. Selective gas adsorption properties and detection of small organic molecules are among the most valuable functional properties of such materials. Here we describe our recent results on synthesis, structural characterization and investigation of functional properties for novel types of metal-organic frameworks.

Isoreticular porous MOFs based on Zn_2–paddle wheels, connected through thiophenedicarboxylate moieties and N-donor linkers (L) $[Zn_2(tdc)_2L]$ are synthesized and characterized. Apart from some structural distortions these frameworks are very similar to the prototypic Zn(II) terephthalate $[Zn_2(bdc)_2dabco]$ compound and so does the general porous properties (pore size, pore volume, specific surface area). However, the substitution of benzene to thiophene linker substantially increases the carbon dioxide adsorption as well as CO_2/N_2 adsorption selectivity. The CO_2 uptake on $[Zn_2(tdc)_2dabco]$ approaches the best values reported in the literature although this compound possesses no basic amine functions nor open metal sites, which is manifested by a low isosteric heat of adsorption. The quantum chemical calculations confirm the definitive role of heterocycles and, particularly, sulfur atoms in CO_2 binding *via* induced dipole interactions. These results emphasize the feasibility of van-der-Waals interactions to effective CO_2 binding while maintaining low heat of adsorption and a general hydrophobicity of the porous material. More importantly, the incorporation of heterocycles into porous structures may be a practical way to improve the adsorption properties of the already known materials.
Substitution of both pyridine and pivalate ligands in $[Li_2Zn_2(piv)_6(py)_2]$ with 4,4′-bipyridine (bpy) and terephthalate bridges (R-bdc^{2-}, R = H, Br, NH_2, NO_2) results in a series of isoreticular porous frameworks $[Li_2Zn_2(R\text{-}bdc)_3(bpy)]\cdot Solv$, in which the eight-connected tetranuclear heterometallic $\{Li_2Zn_2(OOCR)_6L_2\}$ node is linked by dicarboxylate and bpy ligands. The introduction of different substituents R onto the terephthalate linkers affects the free volume of the porous compounds and the N_2 adsorption behavior. The CH_4 and CO_2 adsorption and relative selectivities have been investigated in detail, and interestingly, a fascinating interplay of luminescence properties with wavelength of excitation and nature of the host aromatic guest molecules has been observed.

Acknowledgements - Our work was supported by the Russian Science Foundation (Grant No. 14-23-00013).

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LANTANIDE PYRAZOLECARBOXYLATES: PERSPECTIVE PHOTO- AND ELECTROLUMINESCENT MATERIALS

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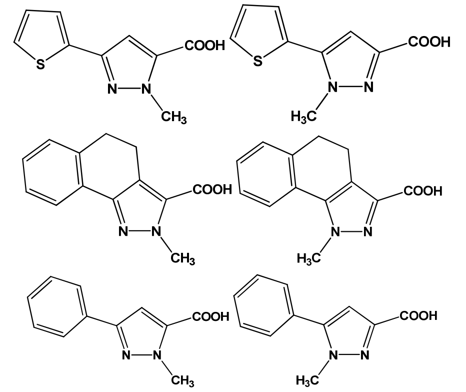
Long excited state lifetimes make lanthanide coordination compounds (LCCs) the ideal materials for bioimaging, whereas the involvement of the triplet state of the ligand in the luminescence makes them promising for organic light-emitting diodes (OLEDs). Aromatic carboxylates are particularly important due to high quantum yields and chemical stability, but they usually demonstrate low solubility due to the formation of coordination polymers, and also usually do not have transport properties, which is important for OLEDs [1].

To increase the solubility, as well as the electronic mobility, we chose anions of pyrazolecarboxylates, containing nitrogen heteroatom in the alpha position relative to the carboxy-group, as ligands. It was found that all the obtained LCCs are well-soluble due to isle structure formation. Terbium pyrazolecarboxylates demonstrated high quantum yields up to 100%, and their transport properties depended on the substituent nature: high electron mobility was demonstrated only by aryl-substituted CCs. It made it possible to successfully use them as emission layers of OLEDs. At the same time, the isomerism exerted a large influence on the luminescent properties of europium CCs. Thus, β-methyl-substituted pyrazolecarboxylates had quantum yields up to 16%, whereas α-methyl-substituted isomers had no luminescence at all because of the presence of a quenching ligand-to-metal charge transfer state caused by the presence of a free electron pair in the beta position.

Anion PA =	**Quantum yield (%) of $Ln(PA)_3(H_2O)_x$, Ln =**		
	Eu	**Tb**	
TPA-α	~0	2	
TPA-β	16	~0	
BIA-α	~0	11	
BIA-β	10	57	
PPA-α	3	40	
PPA-β	14	100	

Cellular studies have shown that europium pyrazolecarboxylates are non-toxic. Since for luminescent bioimaging not only the quantum yield, but also the absorption of CC is important, europium phenylpyrazolecarboxylate demonstrated the greatest intensity of luminescence *in cellulo*. The data obtained make it possible to consider pyrazolecarboxylates of lanthanides as promising luminescent materials for various applications.

[1] VV Utochnikova, NP Kuzmina. Russ. J. Coord. Chem., 2016, 42, 640-656.

Acknowledgements – the authors thank RFBR, grant #16-29-10755

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STRONG LINKS VIA WEAK INTERACTIONS

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The past few years have seen a precipitous growth in the number of publications related to various aspects of weak interactions, both in chemistry and biology. A special issue of *Chemical Reviews* devoted exclusively to non-covalent interactions in chemistry was published in 2016, highlighting the cutting-edge nature of this project.

Compared to covalent bonds, intra- and intermolecular non-covalent interactions are weak. They have much lower energy, fluctuating in the range from several units to several tens of kcal/mol, as well as less directed orientation. Depending on specific chemical elements or building blocks based on these elements, non-covalent interactions are classified into hydrogen, halogen, chalcogen, pnictogen, metallophilic, lp-π interactions, π-stacking, and a number of others; this classification is continuously expanded and refined. Crystal engineering makes extensive use of interactions between multiple non-covalent bonds, allowing the design and production of associates, clusters, extended supramolecular systems and ultimately functional materials.

Despite the low energy of non-covalent interactions, in many cases they act collectively and the sum of their actions can play a significant role in the various transformations of chemical compounds, synthesis and catalysis, including organic catalysis. The talk will consider such types of weak interactions as halogen and chalcogen bonds with special emphasis on how these non-covalent interactions affect the reactivity of chemical compounds. The works carried out in the International Group will be analyzed in the following directions:

- Recognition of novel types of halogen and chalcogen bonds [*Crystal Growth & Design*, **16** (2016) 2979; *CrystEngComm*, **19** (2017) 2517; **18** (2016) 1987; *J. Mater. Chem. C*, **2** (2014) 8285];
- Halogen bond with metal centers including unique bifurcated halogen bonds $HI_2C–I\bullet\bullet\bullet\eta^2_{(Pt–Cl)}$ [*Chem. Commun*., **52** (2016) 5565];
- Halomethanes as useful synthons for crystal engineering [*Crystal Growth & Design*, **17** (2017) 1353; *Phys. Chem. Chem. Phys.*, **18** (2016) 14104];
- New family of heterotetramiric clusters featuring the $(R–Cl)_2\bullet\{\mu_{H,Cl}\text{-}CHR'X_2\}_2$ structural unit with two pairs of simultaneous halogen and hydrogen bonds [*CrystEngComm*, **18** (2016) 5278; *Crystal Growth & Design*, **10** (2010) 4839];
- Effect of chalcogen bonding on regioisomerization of diaminocarbene complexes in solutions [*J. Am. Chem. Soc*., **138** (2016) 14129].

A special emphasis will be placed on the achievements of the International Group established at Saint Petersburg State University under the Russian Science Foundation project 14-43-00017P.

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CHEMICAL DESIGN OF THE (PSEUDO-)MACROPOLYCYCLIC LIGANDS FOR STABILIZATION OF UNUSUALLY HIGH AND LOW OXIDATION NUMBERS AND RARE SPIN STATES OF AN ENCAPSULATED METAL ION

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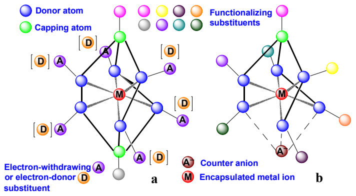
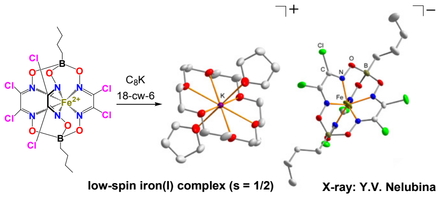
A promising approach to the chemical design of (pseudo-)clathrochelates [1] for accession of unusual oxidation and spin states of their (pseudo-)encapsulated metal ions is based on the use of electron-withdrawing or electron-donating substituents in the ribbed chelate fragments of a quasi-aromatic caging (Scheme 1, **a**) or (pseudo-) encapsulating hydrogen-bonded tripodal (Scheme 1, **b**) ligands combined with variation of the charge of their donor groups (0 or –1). Hexahalogenoclathrochelate [2] and tris-oxalodihydrazide [3] ligands were used for the stabilization of metal(I) (Scheme 2) and metal(IV) (Scheme 3) complexes, respectively, which are possible (electro-) catalytically active intermediates [4,5] and functional metalloenzyme biomimetics [3].

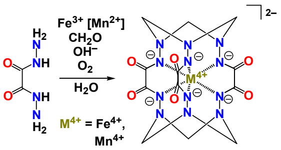


Scheme 1

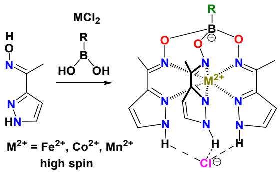


Scheme 2

The designed cobalt(II) pseudoclathrochelates (Scheme 4) possess the largest Co-based axial anisotropy of magnetic susceptibility, which results from their unusual TP geometry and translates into large negative values of the zero-field splitting energy, D. These large D values are high enough to promote paramagnetic pseudocontact shifts at a distance beyond 2 nm; thus, paving the way towards the development of prospective paramagnetic probes and single-ion molecular magnets.[6] Due to a distorted TP geometry of their coordination polyhedra, hexahydrazide clathrochelates (Scheme 4) also possess an unusual inverted configuration of the *3d*-electronic levels. For certain electronic configurations this could result in unusual spin states, *e.g.*, a low-spin d^3 configuration that is inaccessible for octahedral or tetragonal-bipyramidal complexes.



Scheme 3



Scheme 4

1. Y.Z.Voloshin, I.G.Belaya, R.Krämer, *The encapsulation phenomenon: synthesis, reactivity and applications of caged Ions and molecules*, Springer, **2016**; *Cage metal complexes: clathrochelates revisited*, Springer, **2017**
2. Y.Z.Voloshin, O.A.Varzatskii et al. *Angew. Chem. Int. Ed.* **2005**, *44*, 3400
3. S.Tomyn, V.Ksenofontov, I.O.Fritsky et al. *Nat. Commun*. **2017**, *8*, 14099
4. D.P. Halter, F.W.Heinemann, J.Bachmann, K.Meyer, *Nature*, **2016**, *530*, 317
5. M.Malischewski, J.Sutter, K.Meyer, K.Seppelt et al. *Science*, **2016**, *353*, 678
6. V.V.Novikov, Y.Z.Voloshin, R.E.P. Winpenny et al. *JACS* **2015**, *137*, 9792

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ISOLOBAL ANALOGY - «PHYLOSOPHICAL STONE» OF COORDINATION CHEMISTRY

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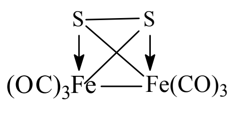
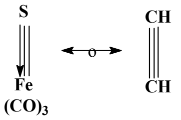
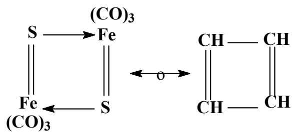
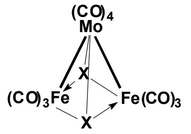
Roald Hoffmann's principle of isolobal analogy of fragments which have near the same frontier orbitals - the higher occupied and the lower unoccupied- and the number of electrons in them unclosed the opportunity to use the organometallic fragments instead of pure organic units: the $^{\cdot}Mn(CO)_5$ and $^{\cdot}CH_3$ **radicals**; the **carbenoids** $Fe(CO)_4$, CH_2 or sulphur atom; the **carbynes** $Co(CO)_3$, CH and nitrogen atom. The combination of isolobal fragments results the analogous of olefines or acetylenes which can coordinate the transition metals. Moreover the $[(CO)_3Fe\equiv S]$ unit appears the **acetylene**-like properties in dimerization to tetrahedron analogous or to cyclobutadiene isomer that in turn can coordinate the transition metals giving cluster chalcogenides as analogous of known organometallic **cyclobutadiene** complexes:

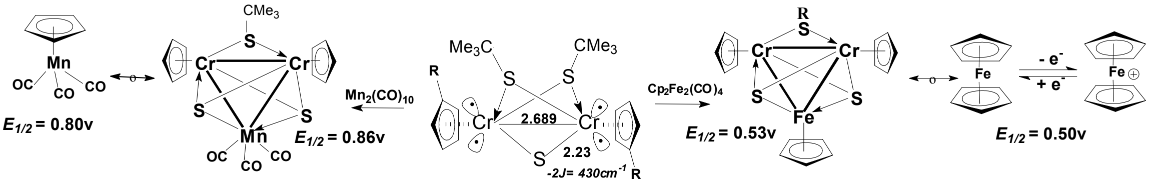




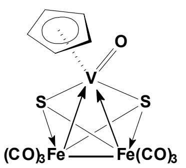


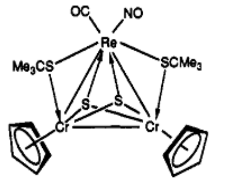


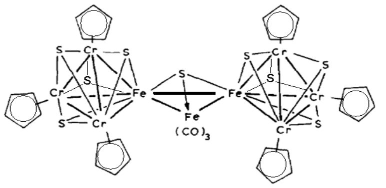
Cluster $(CpCrSCMe_3)_2S$ easily leaves one CMe_3 group and coordinate the different M-containing fragments as five-electron donor by analogy with **cyclopentadienyl** ligand giving mixed-metal clusters ferrocene- or cymantren-like type (including the similarity of electrochemical properties):

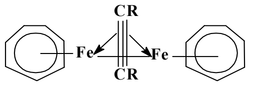


Some of the metal-sulphide fragments are available to give six electrons to metal(V or Re)-containing fragment with **aren**-like complexes formation. In turn the trinuclear tetrasulfides of the 6 group of metals are bonded with two Fe atoms by analogy with **cycloheptatrienyl** ligands (moreover the $(CO)_3FeS$ was added as acetylene-like bridge ligands):









Finally the isolobal analogy between $\mathbf{Re(CO)_3}$ **and** $\mathbf{Me_3Pt}$ units opened to us the way to a raw of Pt-containing mixed-metal complexes, for example, (p-cymene)$Ru(\mu\text{-}Cl)_3PtMe_3$ and (p-cymene)$Ru(\mu\text{-}SBu^t)_3PtMe_3$ as precursors of electrocatalysts.

Such opportunity to have the similar properties at substitution of metal-containing fragments by isolobal units containing different metal atoms could be named as **"philosophical stone" of coordination chemistry.**

Acknowledgements to Russian Foundation of Basic Research for financial support (grant RFBR 16-03-00798).

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REDOX CHEMISTRY OF TRIS(TETRACHLOROSEMIQUINONATO)IRON(III) AND NONCLASSICAL WATER OXIDATION

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Ligand-based redox chemistry is a fundamental property of complexes containing noninnocent quinone ligands. An early example of ligand redox activity was demonstrated for tris(tetrachlorosemiquinonato)chromium(III) ($Cr^{III}(Cl_4SQ)_3$) . Magnetic, spectral, and structural features defined the charge and spin-state of the metal and the radical semiquinone state of the ligands. The complex lies at the center of a redox series with members related by reversible electron transfer steps at the quinone ligands without a change in metal charge. Intermediate members of the series related by stepwise reduction of the SQ ligands have been shown to be Type 2 mixed-valence complexes with Cat→SQ intervalence transfer transitions appearing in the NIR. The related complex of iron, $Fe^{III}(Cl_4SQ)_3$, has been shown to contain *hs*-Fe(III) and undergoes three-electron reduction at the ligands to form $[Fe^{III}(Cl_4Cat)_3]^{3-}$. The appearance of the CV is quite different from that of $Cr^{III}(Cl_4SQ)_3$ as an envelope of charge over a narrow potential range of 330 mV. Spectral properties of intermediate complexes formed upon one- and two-electron reduction of $Fe^{III}(Cl_4SQ)_3$ fail to show IV-transfer transitions typical of Type 2 species. Conproportionation constants (Kc) calculated from electrochemical data are in the 7×10^2 range for the iron complexes, compared with values of 10^7 for the Cr analogs. Interligand coupling through *hs*-Fe(III) is considerably weaker than for Cr(III) resulting in three reversible electron transfer steps at +0.705, +0.547 and +0.371 V (vs Ag/AgCl).

Reactions of $Fe^{III}(Cl_4SQ)_3$ in aqueous solvents suggested water oxidation activity. The addition of $Fe^{III}(Cl_4SQ)_3$ to 95% ethanol led to an immediate reaction with the formation of $[Fe^{III}(Cl_4Cat)_3]^{3-}$ and a decrease in pH. A reaction with PPh_3 in aqueous ethanol was observed to form $Fe^{III}(HCl_4Cat)(Cl_4Cat)(OPPh_3)_3$ as an unexpected product. Other reactions with oxygen-atom acceptors have been studied and, in the absence of pH control, iron oxide and tetrachlorocatechol form over the period of hours. Electrocatalytic substrate oxidation reactions have been studied with the reoxidation of $[Fe^{III}(Cl_4Cat)_3]^{3-}$ to $Fe^{III}(Cl_4SQ)_3$ and reactions with $H_2{}^{18}O$ have been used to show that water is the source of oxygen. As a reaction involving ligand-based electron transfer, without a change in charge at the metal, this may be classified as an example of “nonclasssical” two-electron water oxidation.

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Oral Presentations

CRYSTAL STRUCTURE AND THERMAL BEHAVIOUR OF ISOSTRUCTURAL BINARY COMPLEXES $[Rh(en)_3][Fe(CN)_6]$ AND $[Rh(en)_3][Co(CN)_6]$

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Investigations of the thermal behavior and other properties of binary complex compounds (BCC), i.e. precursors of bimetallic materials, generally involve studying their crystal structures because the latter is one of the chief factors affecting the BCC thermal behavior.

In this work the BCC $[Rh(en)_3][Fe(CN)_6]\cdot 2H_2O$ (**I**) and $[Rh(en)_3][Co(CN)_6]\cdot 2H_2O$ (**II**) have been prepared and characterized by the X-ray diffraction, crystal optic, elemental, and thermal analyses.

The BCC crystal structures **I** and **II** are described within the monoclinic crystal system, are insular and isostructural. The coordination environments of rhodium, iron and cobalt atoms represent virtually regular octahedrons. The cation octahedron consists of six nitrogen atoms belonging to three ethylenediamine cycles with Rh-N bond lengths of about 2.09 Å, whereas the anion coordination octahedrons consist of six carbon atoms belonging to six cyano groups with Fe-C and Co-C bond lengths of 1.95 and 1.91 Å, respectively. The crystal phases **I** and **II** (space group $P2_1/n$) have the following characteristics: a = 8.30052 (16); b = 16.6234 (4); c = 14.6987 (3)Å; V = 2027.60 (7) $Å^3$; Z = 4; d_{calc} = 1.740 g/cm^3 (**I**); a = 8.2699 (16); b = 16.5393(4); c = 14.6970 (3) Å; V = 2009.57 (7) $Å^3$; Z = 4; d_{calc} = 1.766 g/cm^3 (**II**).

The thermograms of both BCCs are extremely similar in both oxidative and inert atmospheras (air and argon), with the only difference being that the II decomposes at higher temperatures. In the air atmosphere after the removal of the ligands, $Rh+1/2Fe_2O_3$ и Rh+Co (460°C) and Rh + Co(500°C) are formed respectively, which upon further heating to 1000°C are converted to $RhFeO_3$ and $RhCoO_{1.5}$, and in the argon atmosphere, the residues from calcination correspond to $Rh+1/2Fe_2O_3$ and Rh+CoO.

For both BCC samples during thermolysis in an oxidizing atmosphere the composition of the gas phase was determined by mass spectrometry. Uniform gaseous products for both BCC are: H_2O, CO/N_2, HCN were fixed, and for **I** NH_3, en and CO_2/N_2O, for **II** other products were not detected.

In general, it can be said that the similarity of the thermal behavior of BCCs **I** and **II** is apparently a consequence of a complete analogy in their structure, but the difference – in the presence of cobalt as central ion.

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HALOGENOIRIDATES(IV): CRYSTALLINE AND ELECTRONIC STRUCTURE, THERMAL AND BARIC PROPERTIES

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Nowadays paramagnetic complexes of iridium(IV) are considered as promising building blocks for design of electronic and magnetic quantum materials [1]. The previous active study of halogenoiridates refers to the early period of the formation of chemistry of coordination compounds. These compounds were synthesized and described at a time when modern research methods were not available, and therefore there is a large gap in the data describing their crystalline and electronic structure, thermal properties. Baric properties have not been studied previously.

We synthesized fluorine, chloro- and bromo- iridates(IV) of alkaline, alkaline-earth metals and some other cations (NH_4^+, Y^{3+}, Ag^+). Some of the compounds were obtained for the first time. In most cases, single crystals have been grown and the structures have been solved by the X-ray diffraction method, while the structural characteristics of the others by the Rietveld method on powder patterns have been refined. Compounds containing water are generally double complex salts. For anhydrous samples the presence of polymorphic modifications was found.

The thermal properties of halogenoiridates primarily depend strongly on the nature of the ligand and, secondly, on the presence of water. Anhydrous fluorocomplexes do not undergo oxidation-reduction conversions; "aqueous" fluorides can form small amounts of metallic iridium and iridium(IV) oxide upon decomposition. Chloroiridates containing water lose it stepwise, and then decompose in accordance with the scheme proposed by Sinitsyn [1]. By a similar scheme bromocomplexes are decomposed.

Recent theoretical predictions of “unprecedented proximity” of the electronic ground state of iridium fluorides to the SU(2) symmetric $j_{eff} = 1/2$ limit [3], relevant for superconductivity in iridates. L_3-edge resonant inelastic x-ray scattering investigation were been performed for $M_2[IrF_6]$ (M = Rb, K, Na, Cs, 1/2Ba). Results are consistent with the Mott insulating scenario predicted by Birol and Haule, but we observe a sizable deviation of the $j_{eff} = 1/2$ state from the SU(2) symmetric limit (ESRF HC-2571 and ESRF HC-2710).

Baric investigations were carried out for $Rb_2[IrF_6]$, $K_2[IrF_6]$, $K_2[IrCl_6]$, and $K_2[IrBr_6]$ up to 40-55 GPa. Data are obtained on the change in the geometry of the coordination anion from the pressure. In the case of $Rb_2[IrF_6]$ up to 50 GPa, no signs of changes in the crystal structure are observed; $K_2[IrCl_6]$ has two phase transitions at 2 and 15 GPa; $K_2[IrBr_6]$ have signs of a phase transition at 0.2-2 GPa (ESRF HC-3095).

The data obtained form the basis of knowledge for the use of both halogenoardates and other iridates as promising materials with unique electrical properties.

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[3] T. Birol, and K. Haule, *Phys. Rev. Lett.*, **2015**, *114*, 096403.

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ANYSOMETRIC TRIS(B-DIKETONATE) LANTHANIDE ADDUCTS

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Coordination compounds of lanthanides(III) are an interesting class of substances that can be used as efficient luminescent materials for various applications [1]. Their main property and advantage is the effective luminescence provided by the Ln(III) ion and not by organic ligands. In such compounds, a central ion possesses poor absorptive capacity, so excitation energy is transferred through surrounding organic ligands ("antenna effect"). The important advantage of anysometric lanthanide complexes is their high solubility in organic solvents and capability to incorporate, in view of some structural resemblance, namely, possessing an anisotropic form and the presence of terminal alkyl chains, into the structure of the conductive conjugated polymers [2].

A new series of anysometric Ln(III) tris(β-diketonate) adducts with different Lewis bases has been synthesized (fig. 1). The structural features of the presented compounds allow to create vitrified optically isotropic and self-organized films with effective luminescence (fig. 2).

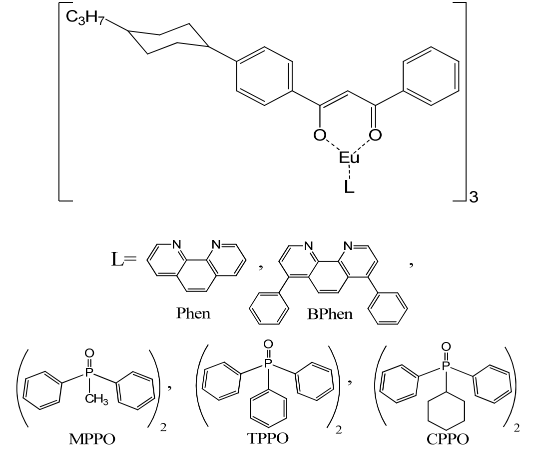

Figure 1. Chemical Structures of Eu(III) Complexes

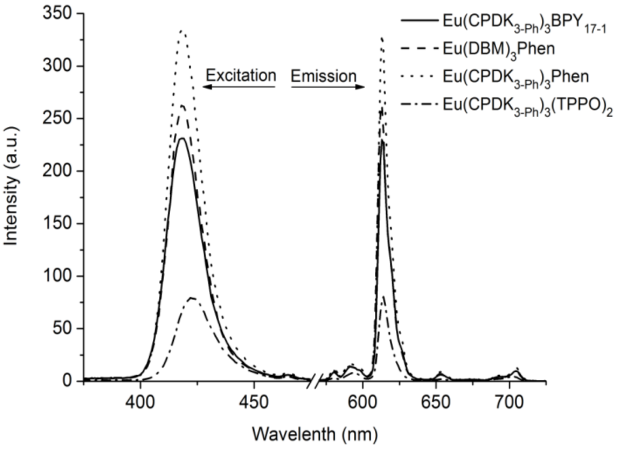

Figure 2. The excitation and luminescence spectra of Eu(III) complexes

Anisometric analogues of well-known Eu(DBM)$_3$Phen complex have been studied to show that the geometry of a complex may exert considerable influence on the luminescence properties of the blends including a conjugated polymer and a Ln(III) complex. It is shown that in blends of PVK and some studied complexes the emission intensity per a complex mole increased by 3.9 times, and intrinsic quantum yield increased by 40% in comparison with individual compounds. The presence of alkyl and cyclohexane substituents in the structure of β-diketone ligands, in contrast to commercial DBM, hinders crystallization, inhibits formation of defects in the structure of films, and demonstrate good dispersibility in PVK films.

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[2] A. Knyazev et al., *Inorg. Chem,* **2017**, *56(11)*, 6067-6075

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3a,6a-DIAZA-1,4-DIPHOSPHAPENTALENE (DDP) – UNIQUE SELF-TUNING LIGAND IN COORDINATION AND ORGANOELEMENT CHEMISTRY

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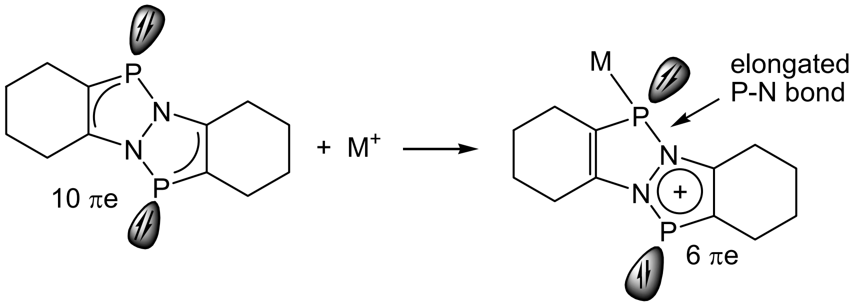
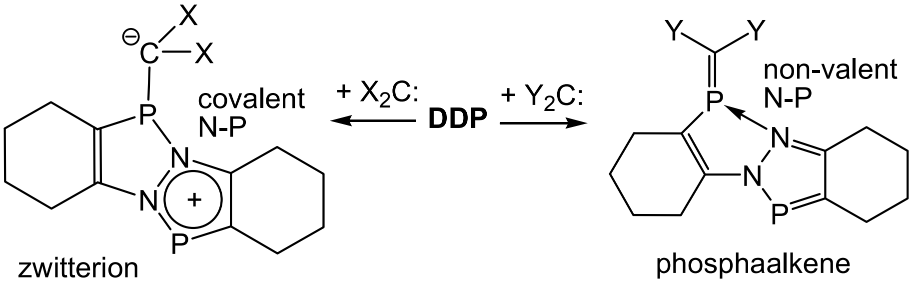
The coordinating activity of DDP is much higher compared to known azaphospholes [1]. This is due to a new type of complexation, such that the lone pair at the phosphorus atom is not involved in the coordination. Instead, the 10π-electron system provides two electrons for the formation of the P→M coordination bond, as we have shown by examples of Hg^{II}, Sn^{II}, Ge^{II}, and Lewis acids (Ph_3B, InI_3).



DDP upon coordination can have an induced high density of negative charge on one of phosphorus atoms due to charge transfer from one phosphorus atom to the other and 6π aromatization of one of the heterocycles. The structure of DDP frame is changed upon coordination. Particularly, X-ray experiment and DFT calculations show elongation of N-P bond. In a special case – complexation of DDP with carbenoids R_2C: - two ways are possible:



- formation of zwitterions (when CX_2 group possesses electron-delocalizing properties) and phosphaalkene, when CY_2 groups do not prone to e-delocalization.

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MONOIMINOACENAPHTHENONES (MIAN) – NEW TYPE OF LIGANDS IN COORDINATION CHEMISTRY: REDOX ACTIVITY AND CHELATING POSSIBILITIES

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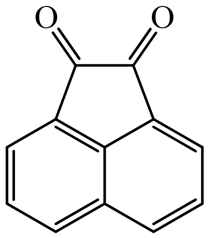
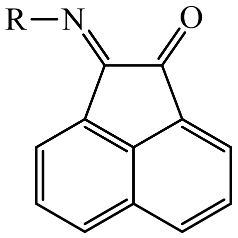
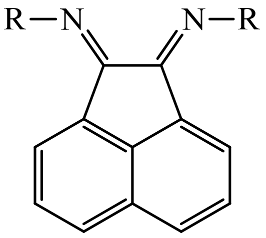
Monoiminoacenaphthenes (MIAN) lie between acenaphthenequinone and acenaphthene-1,2-diimines. Correspondingly, the MIAN steric properties and redox activity are intermediate in this series, suggesting the formation of complexes of new structural types. However, only few examples of metal complexes with MIAN ligands have been known so far.[1, 2]



acenaphthenequinone



mono-iminoacenaphthenone (MIAN)



acenaphthene-1,2-diimine

Here we report on syntheses of a wide number of complexes bearing neutral and reduced 2-(2,6-diisopropylphenylimino)acenaphthen-1-one (dpp-MIAN). The redox properties of this class of ligands have been studied by carrying out chemical reactions with reducing agents (alkali, alkaline earth and rare earth metals, and halides of elements in a low oxidation state), cyclic voltammetry, ESR-spectroelectrochemical reduction and DFT calculations.

We also provide data on the reversible dimerization of MIAN ligands in complexes of transition and non-transition elements, and show how to control this phenomenon.

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VARIETY OF METAL-ORGANIC FRAMEWORKS IN THE ZINC NITRATE-2,5-THIOPHENEDICARBOXYLIC ACID SYSTEM

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Metal-organic frameworks are one- (1D), two- (2D) or three-dimensional (3D) structures composed of metal ions or cluster/polynuclear fragments connected by bridge organic ligands. During last decades these inorganic materials have been attracting great attention of scientists from all over the world because of variety of properties and potential applications in many fields of chemistry and physics as adsorbents, catalysts, sensors, etc. Variety of properties is conditioned by variety of possibilities to influence the formation of frameworks with definite composition, spatial structure or functionalities by choosing a proper metal or ligand or appropriate synthesis conditions.[1]

In this work we obtained eleven new metal-organic frameworks in the zinc nitrate-2,5-thiophendicarboxylic acid system varying synthesis conditions (temperature and duration of a solvothermal synthesis, reagent ratios, solvent composition, medium pH, etc.). After optimization of synthesis conditions seven of these compounds were isolated in a pure phase.

Two interesting four-component compounds $Zn_{12}(EG)_6(tdc)_6(dabco)_3$ (**1**) and $Zn_{12}(G)_6(tdc)_6(dabco)_3$ (**2**) (EG = ethyleneglycol, tdc = 2,5-thiophendicarboxylic acid, dabco = 1,4-diazabicyclo[2.2.2]octane, G = glycerol) were synthesized in a solvent of a complicated composition (N,N-dimethylformamide (DMF), acetonitrile, EG or G) at high temperature (130 °C) and basic pH. The building block of these metal-organic frameworks consists of 12 Zn^{2+} ions connected by deprotonated EG/G molecules: six of these Zn^{2+} ions have a coordination number (c.n.) 4 with two additional positions occupied by tdc connecting the building blocks in a 2D net, other six Zn^{2+} ions have c.n. 5 with one more position occupied by dabco which connects the 2D layers in a 3D structure. In a basic medium a bimetallic metal-organic framework $Na_2Zn(tdc)_2(DMF)_2$ (**3**) was obtained with almost 100 % yield. Addition of dimethyl ammonium chloride in the reaction medium allowed us to get an anionic metal-organic framework $[(CH_3)_2NH_2]_2[Zn_3(tdc)_4]$ (**4**). This material was used to adsorb heavy metal ions from solution. At moderate synthesis temperature (90 °C) $Zn_3(tdc)_3(DMF)_3$ (**5**) was formed. Low synthesis temperatures provide the formation two metal-organic frameworks $Zn_2(tdc)_2(dabco)$ (**6**) and $Zn_6(tdc)_6(dabco)_2(DMF)_2$ (**7**) with hexagonal and triangle (**6**) and distorted hexagonal and triangle (**7**) channels. The luminescence and adsorption properties of the obtained materials were studied.

The variety of obtained compounds in the zinc nitrate-2,5-thiophendicarboxylic acid system clearly demonstrates that synthesis of metal-organic frameworks is very fine science, and sometimes a slight variation of synthesis conditions may results in a new compound completely different in chemical composition and spatial structure.

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Acknowledgements – This investigation is supported by the Russian Science Foundation (project № 14-23-00013).

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SYNTHESIS SUPRAMOLECULAR SYSTEMS OF PORPHYRINS AND PTHALOCYANINES WITH CYCLODEXTRINES

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The construction of supramolecular systems based on the two or more molecules with different properties is a very attractive approach in the building multifunctional materials devoted to applications in different fields. One of these systems intensively studied in the recent years, are conjugates of porphyrins (Por) and phthalocyanines (Pc) with cyclodextrins (CD). The specific biological (tendency to accumulate in cancer tissues) and spectroscopic (high molar absorption, strong fluorescence and good quantum yields) properties of porphyrins and phthalocyanines have been predetermined their medical applications mostly focused on photodynamic diagnostic and photodynamic therapy (PDT). The one of the main problem to use porphyrins and their analogues as photosensitizers is tendency to aggregate in water solutions because of their large aromatic structure. The considerable use of CDs as individualized entities in medicine is undeniably and have a long history. Nevertheless, in the last few years because of the unique capability of forming inclusion complexes in the inner cavities and many other favorable physicochemical and biological properties, CDs and their derivatives have been applied in drug delivery systems to enhance the solubility, stability and absorption. More recently, covalently linked porphyrin-cyclodextrin (Por-CD) and phthalocyanin-cyclodextrin (Pc-CD) conjugates have become new attractive supramolecular systems for the study of biological processes and biomimetic systems and application as drug carriers with recognition and controlled release properties. Moreover, the presence of tetrapyrrolic macrocycle in conjugate with cyclodextrin gives the possibility of additional accurate spectroscopic detectability of the supramolecular systems before and after complexation with guests into cyclodextrin cavities.

The analysis of the experimental data of the synthesis both Por-CD and Pc-CD conjugates shows that the synthetic approaches to prepare most conjugate base on relative difficult ways containing mostly multistep transformations of the cyclodextrins and/or using expensive or synthetically uneasy tetrapyrrolic precursors.

In this review we are show know in detail synthetic approaches to synthesized porphyrin-cyclodextrin and phthalocyanin-cyclodextrin conjugates in which macrocycle and cyclodextrin are covalently linked. Moreover, we present here our study about new approach to simple preparation Por-CD conjugate.

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AMMONIUM PEROXOTELLURATES. SYNTHESIS, STRUCTURE AND APPLICATIONS.

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Tellurium peroxocomplexes were isolated from aqueous hydrogen peroxide solutions and characterized by X-ray analysis, powder diffraction, Raman spectroscopy and thermal analysis [1]. Peroxotellurate anions in isolated ammonium peroxotellurates contain a binuclear $Te_2(\mu\text{-}OO)_2(\mu\text{-}O)$ fragment with one μ-oxo- and two μ-peroxo bridging groups.

This work describes the first-time synthesis of reduced graphene oxide (rGO) supported tin telluride (cubic β-SnTe) and evaluation of its performance as anodes in sodium- and lithium-ion batteries. The SnTe@rGO composite was synthesized by the hydrogen peroxide route [2] from Sn(IV) [3,4] and Te(VI) [1] peroxocomplexes using a wet chemistry protocol and not relying on the overly expensive ball milling or the use of autoclaves. The Te(VI) precursor used in this study is less toxic and less volatile compared to the reduced forms of tellurium, which is an additional incentive for the preference of the hydrogen peroxide route for tellurium processing. The hydrogen peroxide route is very effective for p-block element oxide and sulphide composites preparation [5-8].

SnTe@rGO electrodes exhibit exceptionally high reversible volumetric charge capacities above 3000 and 1300 mAh cm^{-3} at 100 mA g^{-1} charging rate for lithium and sodium ion batteries, respectively, and they show very good rate capabilities retaining 68 and 60% of the respective capacities even at 2000 mA g^{-1} charging rate. The superior electrode performance is attributed to the high conductivity of Te, the mechanical buffering of volume changes by the large row-V host elements, the elasticity of the reduced graphene oxide support, and the very low specific equivalent volumes involved in sodiation and lithiation of SnTe.

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ACENAPHTHENE-1,2-DIIMINE METALLOCOMPLEXES FOR PRODUCING OF BIORESORBABLE POLYMERS

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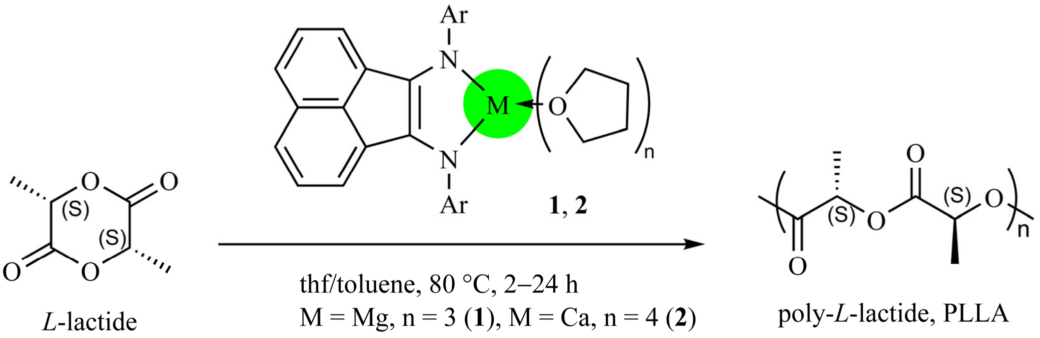
One of the modern trend of bioplastic materials development is bioactive stuff which exceeds metals and ceramics with biodegradability, capacity for functionalization and production technological effectiveness. Osteoplastic materials which are based on biocompatible polyesters have to be possessed of strength, resorbability, osteoconductivity, osteoinductivity. We propose new effective catalysts for ROP of L-lactide based on magnesium and calcium complexes with α-diimine redox-active ligand dpp-bian (Ar=2,6-diisopropylphenyl).



L-lactide

thf/toluene, 80 °C, 2–24 h
M = Mg, n = 3 (**1**), M = Ca, n = 4 (**2**)

poly-*L*-lactide, PLLA

Compounds **1** and **2** can be easily prepared by direct reduction of free diimine dpp-bian with corresponding metal in THF [1]. Reactions of complexes **1** and **2** with L-lactide in THF are accompanied by oxidation of the ligand to the radical anion. In case of magnesium complex **1** the agreement between the experimental and theoretical values of the molecular mass of poly-L-lactide becomes better at high monomer catalyst ratios. Calcium complex **2** demonstrates lower reaction rate compared to the same for **1**. However compounds **1** and **2** reveal high activity in ROP of L-lactide with controllable formation of high molecular weight polymer (up to 200 kDa). The poly-L-lactide prepared using complex **1** exhibits no cytotoxicity in experiments with human dermal fibroblast cultures [2]. Preliminary studies on animals show complete resorption of the implant material with replacement of the defect with bone tissue.

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POLYFUNCTIONAL CATECHOLATO COMPLEXES OF TRIARYLANTIMONY(V)

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The combination of redox-active ligands of o-quinone type with triarylantimony allows to extend redox-properties of the corresponding complex compounds (catecholates, o-amidophenolates) and, in some cases, leads to new unique chemical properties, for example, a reversible binding of molecular oxygen in mild conditions [1-4]. Such type compounds can serve as radical scavengers, inhibitors of radical chain processes like peroxidation of lipids etc [5-8]. The redox behaviour of complexes depends on the electronic properties of substituents in redox-active ligand as well as on the nature of functional groups at the central antimony atom [9-11].

In order to increase the functionality of triarylantimony(V) catecholato complexes we have synthesized a number of 3,5-di-tert-butyl-catechols and the corresponding o-quinones containing a wide raw of functional groups in the 6th position of carbon ring in catechol/o-quinone, and investigated the structure, redox-properties of the corresponding antimony(V) catecholato complexes.

Here we report on the synthesis, investigation of structural features, electrochemical properties of new functionalized catecholato complexes of triarylantimony(V).

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THEORETICAL STUDIES IN CHEMISTRY OF METAL COMPLEXES FEATURING ISOCYANIDE AND NITRILE LIGANDS: REACTIVITY, CATALYSIS, AND NON-COVALENT INTERACTIONS

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Quantum chemical calculations allow the solution of different issues, which often very difficult or even impossible to study experimentally. These issues include, e.g., composition and energies of molecular orbitals, charge distribution, nature of chemical bonding and inter/intramolecular interactions, conformational transitions and rotation barriers of functional groups, elementary reaction steps and their driving forces, thermodynamic and kinetic factors.

Our group conducts a multidisciplinary research at the intersection of experimental and theoretical chemistry. We applied modern advanced quantum chemical methods (*ab initio* and DFT) as well as some special techniques (QTAIM, NBO, CDA, BSSE-correction, isodesmic reactions, HSAB principle theoretical model, Hirshfeld surface analysis) upon studies of organometallic and coordination compounds, their reactivity, and catalytic transformations.

Our particular interest include (*i*) the nucleophilic addition and cycloaddition reactions involving substrates featuring the C≡N moiety, viz., isocyanide and nitrile ligands (mechanisms, driving forces, kinetics and thermodynamics, isomerism, properties of coordination bonds, orbital/charge factors) [1–2]; (*ii*) photophysical properties of platinum group coordination compounds [3]; (*iii*) studies of non-covalent interactions, viz. hydrogen, halogen and chalcogen bonds, anagostic and metallophilic interactions, stacking [4–6].

The obtained results are potentially useful for biochemistry (understanding the nature of proteins folding), medicine (synthesis of antibacterial, antiviral, and antitumor drugs), chemical industry and technology (catalysis of cross-coupling and multicomponent reactions), materials science (design of smart materials with valuable electronic, thermal, magnetic and optical parameters).

In this report, main results of our group for the past five years will be analyzed.

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COPPER (II) COMPLEXES OF PYRIDYL CONTAINING PHOPSHOLANE OXIDES

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Complexes of pyridyl containing phosphine oxides are attractive as applicants for catalitycal processes such as olefins epoxidation [1], radiopharmaceuticals [2], and as emitters sourses for OLED devices [3]. In spite of wide range of application fields, complexes of pyridyl containing phosphine oxides are represented by a scattered variety of transition metal-ions. In another hand it is observed that this class of ligands mainly represented by pyridyl diphenyl phosphine oxide. Thus, the synthesis of novel P-oxides of phosphinopyridines and their complexes with transition metals, and the study of their properties became an interesting opportunity for organoelement and coordination chemistry.

Recently we’ve synthesized P-oxides of phospholanopyridines and their complexes with Ni(II) [4]. Herein we represent a synthesis of novel copper (II) complexes based on these perspective hybride ligands.

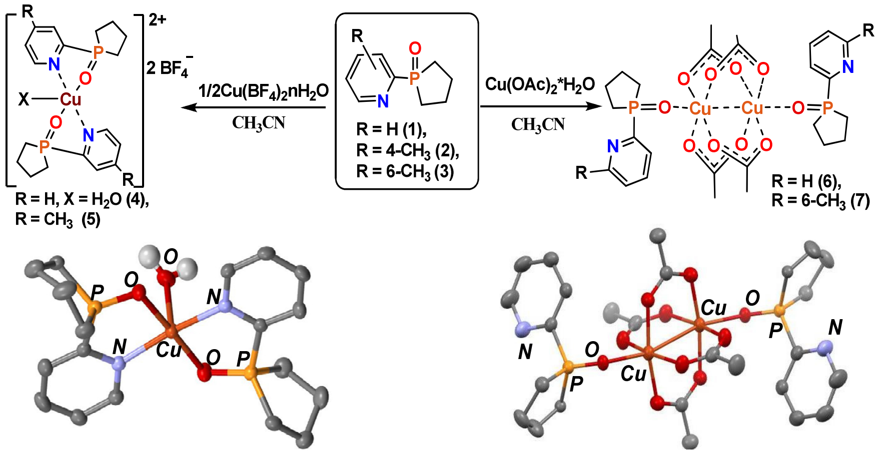

*Fig. 1. Molecular structure of cation of complex **4***

*Fig. 2. Molecular structure of complex **6***

Scheme 1. Copper (II) complexes of pyridyl containing phospholane oxides.

Interaction between ligands **1 - 3** and copper (II) salts in different molar ratio resulted to complexes **4 – 7** (Scheme 1). The structure of compounds **4 – 7** was detremined by IR-, ESR-spectroscopy, mass-spectrometry, elemental and thermogravimetric analysis, and X-Ray diffraction (*Fig. 1* and *2*). Pyridyl containing phospholane oxides exhibit different coordination modes in obtained complexes **4 – 7**: N,O-*bis* chelate (**4, 5**) or O-monodentate (**6, 7**) depending on initial copper (II) source. Metal ions in obtained complexes represent two types of geometry: square-pyramidal or square-planar (without Cu…Cu interaction). All complexes demonstrate well solubility in common organic solvents and also in water that makes them perspective candidates for catalytical processes, alcohols oxidation as example.

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SELF-ASSEMBLING TRITON-BASED MICELLAR COORDINATION CLUSTERS: FORMATION FEATURES, STRATEGIES OF MODIFICATION AND APPLICATION FOR HYDROPHOBIC MOLECULES SOLUBILIZATION

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Low aqueous solubility of many compounds is usually a major obstacle in the development of therapeutic agents, drug delivery, sensing or during investigation of properties of materials. There are many approaches commonly used to enhance the solubility of poorly soluble drugs exist. Micellar solubilization is a widely used alternative for the dissolution of many hydrophobic compounds. However, not always using of pure micellar aqueous solutions is suitable for solubilization. The concept of micellar conjugation followed by clusters formation showed a great potential in the aspect of hydrophobic compounds solubilization beyond their solubilization limit. With the aim to extend the application fields of micellar clusters, we explored a new features and schemes for micellar clusterization for some detergents of Tritons group. Proposed strategies allowed us to sufficiently increase solubility of some hydrophobic toxic compounds, anticancer peptide drug conjugates and fluorescent dyes in aqueous media, so that the latter even may serve as micellar clusterization support agents. Hydrophobic fluorescent compounds-loaded micellar complexes demonstrate good optical response in aqueous media without crystallization beyond their solubilization limit in aqueous phase. We also showed that clusters are also very tunable and can be modified by various nanoparticles of noble metals or magnet nanoparticles. Therefore, the conception of micellar clusters modifying allowed to obtain various nanosystems, such as fluoromagnetic clusters or drug-loaded composites that open a new horizons for new advanced functional materials creation.

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DFT STUDY OF DIAMAGNETIC TRANSITION METAL COMPLEXES WITH RADICAL-TYPE REDOX-ACTIVE LIGANDS

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Transition metal coordination compounds with redox-active ligands play an important role in biological processes, serve as efficient catalysts of various organic reactions, represent promising basis for the development of new polyfunctional materials. The possibility of controlling magnetic properties determined in these complexes by unpaired *d*-electrons of transition metals and radical-anion forms of redox-active ligands opens the prospects of using them in molecular electronics and spintronics.

The principal methods of studying such type paramagnetic compounds are X-ray structural analysis, magnetochemistry and EPR spectroscopy, which allow in most cases to make an unambiguous conclusion about their structure and the distribution of unpaired electrons. At the same time there are complexes, in which deviations of geometry parameters of the ligands from those expected for the specific oxidation level are observed and strong antiferromagnetic exchange interactions resulting in diamagnetism prevent from applying magnetic measurements for the ascertainment of metal and ligand states.

Quantum-chemical study is one of the reliable approaches of investigating coordination compounds with unusual magnetic properties. A comprehensive analysis of the calculation results of the isomers with different electronic states and also model simplified structures makes it possible to explain the magnetic properties of such systems.

This report will outline the results of density functional theory calculations of diamagnetic copper, nickel and cobalt complexes, for which the experimental studies have not succeeded in determination of the electronic states of the metal and redox-active ligand. Detailed study of the electromeric forms and exchange interactions between unpaired electrons enables to clarify the observed behaviour of the considered compounds.

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QUANTUM-CHEMICAL INSIGHT INTO MAGNETIC BEHAVIOR OF IRON AND COBALT DIOXOLENE COMPLEXES

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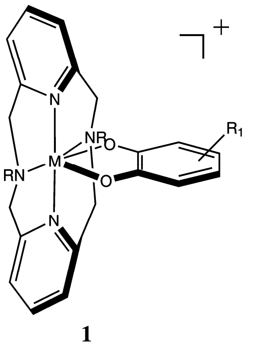
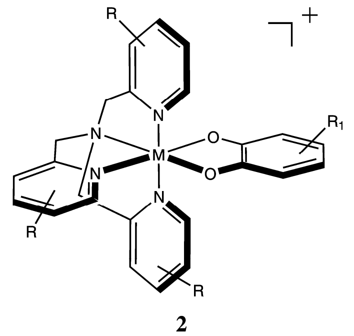
Coordination compounds with switchable magnetic properties can find applications in molecular electronics and spintronics. The most versatile mechanisms driving the changes of spin states of transition metal complexes are spin-crossover (SCO) caused by the electronic rearrangement within a metal ion between its low-spin and high-spin states [1] and valence tautomerism (VT), or redox-isomerism, which is an intramolecular process consisting in reversible electron transfers between a metal ion and a redox-active ligand [2].

Recently, cationic cobalt-dioxolene complexes with ancillary tetraazamacrocyclic ligands exhibiting VT [3-5] and SCO transitions [6] have been synthesized. The interpretation of magnetochemical data in such compounds is complicated by coexistence of two processes: conversion of a molecule to the high-spin state and the exchange interactions between unpaired electrons of the semiquinonate form of the redox-active ligand and the metal ion.

To elucidate the magnetic behavior and the possibility of the occurrence of SCO and/or VT rearrangements, density functional theory UTPSSh/6-311++G(d,p) quantum-chemical calculations of the complexes **1** [7] and **2** have been performed.



1



2

M= Fe, Co; R=H, CH_3, t-Bu; R_1= Cl

It has been shown that the type of spin-state switching mechanism and the nature of the exchange interactions between the metal center and semiquinone depend on the ancillary nitrogen-centered ligand and the substituents in dioxolene.

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THEORETICAL STUDY OF THE AXIAL LIGANDS EFFECT ON THE GEOMETRY, SPIN-STATES AND ABSORPTION SPECTRA IN MONONUCLEAR RUTHENIUM, IRON AND COBALT QUATERPYRIDINE COMPLEXES

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In this research, we study the [M(dcqtpy)E_2] complexes, where M is Ru(II)/(III), Fe(II)/(III) or Co(II)/(III), dcqtpy is 4′,4′′-dicarboxyl-4,4'''-dimethyl-2,2′:6′,2′′:6′′,2′′′-quaterpyridine ligand, and E is I^-, SCN^-,Cl^-, NCS^-, CN^-, NO^- ligands. DFT and time-dependent DFT (TD-DFT) calculations were performed on the full sequence of generated [M(dcqtpy)E_2] complexes, by changing type of metal (M) and its oxidation state and the spin-state of the complex. The electron structure, total and relative energy of different spin-states, as well as absorption spectrum were calculated by optimizing functional and basis sets to reach a good match with experimental data available in the literature.

The calculated relative stabilities of high spin (HS) and low spin (LS) states depend on the amount of Hartree−Fock (HF) exact exchange used in the hybrid functional [1], such as B3LYP. In this case the amount of HF exchange is the subject of some variation, when describing the ionic complexes of the first-row transition elements, because such hybrid functional often incorrectly favors the HS state as the ground state [2].The values of ΔE_{HS-LS} were calculated for iron and cobalt coordination compounds taking different amount of HF exact exchange in the B3LYP functional, namely, 5, 10, 15, 20 and 25%.

The dependences of ΔE_{HS-LS} on HF exact exchange for Fe(II)-based complexes are matching well. It is evident from the plot, that $C = 0.15$ is optimum value of HF for calculation of iron-based complexes in different spin-states, in accordance to what has been reported by other authors [3]. The dependency lines for compounds of Fe(III) and Co(III) are arranged in parallel to each other in respect to the difference in the ligand field strength created by the CNS ligand coordination arrangement (from isothiocyanate to thiocyanate). The calculated energies for HS and LS states for Ru(II) complexes show that the most stable spin state is that of LS. Respective ΔE_{HS-LS} value is higher than 50 kcal/mol. The oxidation of Co(II) complexes to Co(III) form with CNS ligands leads to the spin change form HS state to LS states. Theoretical study of iron(II) coordination complexes revealed the profitableness of the HS state for E = Cl^-, NO^-, NCS^-, and I^- and the LS state for E = CN^-. The HOMO—LUMO energy difference calculated for the complexes in question increases in the following order of E: $NO^- < NCS^- < Cl^- < I^- < CN^-$.

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REACTIONS OF COORDINATED LIGANDS AND *E,Z*-IZOMERISATION OF OXIMES IN URANYL COMPLEXES

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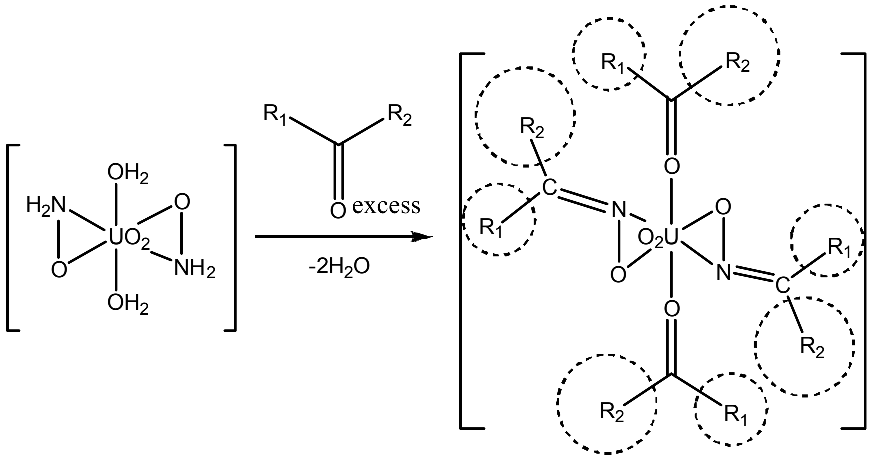
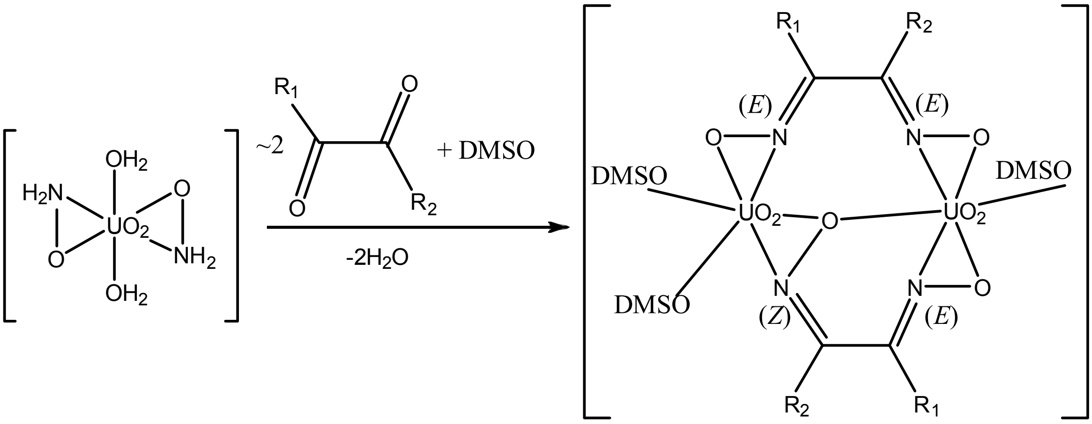
For the first time, the reactions of coordinated ligands in uranyl complexes, i.e., condensation of coordinated hydroxylamine with aldehydes and ketones of various structures, have been studied. It was shown that these interactions have some peculiarities characteristic of only uranium(VI) coordination compounds.

Thus, when the interaction follows the scheme:



the geometric parameters of the radicals of monocarbonyl compounds (there are 8 of then in this case) located in equatorial plane of the uranyl group of the oximate complex influence the reaction pathway (for example *E,Z*-isomer formation). Nevertheless, an analogous reaction of uranium coordinated hydroxylamine with α-diketones does not depend on the structure of the radicals and results in the formation of one type of uranyl complexes with a double *anti-, amphy-*dioximate bridge fragment, i.e. in the formation of two dioxime isomers (in the ratio 1 : 1).



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NONSTEROTYPEC IDEAS AND PENETRATION OF THE NATURE OF SPECIFIC INTERACTIONS OF THE BACE CLASS OF ORGANIC COMPOUNDS

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At this lecture we substantiate the necessity to proposal a new, non-stereotypic ideas, secured expose of the nature of specific intermolecular interactions and penetration in more deep their understanding and apprehension for substantiation and development of theory their interactions at which scientists were required so march and for which have been turned aspirations:

1. Pentacoordinated carbon atom at specific intermolecular interaction;
2. Novel kind of intramolecular interaction - rivers dative bond between carbon atom C alkyl ligand R and central atom A in complex AR_k C(2e)→A(0e), in its electron structure is consist;
3. Substantiated refusal from sp^3(c)-hybridization model of electron configuration of carbon atom;
4. Existence of essential nondivided $2s^2$(c)-electron pair,
5. All bonding vacancies of a molecule must take part at a formation of specific intermolecular interactions;
6. Enthalpy (entropy) vaporation (sublimation) is interconnected with a number and energy of specific intermolecular interactions.

We expose of the nature of specific intermolecular interactions with participation of pentacoordinated carbon atom and discussed structural energetic conformity of formed structures with a network of specific interactions of ethers with symmetrical and unsymmetrical of their representatives, normal and iso-structural fragments, different cyclic onsides. Received energies of different types of specific interactions are described by low government of their stabilization, Settle dunning on the results of fulfilled thermodynamic analysis of different series ketones, alcohols, acids, aldehydes with different length of chine, saturated and unsaturated ligands, number of carbon atoms at cyclic and neither series compounds, we discuss problem of the determination of energetic parameters of specific intermolecular interactions and the problem of stabilization energies of formed different types of specific interactions and hydrogen bonds at low government rood from the influence different factors.

It was established, that at mane atomic ketones and acetylene alcohols with fragments from four carbon atoms of chain, turned upon by isostructural methyl groups, prototypic proteins, take pat at the distribution of electron density and display exstrastabilysing effect, dependented on decreasing of the contribution of energies at vaporization enthalpy till values of the contribution of energy one methylene group of chine ($\approx$ 5.1 kJ mol^{-1}) and more less (2.53 kJ mol^{-1}).

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THE THERMOCHEMICAL BEHAVIOR OF THE TRISODIUM MONOHYDROGEN-NITRILO-TRIS-METHYLENEPHOSPHONATO-HYDROXYLAMINATO-NITROSYL-MOLYBDATE $Na_3[Mo(NO)(NH_2O)\{N(CH_2PO_3)_3H\}]\cdot 8H_2O$ IN THE COMPACT STATE AND IN THE ADSORBED LAYERS ON THE STEEL SURFACE ACCORDING TO XPS *IN SITU*

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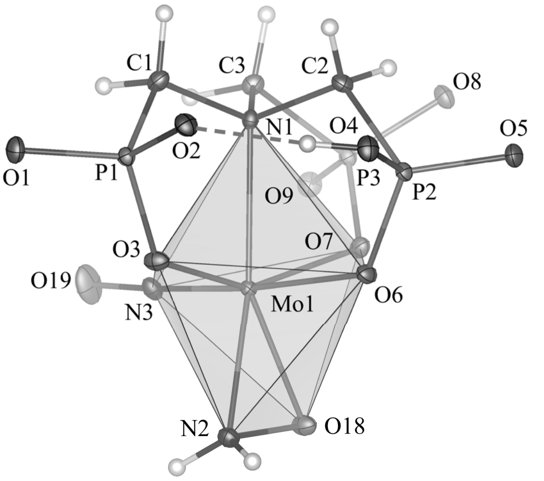
The heteroleptic complex of molybdenum with nitrilotrismethylenephosphonic acid, hydroxylamine and nitrogen(II) oxide $Na_3[Mo(NO)(NH_2O)\{N(CH_2PO_3)_3H\}]\cdot 8H_2O$ (I) was synthesized, isolated and characterized by the single-crystal X-ray diffraction. The thermochemical behavior of it in the compact state and in the adsorbed layers on the steel surface is investigated by XPS *in situ*.



It is established that, despite the formal oxidation state of molybdenum +3, the charge on Mo atom in crystal complexes is near +1*e*. By data of X-ray diffraction, electronic density is mostly localized in the Mo–NO bond, and distribution of electronic density indicates formation of π-bond. Under thermal action the complex (I) eliminate the NH_2OH (at 220–240 °C) and the NO (at 280–400 °C); charge on Mo atom in same time decrease to 0.6*e*.

The adsorption of complex (I) from water solutions on the steel surface is followed by change of a charge on Mo atom to +1.6*e* (or formal oxidation state +5). According to us, it is caused by elimination of NO molecules from corresponding Mo atoms what leads to increase of a charge on Mo atom to +1.6*e*. The molecules of a complex (I) which link to steel surface by the PO_3 groups keep the molecule NO and a charge near +1*e* on Mo atom. Thus at adsorption (I) on the steel surface there is competition between the NO molecule and the steel surface for possession of Mo atom. Under thermal action in the adsorbed layer there is an redox process, leading (at 120 °C) to decrease of charge on the Mo atom to +0.6e (what correspond to formal oxidation state of Mo is +2) and further (over 280 °C) to metal state of Mo. In same time, the iron oxides on the steel surface practically no observed. In our opinion, as reduction agent in this redox process participate are fragments of carbon skeleton of the nitrilotrismethylenephosphonic acid molecule.

The received results show features of behavior of a non-innocent ligand in the adsorption process of a heteroleptic complex on a metal surface, and give an example of the competition between a non-innocent ligand and a metal surface at surface complexation.

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ORGANIC AND METALLOORGANIC SYSTEMS FOR CHEMICAL SENSING IN LIQUID AND GAS MEDIA

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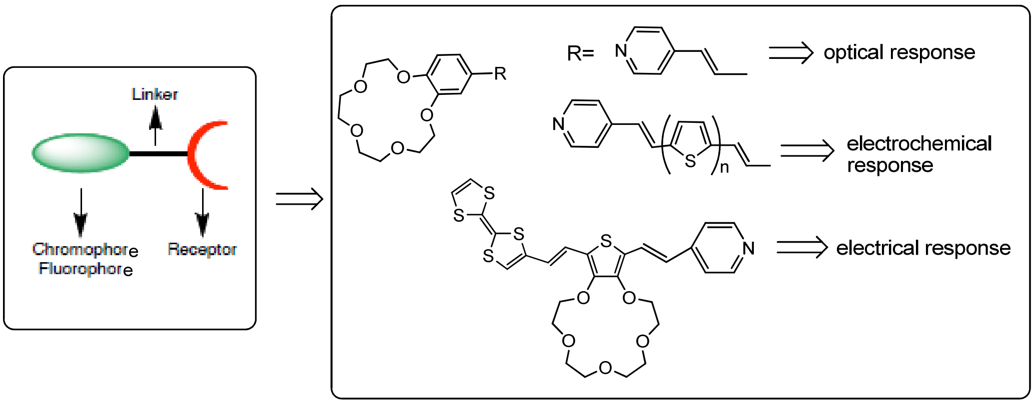
Sensors belong to the modern world like the mobile phone, the compact disc or the personal computer. A chemical sensor is a device that transforms chemical information, ranging from concentration of a specific sample component to total composition analysis, into an analytically useful signal. The sensor element in such device contains receptor group for recognition of analyte and transducer group providing the type of observed signal. Based of signal transduction the sensor groups could be defined as optical sensors, electrochemical sensors, electrical sensors, mass sensitive sensors, magnetic sensors, ect.

In the present research we showed the ways of the applying of proper design to obtain the molecular sensors demonstrated different types of sensor signals.



Donor-acceptor systems, either molecules or supramolecular assemblies such as compounds presented at scheme, have been identified as ideal chemosensors, i.e. components which translate the presence of the analyte into an appropriate optical response, in some cases also into an electrical response. The system is designed such that it is highly modular, i.e. receptor units, linker and chromophore may be exchanged and combined, and even different chromphores may be employed. The chemical, optical and conductive properties of these systems depend strongly on the extent of the donor-acceptor interplay because of charge-transfer, charge-shift, or charge-separation processes. Thus, if either the donor or the acceptor unit interacts with the analyte, in most cases upon complexation, this recognition event leads to a significant change of the optical properties or electrical conductivity, allowing to monitor the process by absorption or emission spectroscopy, conductivity measurements or even by the determination of molecular electronics or photodynamics.

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STRUCTURAL DIVERSITY OF NEW POLYNUCLEAR SELF-ASSEMBLED ORGANOMETALLOGERMOXANES

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Organometallogermoxanes is the new class of polynuclear clusters with atoms of transition and rare-earth metals. From structural point of view compound of this family can be described as closest analogues of organometallosiloxanes [1]. Indeed, silicon and germanium atoms have very close covalent radii, so it is reasonable to expect similar cluster frameworks formed by $RSi(Ge)O_3$ moieties. To prepare the compounds under consideration we used the synthetic route similar to that for organometallosiloxanes. The hydrolysis of $RGe(OR')_3$ (R = Ph, R' = Me) with subsequent addition of transition or rare-earth metal chlorides in polar solvents afforded the number of polynuclear complexes containing several metal atoms and macrocyclic organogermanium ligands [2].

Our X-ray diffraction studies have shown that the nature of transition (or rare-earth) metal atoms is the principle factor responsible for the shape of polynuclear cage and the amount of macrocyclic organogermanium ligands. Thus, herein we report crystal structures of title compounds and discuss their structural diversity in comparison with organometallosiloxanes. In addition, especial attention will be paid to the size of organogermanium ligands. As a rule, the majority of studied organometallogermoxanes contains the decamembered $[RGeO_{1.5}]_5$ ligand while in the case of its silicon analogues the twelvemembered ligand $[RSiO_{1.5}]_6$ is the most abundant. To give insight on the problem of stability of macrocyclic anionic organosilicon and organogermanium ligands and some aspect of their self-assembling theoretical DFT calculations were carried out. The final point of our presentation is the design of coordination polymers and other types of supramolecular architectures constructed via weak interactions (H-bonds or stacking interactions).

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NEW APPROACHES TO THE SYNTHESIS OF CLUSTER COMPLEXES OF MOLYBDENUM, TUNGSTEN AND RENIUM: SYNTHESIS, STRUCTURE AND PROPERTIES

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This work is aimed at finding new, highly efficient approaches to the synthesis of cluster complexes of transition metals and a detailed study of their structure and properties.

In the course of the work, the interaction in the system metal oxide -X-KCN where X = S, Se, Te, P, As, and also in the system metal iodide -X-KCN where X = P, As were studied. A new type of tungsten cluster complexes, namely, bitetrahedral complexes, was obtained for the first time, and pnictogen-containing cluster complexes of these metals were obtained. All the compounds obtained were characterized by IR, NMR, UV-Vis spectroscopy, and the structure was determined by X-ray diffraction on single crystals.

The obtained results are of interest for cluster chemistry as a whole as new fundamental knowledge that can be directed to further research on the possibility of using oxides and halides for other cluster-forming metals.

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NICKEL COMPLEXES WITH P,N AND N,N – LIGANDS AS PROMISING ELECTROCATALYSTS FOR HYDROGEN EVOLUTION

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The nickel, iron, cobalt complexes $[M(PR_2NR_2)_2]^{2+}$, where PR_2NR_2 – 1,5-diaza-3,7-diphosphacyclooctane have proven to be as effective as catalysts for recovery of proton in hydrogen and for reversible oxidation of hydrogen with low overpotentials. A key feature of these catalysts is a positioned pendant amine that functions as a proton relay in close proximity to a vacant coordination site of a redox active metal center, which permits bifunctional activation of H2 during the heterolytic cleavage or formation of the H−H bond. Recently, polypyridyl nickel complex was reported for photocatalytic hydrogen production with high activity. The changing polypyridyl ligands on bis-iminoacenaphtene (BIAN) seems promising step to construction of efficient catalytic system. Furthermore, analogous BIAN-cobaloxime was used as electrocatalyst for hydrogen evolution.

The present work is focused on the seeking of the new representative of hydrogen evolution catalysts based on the combination of aminomethylphosphine and BIAN ligands in nickel complexes.

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FROM MONO- TO POLYNUCLEAR COMPLEXES ON THE BASIS OF OXIME LIGANDS

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The basic task of contemporary chemical synthesis is to obtain materials and technologies based on new compounds with distinct structure and properties. Due to the various possibilities of combining inorganic and organic compounds, the coordination chemistry is a field that obtains new materials with various useful properties. Final products are often characterized by composition, structure, and properties completely different from those predicted (a phenomenon that largely depends on the modeling of synthesis conditions). The combination of transition metals with organic ligands can lead to the emergence of unexpected properties. Inorganic and organic bridges (dipyridine, dicarboxylic, pyridine-carboxylic, pyridine-oxime, oxime-carboxylic etc.) are used for the production of polynuclear compounds with oxime ligands.

There were obtained mono- and polynuclear compounds of manganese(II), cobalt(II/III), nickel(II), copper(II), zinc(II) and cadmium(II) which composition and structure had been determined (IR, NMR, X-ray etc.). There were also obtained *mono*-, *bis*- and *tris*-oxime complexes depending on the nature of the ligands and the synthesis conditions [1,2]. The presence of electron donor atoms and their topology in the ligand molecule as well as the combination of different ligands within the same complex allow the molecular design of the synthesized complexes to be varied and also influence the coordination number of the metal atom. The configuration of the polymer chain of some compounds allows the formation of intermolecular cavities, which lead to obtaining porous materials with adsorbing properties. There has been studied the influence of the solvent nature on the polymer chain formation. The use of new oxime-carboxylic ligands, due to coordination with both oximetic and carboxyl groups (also selectively with different metals) opens perspectives for the synthesis of heterometallic materials.

In order to investigate the ligand competition capacity in the coordinating process to the central atom, the substitution properties of ligands in the complex was studied experimentally and simulation by the quantum-chemical calculation [3]. There was analyzed the coordination capacity of dioxime, monoxime, pyridine, carboxylic, amine etc. groups to the metal atom under competitive conditions. On the basis of both commercial and the new ligands by using block combinations there were assembled binuclear coordinative compounds [4].

The obtained compounds were studied to determine useful properties: growth promoters for some organisms, substances with luminescent properties, mechanical hardness, corrosion inhibitors for steels, etc.

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REACTIONS OF AMIDOXIMES WITH NITRILE LIGANDS

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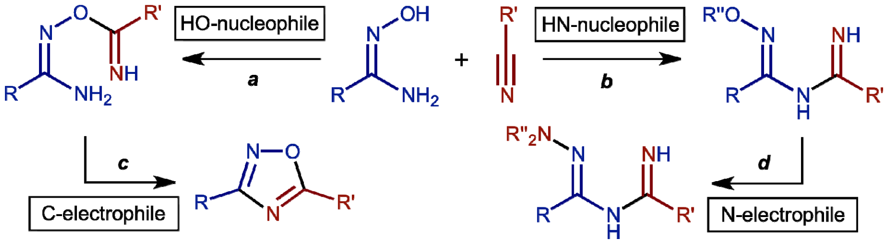
In general, nucleophilic addition to nitriles, RCN, is an attractive route to new organic and coordination compounds with a variety of laboratory and industrial applications. These compounds – in particular, unreactive RCN species bearing donor R groups – should be subjected to additional electrophilic activation in order to perform the nucleophilic addition at the nitrile C atom. One of the most effective routes to achieve this activation is coordination of RCN to a metal center.

In the framework of our project, reactions of amidoximes with nitrile ligands at boron(III) [1], zinc(II) [2, 3], platinum(II) [4-7], and platinum(IV) [8] metal centers were studied. We observed that depending on reaction conditions, nature of metal-bound substrate, and a metal center, amidoximes serve as HO-nucleophiles (***a***) [2, 5, 8], HN-nucleophiles (***b***) [4, 7], C-electrophiles (***c***) [2, 8], and N-electrophiles (***d***) [7]. In addition, amidoximes appeared to be more reactive toward nucleophilic addition to nitrile ligands than conventional ket- and aldoximes due to high +*M* effect of the amide group. For almost all studied reactions postulated mechanisms were confirmed theoretically.



All these reactions allow the preparation of a broad spectrum of coordination and organic compounds and all these transformations will be discussed in the talk.

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MIXED-LIGAND COMPLEXES OF ALKALINE, ALKALINE EARTH AND RARE EARTH ELEMENTS IN CHEMICAL DEPOSITION OF INORGANIC FUNCTIONAL THIN FILMS

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Application of many kinds of functional materials (e.g. superconductors, insulators, high-K materials, MIT layers, multiferroics, optical materials, etc.) in a form of thin films is of high interest. The development of simple, cost effective, easy scalable and universal technique of thin films production remains an important task for material sciences. Nowadays the chemical methods of deposition from either vapor phase or solution of metal-organic precursors, MOCVD and MOCSD respectively, seems to be most perspective, scalable and flexible for fabrication of functional material thin films. MOCSD allows easy and precise control of thin film stoichiometry that is especially important for complex oxide and fluoride materials, but it requires the initial precursor solutions.

Here, we proposed the alkaline (AE), alkaline earth (AEE) and rare earth element (REE) carboxylates (lactates, pivalates, isovalerates, propionates, trifluoroacetates and pentafluoropropionates) as well as beta-diketonates and their mixed-ligand complexes with ancillary neutral donor ligands (polyglymes and polyamines) as metal-organic precursors for MOCSD. The aforementioned homo- and mixed-ligand complexes were synthesized via ligand exchange reactions in either aqua or anhydrous conditions with the high yield and characterized by IR, NMR, elemental analysis, powder and single crystal XRD. Thermal behavior was studied by TGA.

The radius of central ion, anionic ligand nature and denticity of ancillary ligand affects structure and chemical properties of these related compounds. Thus, for AE and AEE complexes with molecular structures and different nuclearity were obtained depending on denticity of ancillary ligands. REE carboxylates demonstrate variety of crystal structure: 1D polymeric for pivalates and propionates; dimeric for isovalerates; dimeric or polymeric structure for light REE lactates and mononuclear motif for other lactates.

Reaction of REE carboxylates with aliphatic N-donor ligands, e.g. diethilenetriamine, is split two ways: formation of mixed ligand complexes and formation of hydroxogels. The DFT calculations and further synthesis show that for non-fluorinated REE carboxylates the hydrolysis is most favorable for REE = Pr-Dy and leads to formation of hexanuclear complexes $[REE_6(OH)_8O_x(Carb)_{10-2x}]$. Fluorinated REE carboxylates are more susceptible to interaction with water traces and polynuclear hydroxocomplexes were isolated even for La. Controlled hydrolysis of mixed-ligand complexes allows us to stabilize the precursor solution, to decrease the decomposition temperature down to 400-600°C and to obtain by MOCSD thin films of Y_2O_3, $LaLuO_3$, $LaAlO_3$, $LaNiO_3$, LaF_3, CaF_2, SrF_2, BaF_2 and $NaYF_4$:Tm,Yb.

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ELECTROCHEMICAL REACTIONS OF TRANSITION METAL COMPLEXES AS A WAY TO NEW CATALYSTS AND MATERIALS

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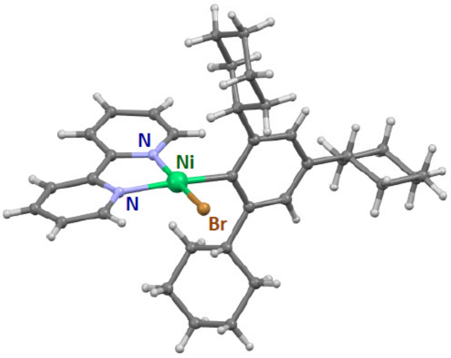
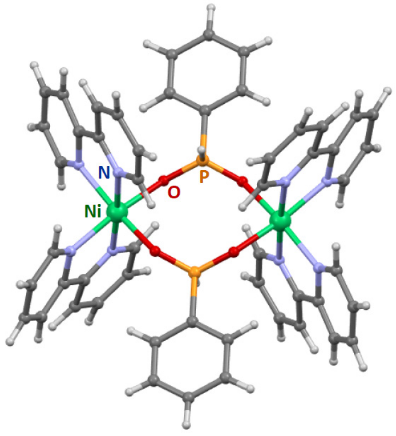
The creation and design of new molecules bearing unique catalytic and magnetic properties are one of key research priorities of modern synthetic chemistry. The combination of synthetic electrochemical techniques and coordination chemistry can be considered as new powerful tool in preparation of various types of catalytically and magnetically active materials and nanosized species based on transition metals. The mild conditions, single-stage process, cyclic regeneration of the catalyst, and convenient and relatively inexpensive form of the energy used are the main advantages of electrochemical methods.

The application of the electrochemical techniques allowed us to elaborate new methods for preparation and modification of various types of organometallic complexes [1-3] and dinuclear nickel [4] and cobalt [5,6] derivatives.





Herein, we present our recent results obtained by using of the electrochemical techniques in application towards preparation of active catalysts, based of organonickel sigma-complexes, and polynuclear materials.

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MACROLIGAND PROPERTIES OF ORGANIC SUBSTANCES OF HUMUS NATURE WITH RESPECT TO METAL IONS IN A COMPETITIVE SYSTEM

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Some authors point to the similarity of the migration properties of nickel and cobalt ions in natural waters [1-2]. However, also the results of studies of the interaction of nickel and cobalt ions with natural high-molecular acids by electrochemical methods are reflected significant differences in the stability constants of the complexes of these metals and presented.

The aim of the work was a voltammetric study of the processes of binding of nickel and cobalt ions to fulvic acids (FA) isolated from certain soils in the following systems: Co(II) -FA, Ni(II) -FA, Co(II) -FA-Ni (II).

The isolation of FA was carried out according to the classical technique of Orlov [3] by successive extraction with ion-exchange purification. Gleic-podzolic soils were chosen, FA of which contain a sufficient number of carboxyl and carbonyl groups. Also, chernozem FA that contain more nitrogen-containing fragments and are enriched in hydrocarbon groups were selected [1-4].

Definitions of the stability constants of complex systems were carried out using a voltammeter TA-4 [1-4] using a mercury-film electrode in a solution of 1 M KCl. Concentrations of FC from $1 * 10^{-3}$ to $0,3 * 10^{-2}$ mmol / l. Concentrations of metal ions were $1 * 10^{-3}$ mmol / l and $5 * 10^{-2}$ mmol / l. The constants were calculated from the displacement of the half-wave potential [4].

The results of a voltammetric study of individual systems have shown that the logarithms of the stability constants of the complexes of Ni(II) and Co(II) ions with FA (Gleic-podzolic soils) are 4.40 and 5.82 (± 0.05), respectively, with FA (chernozem) for Ni(II) 4.90 and Co(II) 3.92 (± 0.05). In the study of mixed systems, the following features were revealed: in the Co-FA-Ni system (Gleic-podzolic soils), the logarithm of the stability constant for Ni (II) decreased to 3.5 (± 0.07), and for Co (II) it was 6.03 (± 0, 05).

In the case of studying the same system with FA of chernozem, the following data were obtained: the logarithm of the stability constant for Ni(II) was 6.05 (± 0.03), and for Co(II) 2.5 (± 0.06). Conducted voltammetric studies indicate the possible mutual influence of both metal ions and functional groups (and their location in the structure of the FA) on the spatial symmetry of natural complexes and stability in the system.

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PLATINUM(II) AS A LEWIS BASE FOR HALOGEN BONDING

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The halogen bond (XB) formation together with other non-covalent interactions is actively applied in crystal engineering, supramolecular chemistry, stabilization of explosives and biochemistry. The metal complexes are perspective building blocks in the design of ordered systems using XBs. However, in most previously described metal-containing systems, metal atoms themselves were not involved in XBs, and these non-covalent interactions were realized *via* coordinated ligands.

The metal•••halogen interaction, where metal is a Lewis base and halogen is a Lewis acid, were previously described only for one type of platinum(II) complexes and molecular iodine [1]. In this case, the $Pt^{II}{\cdots}I_2$ contact is strong enough to be treated as the I–I←Pt coordination bond.

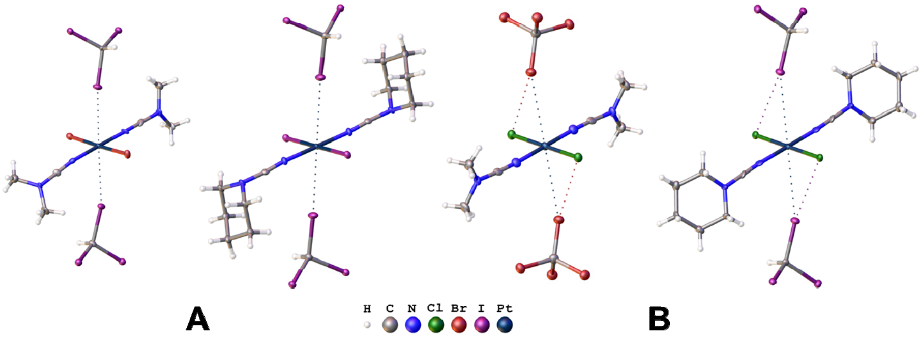

Figure 1. Two types of metal-involving XBs between the PtX_2 (X = Cl, Br, I) linear fragment and the halomethanes (R–X' = HI_2C–I, Br_3C–Br).

In this work, we, firstly, found that the platinum(II) complexes *trans*-$[PtX_2(NCNR_2)_2]$ (X = Cl, Br, I) behave as good XB acceptors *via* both halide ligands and metal centers in the adducts with CHI_3 [2] and CBr_4 taken as XB donors forming:

- the HI_2C–I•••Pt metal-involving XBs, (Fig. 1, **A**);
- the bifurcated R–X'•••(Cl–Pt) (R–X' = HI_2C–I, Br_3C–Br) XBs, were chloride and platinum(II) act as simultaneous Lewis bases for one halogen atom (Fig. 1, **B**);
- numerous R–X'•••X–Pt (R–X' = HI_2C–I, Br_3C–Br; X = Cl, Br, I) XBs.

Upon variable-temperature XRD experiment for the bifurcated HI_2C–I•••(Cl–Pt) XB we also observed the reversible thermal-induced isomerization $HI_2C\text{–}I{\cdots}\eta^2_{(Pt\text{–}Cl)} \rightleftarrows HI_2C\text{–}I{\cdots}\eta^1_{(Pt)}$. All adducts were studied by single-crystal XRD experiments followed by DFT calculations.

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HETEROMETALLIC COMPOUNDS V(IV)-Ln(III) WITH CYCLOBUTANE-1,1-DICARBOXYLATE ANIONS: SYNTHESIS FROM «BUILDING BLOCKS», CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES

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Design of heterometallic 3d-4f complexes is one of the intensively developing fields of coordination chemistry. This is due to the possibility to create new substances and materials with useful physicochemical characteristics, such as photoluminescence activity [1] and unusual magnetic behavior [2]. One of the synthetic approaches to obtain 3d-4f compounds is the use of stable "metal-organic blocks". These are mononuclear 3d metal complexes with organic ligands, containing free functional groups, which are able to link the "blocks" with 4f metal atoms. In the present work by the example of oxovanadium(IV) we showed the possibilities of construction of 3d-4f compounds based on cyclobutane-1,1-dicarboxylic acid (H_2cbdc) anions, which form stable bis-chelate anionic complex $[VO(cbdc)_2(H_2O)]^{2-}$ with V^{IV} atom.

It was found that the interaction of $VOSO_4$ with K_2cbdc and $Ln(NO_3)_3$ (Ln varies from La^{III} to Lu^{III}) results in three types of heterometallic compounds V^{IV}-Ln^{III}, which structure depends on lanthanide(III) ion radius. In case of La^{III} and Ce^{III} (r_{ion} = 1.115 and 1.081 Å respectively) two types of crystals are formed: $\{[Ln(VO)(cbdc)_2(H_2O)_7]\cdot½[VO(cbdc)_2(H_2O)]\}_n$ (I) and $\{[KLn(VO)_2(cbdc)_4(H_2O)_9]\cdot3.5H_2O\}_n$ (II). Structures of the first type contain 1D-polymeric cations, in which $\{VO(cbdc)_2(H_2O)\}$ units are bound to Ln^{III} due to coordination of the free carboxylate oxygen atoms. In compounds of the second type two non-equivalent vanadyl-containing bis-chelate units are coordinated to one Ln^{III} atom forming trinuclear anions, which are linked by K^+ cations in 3D polymeric crystal structure. If Ln^{III} is Pr, Nd, Sm, Eu, Gd, Tb and Ho (r_{ion} in the series decreases from 1.052 to 0.926 Å) only the crystals of compounds II are formed. The third type of V^{IV}-Ln^{III} compounds, $[KLn(VO)_2(cbdc)_4(H_2O)_{11}]\cdot2H_2O$ (III), was obtained for the end of the lanthanide series, Er, Tm, Yb and Lu (r_{ion} decreases from 0.911 to 0.867 Å). In structure III only one of two $\{VO(cbdc)_2(H_2O)\}$ fragments is coordinated to Ln^{III}, forming binuclear V^{IV}-Ln^{III} cation. The other one is bound to the V^{IV}-Ln^{III} cation due to ionic interactions with K^+ ion.

Magnetic properties of all compounds have been investigated in temperature range of 2-300 K. The behavior of the $\chi T(T)$ dependence for V^{IV}-Gd^{III} compound indicates domination of ferromagnetic-type exchange coupling between V^{IV} and Gd^{III} ions.

[1] L. Liu, H. Li, W. Feng, G. Fu, X. Lü, W.-K. Wong, and R. A. Jones, *Opt. Mater.*, **2017**, *64*, 106-113.
[2] H. L.C. Feltham, S. Brooker, *Coord. Chem. Rev.*, **2014**, *276*, 1-33.

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MONONUCLEAR METAL PIVALATES

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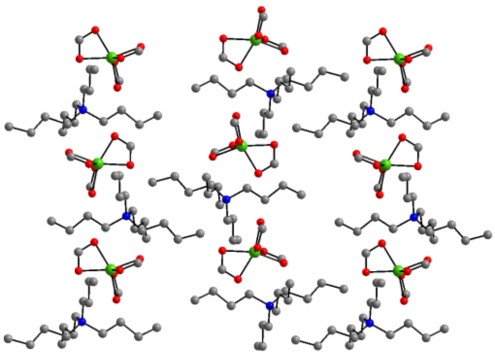
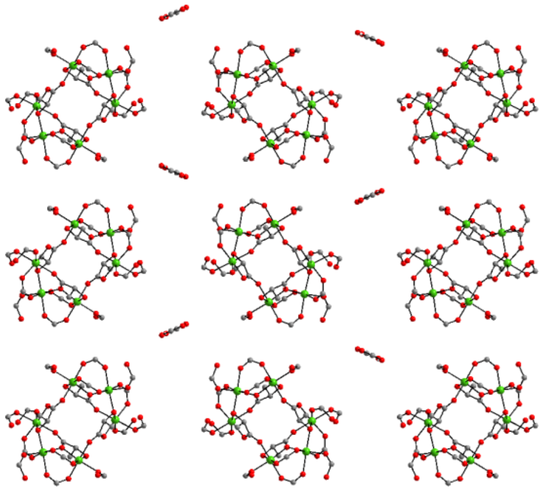
Mononuclear transition metal complexes with chelating carboxylate ligands, leading to the formation of four-membered chelate rings, are extremely rare. A novel complex anion of this type was isolated in the form of tetrabutylammonium salt [N(C_4H_9)$_4$][MPiv$_3$], where M are Ni(II), Mn(II), Co(II), Cu(II); and Piv is pivalate.

In the structure of the [NiPiv$_3$], [MnPiv$_3$] and [CoPiv$_3$] coordination units, the environment of the central atom was found to be close to a trigonal prism. In the synthesis of NBu$_4$[CoPiv$_3$] and NBu$_4$[CuPiv$_3$], new compounds, namely, tetranuclear (NBu$_4$)$_2$[Co$_4$Piv$_8$(AcO)$_2$(H$_2$O)$_4$] and (NBu$_4$)$_2$[Cu$_4$Piv$_8$(AcO)$_2$(H$_2$O)$_2$], respectively, formed along with the major product. Due to high kinetic persistence of mononuclear [MPiv$_3$], the reason of polynuclear complexes formation is a presence of nonmononuclear species in reaction media.

It was found that [N(C_4H_9)$_4$][NiPiv$_3$], reacting with ordinary Ni(II) salts in organic media, can initiate an unusual process, forming a hexanuclear complex [Ni$_6$L$_2$(HL)$_2$Piv$_6$(HPiv)$_8$]·2HPiv, where L and HL are the lactic acid di- and monoanions, respectively. [Ni$_6$L$_2$(HL)$_2$Piv$_6$(HPiv)$_8$] is the first hexanuclear transition metal complex with lactate anions in the ligand shell.



Fragment of the structure of
[N(C_4H_9)$_4$][NiPiv$_3$]



Fragment of the structure of
[Ni$_6$L$_2$(HL)$_2$Piv$_6$(HPiv)$_8$]·2HPiv

Acknowledgements - This work was supported by RScF (17-13-01022), FASO Russia.

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PHOTOPHYSICS AND PHOTOCHEMISTRY OF MIXED-LIGAND Pt(IV) COMPLEXES PROSPECTIVE IN PHOTODYNAMIC THERAPY OF TUMORS

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Synthesis and investigation of photochemical properties of Pt(IV) complexes prospective as prodrugs in photodynamic therapy (PDT) of tumors is an attractive task in modern coordination chemistry. The application of these complexes is based on the photoreduction of Pt(IV) to Pt(II) giving rise to the complexes which can platinate DNA similar to well-known anticancer drug cisplatin [1]. Diiodo and diazido complexes of Pt(IV) comprised the first and second generations of photoactive Pt(IV) compounds correspondingly [2, 3]. For successful applications, the mechanisms of photochemical reactions for the corresponding complexes should be known in detail. In this work mixed-ligand complexes of Pt(IV) - *cis, trans*-$[Pt(en)(I)_2(OH)_2]$ (**1**), *cis, trans*-$[Pt(en)(I)_2(CH_3COO)_2]$ (**2**), *cis,trans,cis*-$[Pt(N_3)_2(OH)_2(NH_3)_2]$ (**3**) and *trans,trans,trans*-$[Pt(N_3)_2(OH)_2(NH_3)_2]$ (**4**) prospective as prodrugs in PDT processes were studied by means of ultrafast (femtosecond) kinetic spectroscopy, nanosecond laser flash photolysis and stationary photolysis.

For diiodo complexes (**1**) and (**2**) irradiation in the near UV spectral range was shown to result in the consecutive exchange of I^- to H_2O / OH^-. The photoexchange processes were found to be completed in the time range of ca. 100 ps. For both complexes multiexponential dynamics of ultrafast processes was observed which was explained by transition of the initial Frank-Condon excited state to the lowest electronic excited state (0.5 – 1 ps), its vibrational cooling (3 – 8 ps) and decay to final photoproducts (20-80 ps). Photoreduction of Pt(IV) to Pt(II) is the result of the secondary photochemical processes.

For diazido complexes (**3**) and (**4**) the first process is the exchange of N_3^- to H_2O. This process is a chain reaction with the concentration-dependent quantum yield. Pt(III) intermediates responsible for chain development were recorded using nanosecond laser flash photolysis and ultrafast kinetic spectroscopy. Disproportionation of Pt^{III} intermediates results in formation of final Pt^{II} products, providing the therapeutic effect of the initial compounds.

Finally, photochemistry of Pt(IV) complexes prospective for PDT was studied in wide time range, from absorption of light quanta to the formation of final photolysis products.

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A NEW APPROACH TO THE SYNTHESIS OF METAL COMPLEX CATALYSTS FOR OXIDATION REACTIONS OF NATURAL COMPOUNDS

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Research Institute of Macrogeterocyclic Compounds, Ivanovo, Russia

In recent decades, metal-organic frameworks (MOF) - nanomaterials with unique properties were actively studied. These materials can be synthesized using suitable building blocks, for example, metal phthalocyaninates. These compounds are synthetically available and characterized by high stability and big absorption coefficients, which makes them promising materials for preparation of new materials [1].

The metal centers play an important role in catalytic reactions. Despite the advantages of metal-organic frameworks, the synthesis of compounds with active metal centers is the serious problem, since metal clusters often tend to coordination with organic ligands [2]. We use copper and cobalt octacarboxyphthalocyaninates as a starting material for the synthesis of new nanomaterial. The structure and properties of these compounds were investigated using various methods, such as spectrophotometry, derivatography, and SEM.

The catalytic properties of the obtained materials were investigated in the reactions of oxidation of several organic compounds by air oxygen. The ascorbic acid as a model compound was used. The kinetic parameters of the reaction were determined. It was noted that the limiting stage of the reaction is the coordination of oxygen at the catalyst metal centers with their activation. However, an increase the concentration of ascorbic acid, a substrate "poisoning" takes place. Very importantly fact is that those catalysts are a stable during by several catalytic cycles.

The obtained results demonstrated the big perceptivity of investigations of these materials as effective catalysis by dioxide. The results obtained open up broad prospects for further work in this direction - it should be expected that by varying the nature of the central and peripheral metal cations, it will be possible to obtain materials with different catalytic properties.

[1] Wen-Yang G., Chrzanowski M. Chem. Soc. Rev. 2014. №43. P. 5841-5866.
[2] Gascon J. The Royal society of chem. 2013. P. 237-263.

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STRUCTURAL-CHEMICAL ASPECTS OF PLATINUM AND RHODIUM COMPLEXES WITH CALIXPHOSPHINES

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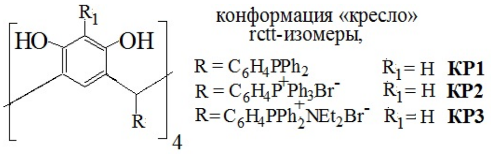
We have previously described [1] the complexes $PtCl_4$ (**1**) and $[Rh_2(OAc)_4{\cdot}2H_2O]$ (**2**) with the calixphosphine **KP1** isolated from EtOH and Me_2CO: {**KP1**$\cdot 2[PtCl_4]$} (**4**) and {**KP1**$\cdot 2[Rh_2(AcO)_4]$} (**5**). **KP1** forms a complex of the composition {**KP1** $[Rh_2Cl_6]$} (**6**) with $RhCl_3{\cdot}nH_2O$ (**3**) in EtOH, and in Me_2CO it forms a paramagnetic complex {**KP1**$\cdot 4[Rh^{III}(O_2^-)\cdot 2(Cl^-)]$}(**7**). Depending on the type of initial compound, complex formation proceeds by the nucleophilic either addition or substitution reaction. In the interaction of **1-3** with the supramolecular quasiphosphonium salts of **KP2** and **KP3** in polar Me_2CO, a heterolytic rupture of one of the P-Ph bonds occurs with the cleavage of PhBr and conversion into the calixphosphines **KP2'** and **KP3'** with aryldiphenylphosphine and aryldiethylaminophenylphosphine groups, respectively (schemes 1, 2).



In the presented report, the donor-acceptor properties of phosphorus atoms and the structural-chemical aspects of complexes **4-7** with **KP1** and calixphosphines **KP2'** and **KP3'** were examined and compared using the spectral parameters $NMR^{31}R$ (δ_P, $\Delta\delta_P$, ppm, $^1J_{M\text{-}P}$, Hz) and IR {ν ($M\text{-}Cl_{term}$), ν (MμCl)} of synthesized compounds.

Схема 1

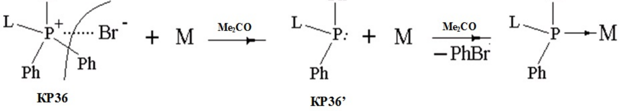
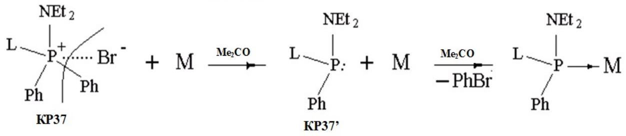
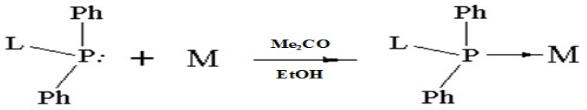


Схема 2





According to the parameters of the $NMR^{31}R$ spectrum (δ_P, $\Delta\delta_P$, $^1J_{M\text{-}P}$: **4** - 25.47, 32.47, 3751; **5** - 25.00, 32.00, 213; **6** - 25.98, 33.98, 163; **7** - 26.12, 33.12, 208), the enhancing of phosphorus nuclei screening (**KP1** - δ_P = -7.00) is observed under complexation. This indicates more pronounced σ-donor properties of the phosphorus atoms of the diphenylphosphine **KP1** groups as compared to π-acceptor ones, which do not depend on the nature of 1-3, but are determined by the polarizing properties of P^{III} and the steric factor, namely, aryl groups, creating a specific conic angle for interaction.

Dependences between the donor-acceptor properties of the phosphorus atom in **KP1** and the *cis-trans* isomerism of the coordination site in complexes **4-7** are not observed: **4**, **5**, **7** – *trans*-isomers, and **6** - *cis*-isomer.

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COMPLEXES OF Cu(II), Zn(II) AND Cd(II) WITH 2-(N-ACETYLAMINO)PYRIDINES: CYTOTOXIC ACTIVITY AND FLUORESCENCE

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Metal complexes have recently received considerable attention, as they have been shown to exhibit various types of biological activity. There is a strong need of the design of novel potential therapeutic candidates based on coordination metal complexes. It is considered that cisplatin is the most active chemotherapeutic agent among of the existing chemotherapeutic drugs. However, due to its efficient cytotoxic effects, cisplatin has adverse drug effects and chemo-resistance. Constant interest to the pyridine derivatives is explained by the fact that many of them, natural and synthetic, display significant physiological activity.

This work is devoted to the synthesis and characterization of new coordination compounds of copper(II), zinc(II), and cadmium(II) with methyl-substituted 2-(N-acetylamino)pyridine derivatives [1, 2]. All of the complexes have been identified and characterized by a set of methods including elemental analysis, IR-spectroscopy, single-crystal X-ray diffraction analysis, and magnetic susceptibility measurements in the range 5 – 300 K. The fluorescence and cytotoxic activity of the complexes in comparison with cisplatin on several human cell lines have been investigated.

Comprehensive studies of photoluminescence for the ligands and complexes of zinc(II) and cadmium(II) were carried out. It was detected quantum yield increasing of luminescence for film samples and mesoporous structures in comparison with polycrystalline complexes [3].

The cytotoxicity some of the complexes in comparison with cisplatin was investigated in vitro against human cancer cell lines: HEK 293 (human embryonic kidney) and U937 (leukemic). Our results showed that cisplatin and complexes inhibit HEK 293 cell line in a dose and time dependent manner, toxicity of complexes is similar to that of cisplatin. The U937 cell line is significantly less sensitive to complexes compared to cisplatin. However, this selective sensitivity can be useful for the selection of drugs with reduced sensitivity to normal cells.

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[3] A.S. Berezin, O.V. Antonova, E.V. Lider, A.I. Smolentsev, V.A. Nadolinny, M.S. Mel'gunov, *Journal of Luminescence*, **2017**, *190*, 261–266.

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SYNTHESIS AND PROPERTIES OF SOME PLATINUM GROUP METAL COMPLEXES WITH TETRAZOLE LIGANDS

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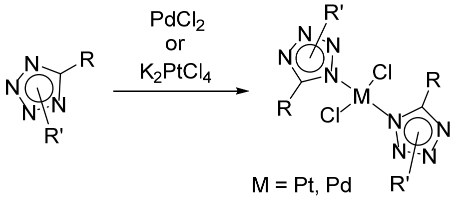
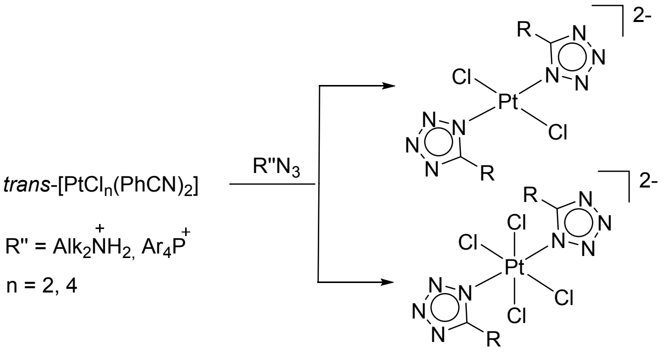
[c]*RI for Physical Chemical Problems, Belarusian State University, Minsk, BELARUS*
[d]*ITMO University, St. Petersburg, RUSSIA.*

In recent years the number of publications describing the targeted synthesis, investigations of the structure, physico-chemical and biological properties of metal complexes bearing in their structure tetrazole heterocyclic fragment has grown intensively [1]. Among them tetrazole-containing platinum group metal complexes are considered as objects of medicinal chemistry.

These complexes can be obtained by reaction of tetrazoles with metal {Pt(II), Pt(IV), Pd(II)} salts.



An alternative method for the synthesis of the complexes featuring tetrazoles is the interaction of coordinated nitriles with azides or. coordinated azides with nitriles [2].



DSC/TG analysis showed that these compounds may be regarded as fairly thermally stable and relatively safe in handling substances. Preliminary biological studies and molecular docking allow to consider the platinum group metals complexes with tetrazole ligands as potential cytostatics.

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METAL HEXAFLUOROACETYLACETONATE COMPLEXATION WITH ALKOXYAMINES: A NEW WAY TO TRIGGER C–ON BOND HOMOLYSIS AND TO CONTROL NITROXIDE MEDIATED POLYMERIZATION

G. Audran[a], E. Bagryanskaya[b], I. Bagryanskaya[b], M. Edeleva[b], S. R. A. Marque[a,b], D. Parkhomenko[b], E. Tretyakov[b] and S. Zhivetyeva[b]

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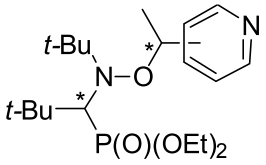
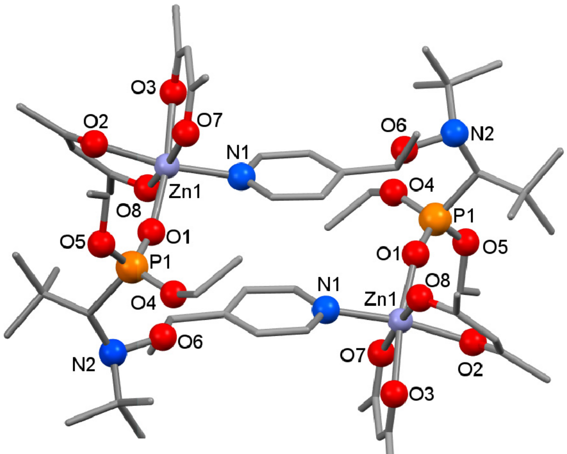
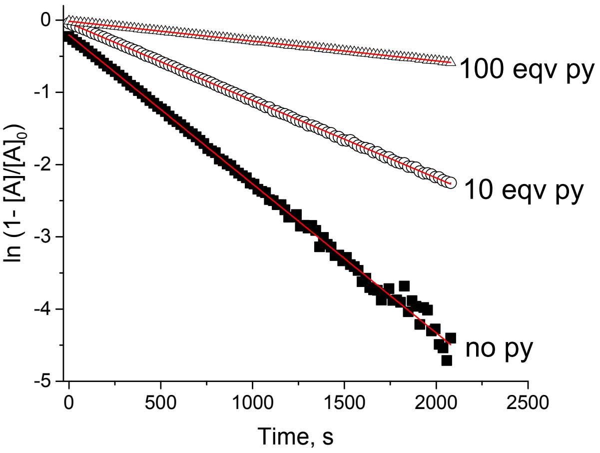
In this work, we demonstrate for the first time that an alkoxyamine’s homolysis can be effectively triggered by complexation with a metal. Complexes of M(hfac)$_n$ (M = Cu^{2+}, Zn^{2+}, Tb^{3+}) with *RS*(*SR*)- or *RR*(*SS*)-(diethyl(2,2-dimethyl-1-(*tert*-butyl-(1-pyridylethoxy)amino)propyl)phosphonate) diastereoisomers **1–3** having pyridyl moiety bound at *ortho*, *meta* or *para* position were synthesized [1]. XRD, ^{1}H and ^{31}P NMR spectra show very different structures for each complex in solid state and in solution depending on the diastereosiomers and on the regioisomers. In solution, kinetic measurements revealed up to a 30-fold increase in homolysis rate constants k_d. Moreover, the activation is also controlled by the amount of pyridine, used as a ligand competitor. Taking this into account, the M(hfac)$_n$ complexes with alkoxyamines exhibit a high potential of application for the use in Nitroxide Mediated Polymerization.



1–3



para-(Zn-*RS*/*SR*)



[1] G. Audran, E. Bagryanskaya, I. Bagryanskaya, P. Brémond, M. Edeleva, S. R. A. Marque, D. Parkhomenko, E. Tretyakov, and S. Zhivetyeva. *Inorg. Chem. Front.*, **2016**, *3*, 1464–1472.

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COORDINATION COMPOUNDS OF Zn^{II} WITH THE ANIONS OF SUBSTITUTED MALONIC ACIDS: SINTHESIS, STRUCTURE AND PROPERTIES

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Substituted malonic acids are the suitable ligands for construction of a great variety of crystal structures ranging from mononuclear species to three-dimensional networks. The structure of products that can be built with the malonate ligand depending on the nature of substitutes at the carbon atom in acid, metal ions and on the presence of coligands.

Zn^{II} malonates in the absence of additional ligands are characterized by the formation of dianionic fragments $\{Zn^{II}Mal_2\}$ (Mal = malonate or substituted malonate). This fragment can be easily assembled in structures by linking with alkaline, alkaline-earth, or transition metal ions. For example, it has been found that the reactions of zinc(II) sulfate with barium salt of dimethylmalonic (H_2Me_2Mal) or allylmalonic (H_2AlMal) acid in aqueous solutions give crystals of the 3D-polimeric compounds $[BaZn(H_2O)_5(Me_2mal)_2]_n$ (**1**) and $[BaZn(H_2O)_3(Almal)_2]_n$ (**2**), respectively. The crystal packing of **1** and **2** contains cyclic moieties formed by six $\{M(H_2O)(Rmal)_2\}^{2-}$ dianions linked pairwise through barium atoms. The methyl substituents of the dianions of acids are oriented inward the «rings». One more advantage of malonates is their high thermal stability, which is essential for studies of thermal dehydration. It has been shown that total thermal decomposition of complexes **1** result in the formation of mixed $BaZnO_2$ oxide. The content of this oxide in the solid product depends on the thermolysis conditions: atmosphere, feed rate of the external gas, final temperature and existence of an isothermal segment at the end of the process [1].

We have obtained new Zn^{II} compounds with the anions of dimethylmalonic and diethylmalonic (H_2Et_2Mal) acids with N-donor bridging ligands (such as 4,4'-bipyridine, 1,2-di(pyridin-4-yl)ethane, 1,2-di(pyridin-4-yl)ethylene (*bpe*)). These complexes represent a polymers with a diverse structure, with the exception of molecular $[Zn(H_2O\text{-}\kappa O)_4(bpe)_2]\cdot 2HEt_2mal$ (**3**). The structure of product is in some cases affected by the initial zinc(II) salt (acetate or nitrate). The greatest attention is attracted to two complexes containing 1,2-di(pyridin-4-yl)ethylene – $\{[Zn(bpe)(Me_2mal)]\cdot H_2O\}_n$ (**4**) and **3**, which are able to react the single-crystal-to-single-crystal [2+2] cycloaddition reaction with formation of new compounds.

[1] M.A. Ryumin, Zh.V. Dobrokhotova , A.L. Emelina , M.A. Bukov, N.V. Gogoleva, K.S. Gavrichev, E.N. Zorina-Tikhonova et al, *Polyhedron*, **2015**, *87*, 28-37.

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SPECIAL ASPECTS OF THE COORDINATION CHEMISTRY OF MACROCYCLIC AMINOMETHYLPHOSPHINE LIGANDS.

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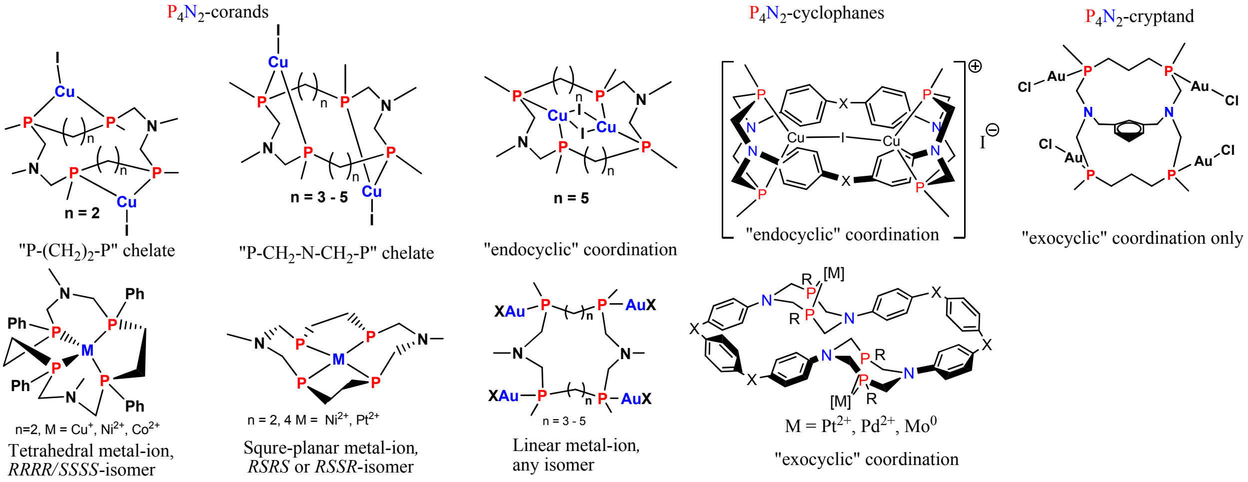
Macrocyclic complexes are typically very stable species and this can give rise to unusual structural, electronic and electrochemical properties of materials on their base. There are many examples incorporating N, O or S donor atoms into macrocyclic skeleton whereas examples involving phosphine functions are significantly less presented. Incorporation of phosphorus atoms as donor atoms in the macrocycle should result in specific properties and thus expand the possibilities of their utilization.

The synthetic methodology of mixed donor P_4N_2 macrocycles based on the condensation reactions of secondary bisphosphine or primary phosphine, formaldehyde and primary amine or secondary bis-amine was developed in our laboratory [1]. The coordination chemistry of various P_4N_2 ligands including corands, cryptands and cyclophanes has been studied and the wide row of different macrocyclic complexes was obtained.



Specific aspects of coordination of P_4N_2 aminomethylphosphine ligands was found. So, the complexation mode depends on the following factors: the macrocycle size (different coordination mode in P,P-chelates of 14-, 16-, 18- and 20-membered P_4N_2 corands, "endo"- or "exocyclic" coordination); the phosphorus configuration (preorganization of the ligand to coordination of tetrahedral or square-planar metal-ion); the ability of P_4N_2 macrocycle to change its conformation and even the structure in the course of coordination (interconversion of stereoisomers, the cycle size changing); the macrocycle flexibility (various conformation of complexes in crystal); type of the metal ion (size, geometry, coordination number etc.)

[1] A.A. Karasik and O.G. Sinyashin, *Phosphorus Compounds Advanced Tools in Catalysis and Material Sciences*, ed. M. Peruzzini, L. Gonsalvi, Springer, Netherlands, **2011**, *37*, 12, 375.

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BI- AND POLYNUCLEAR COORDINATION COMPLEXES OF D-ELEMENTS IN THE OXIDATION REACTIONS OF THIOLS

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Synthesis, the determination of a structure of coordination complexes of d-elements and revealing of their role in reactions of catalytic oxidation of organic compounds are important aspects of modern coordination chemistry. Among such catalytic processes in recent years much attention has been paid to the physiologically significant reactions of living organisms that are related to the oxidation-reduction regulation of processes of an intracellular signaling. These processes are based on a post-transmitting oxidizing modification of sulfur-containing proteins and are carried out in living organisms due to the endogenous oxidizers (ROS etc.) and can be catalyzed by the enzymes including active centers containing d-elements.

One of the natural endogenous oxidizers is hydrogen peroxide which is the secondary intermediary in a transduction of various signals. First of all hydrogen peroxide's targets are thiolate – the SH groups of proteinaceous molecules belonging to side chains of the remains of cysteine, nowadays it is considered that one of the most important is tripeptide glutathione – L-γ-glutamide-L-cysteinylglycine.

In this report the coordination complexes of d-elements capable to accelerate process of the thiolate groups' homogeneous oxidation of thioamines and thioamino acids will be discussed. At the same time the course of the processes which result can be not only a formation of disulfides (R-S-S-R) but also more oxidized products, such as sulfenyl (R-SOH), sulfinyl (R-SO_2H) and sulfone (R-SO_3H) acids is possible depending on the nature and concentration of the catalytic agent. At the same time, glutathione oxidation process solely to the disulfide form1 is the most significant one. Therefore, the creation of catalytic systems on the basis of coordination compounds of the d-elements that allow selective oxidation of glutathione with hydrogen peroxide can be considered as the urgent tasks of application-oriented coordination chemistry.

The role of the structure of coordination compounds of the d-elements (such as Ni, Pd, Pt, Cu, Fe, Rh, and Ir) in the formation of catalytic systems which are capable to the selective oxidation of thiolate groups of biological substrates will be demonstrated. This role will be used to develop fundamental bases of the creation of highly effective modulators of pharmacological activity for already existing pharmaceuticals and biologically active compounds.

[1] Molecular Biology of the Cell, 4th edition. Alberts B., Johnson A., Lewis J., Raff M., Roberts K., and Walter P. New York: Garland Science. 2002

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DIPOLE MOMENTS AND SOLVATOCHROMISM OF METAL COMPLEXES: PRINCIPLE PHOTOPHYSICAL AND THEORETICAL APPROACH

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Organometallic complexes of titanium subgroup (Ti, Zr, Hf) represent key compounds for modern organometallic chemistry and metal complex catalysis. Knowledge on the ground and excited-state properties of coordination compounds is essential, as attributed to the fundamentals and advances of molecular photonics, design of non-linear optical materials, and so on. The present study suggests a combined systematic experimental and theoretical strategy for estimate of electric dipole moments (μ) and their difference for metal-based compounds in the ground and emissive states and shed light on the solvatochromism of organometallic complexes. The associated approach, based on the Bakhshiev, Bilot-Kawski, and McRae solvatochromic models and theoretical calculations, is sought to be universal, promising, enough simple, and easily accessible for unraveling properties of complex solutes.

Thus, the study was conducted with use of zirconocene(IV) dichlorides: sterically hindered *rac*-$C_6H_{10}(IndH_4)_2ZrCl_2$ [1], possessing unique phosphorescent in liquids ligand-to-metal charge transfer excited states, and "structurally simple" Cp_2ZrCl_2 [2]. Details of the treatment are given in below cited references [3-4]. For instance, for *rac*-$C_6H_{10}(IndH_4)_2ZrCl_2$, the experimentally derived gas-phase values are: $\mu_g = 5.3$ D and $\mu_e = 8.7$ D; the computed gas-phase values are: $\mu_{g(DFT)} = 5.46$ D and $\mu_{e(DFT)} = 8.07$ D. The experimental ratio $\mu_e/\mu_{g(exp)}$ is 1.64, while the theoretical ratio $\mu_e/\mu_{g(DFT)}$ varies from 1.48 (in gas) to 1.55 (in CCl_4) that is in excellent correspondence with the experimental result. Our calculations reveal that solvent drastically affects magnitude of electric dipole moments of the target solutes both in S_0 and T_1-states. An increase in the solvent polarity parameters is accompanied by increase in the dipole moment of the solutes in S_0 and T_1 states, as well as in the difference between excited-state and ground-state dipole moments $\Delta\mu$.

In summary, for metal-based compounds, the ground- and excited-state dipole moments and difference thereof are for the first time obtained both experimentally and theoretically using solvatochromic equations and DFT/B3LYP calculations, also evidence correspondence and complementarily of the data, derived in the theoretical and photophysical studies, and, importantly, the unity of the suggested approach.

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[3] G. Loukova, A. Milov, V. Vasiliev and V. Minkin, *Phys. Chem. Chem. Phys*., **2016**, *18*, 17822-17826.
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Acknowledgements – The study was performed under financial support from Presidium of Russian Academy of Sciences and the Russian Foundation for Basic Research (projects N 15-03-08003). The study was conducted in the framework of state contracts 0089-2014-0008 and 007–01114–16 PR 0256–2014–0009, SFU contract 1.5056.2017.VU, and SEC "High-Energy Chemistry" of Lomonosov Moscow State University.

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PRESSURE INDUSED SPIN TRANSITIONS IN BREATHING CRYSTALS

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A family of heterospin complexes based on copper(II) hexafluoroacetylacetonate Cu(hfac)$_2$ with persistent nitronyl nitroxides L^R was named as *breathing crystals* due to their ability to undergo reversible 'Single-Crystal-to-Single-Crystal' phase transformations. Studying of these processes facilitates a detail investigation and understanding of solid dynamics. Phase transitions occur as a consequence of the P- and/or T-induced structural reorganization of exchange clusters 'Cu-O•-N' or 'N-•O-Cu-O•-N'. This reorganization causes an appearance of magnetic anomalies on the dependence of the effective magnetic moment *vs* temperature (or pressure) [1-3]. It was shown that both pressure induced and temperature induced phenomena provide valuable information on the spin state in heterospin solid.

For the chain-polymer complexes [Cu(hfac)$_2L^R$], where hfac is the hexafluoroacetylacetonate anion (L^R is 2-(1-R-1*H*-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl, R = Me, Et, Allyl) with the head-to-head chain motif, the temperature dependence of the effective magnetic moment at increased pressure, as well as the temperature and compression dynamics of the structure, were studied. It was shown that pressure variation provokes another structural reorganization in compare with temperature induced structural changing. Due to the high sensitivity of the structure and magnetic anomalies of breathing crystals to applied pressure they could serve as a new type of a pressure sensor.

[1] Victor Ovcharenko, Elena Bagryanskaya. In: *Spin-Crossover Materials: Properties and Applications*, Ed M. A. Halcrow, Wiley-VCH, New York, **2013**, 546 p.
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[3] N. A. Artiukhova, G. V. Romanenko, A. S. Bogomyakov, I. Yu. Barskaya, S. L. Veber, M. V. Fedin, K. Yu. Maryunina, K. Inoue, V. I. Ovcharenko. *J. Mater. Chem. C*, **2016**, *4*, 11157-11163.

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SYNTHESIS OF NOVEL RUTHENIUM CARBORANE CLUSTERS WITH LABILE ACETONITRILE LIGAND

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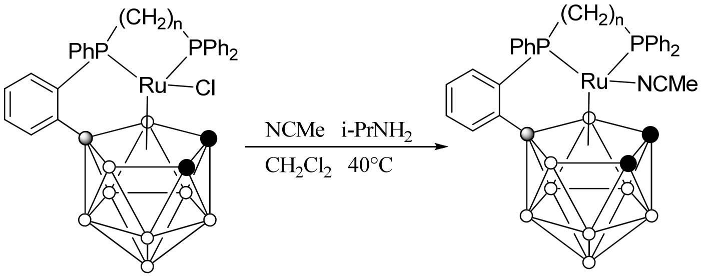
Metallacarboranes is an interesting class of coordination compounds which show high catalytic performance in different reactions in organic chemistry, such as amination, hydroformylation, radical reactions and so on. Every catalytic cycle includes stages of addition of substrates to metal centre and consecutive elimination of products. So coordination compound should have a vacant coordination cite to act catalyst. From this point of view compounds with weakly bounded ligands are usually used as catalyst precursors. Our recent results indicate that ruthenacarborane clusters are effective catalysts of Atom Transfer Radical Polymerization. The latter process conducts through formation of active 16-electron species which conduct process in controlled mode [1]. In this work a novel ruthenacarboranes with weakly bounded acetonitrile ligands capable to generate 16-electron species were synthethised.



The reaction of stable 17-electron compounds with aliphatic amines in CH_2Cl_2/acetonitrile solution gives corresponding 18-electron species. The reaction completes in 2-4 hours at 25-40°C giving final products in 75-95 % yield. Novel ruthenacarboranes were isolated as yellow solids stable on air. The products were characterized by X-ray, NMR, IR-spectroscopy and elemental analysis. The developed method was applied to the synthesis of series derivatives of carbon-substituted and non-substituted complexes

Cyclic voltammetry study of obtained complexes showed the ability of obtained complexes of ruthenium (II) to undergo reversible oxidation to Ru(III) species. In case of complexes with bis ortho-cycloboronated ligands two consecutive reversible oxidations are observed.

The obtained complexes were used as catalysts of methyl methacrylate polymerization. Polymerisation catalysed by obtained complexes proceeds in controlled mode and is accompanied by increase of molecular weight with conversion.

[1] I. D. Grishin, N.E. Kiselyova, D. I. Dyachikhin, I. T. Chizhevsky, D. F. Grishin, *Russ. Chem. Bull. Int. Ed.,* **2015**, *8,* 1942-1948.

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CYCLOPENTADIENYL Ir(I) COMPLEXES [Ir(COD)Cp^{X}]: SYNTHESIS, THERMAL PROPERTIES AND APLICATION IN MOCVD PROCESSES

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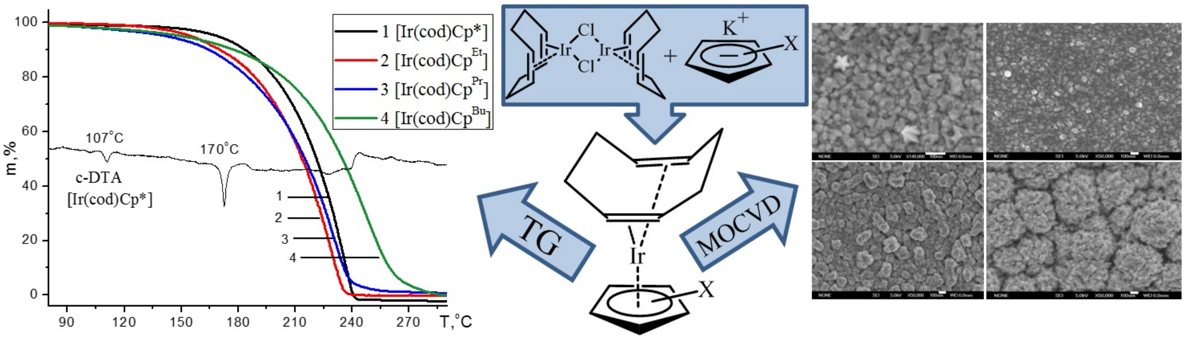
Iridium based coatings have found a broad range of applications which include their use in protecting refractory materials in high-temperature processes of glass melting or crystal growth, in rocket technologies for the protection of combustion chambers in engines and turbine blades, in various areas of catalysis and as electrical contacts. Metal-Organic Chemical Vapor Deposition (MOCVD) is one of the most promising technique to produce iridium based coatings due to the possibility of making them uniform with required characteristics on complex shape substrates at relatively low temperatures. The conditions of MOCVD process and therefore the properties of the produced coating are strongly depend on the precursor, or rather its thermochemical properties. So the expanding the range of precursors to satisfy any requirements of the MOCVD process is important task for developing of this method. This work is focused on studying cyclopentadienyl Ir(I) complexes [Ir(cod)Cp^{X}] (Cod – cyclooctadiene; Cp^{X} – substituted cyclopentadienyl; X – ethyl, propyl, butyl, pentametyl) and the influence of the substituents in Cp ligand on thermal properties of the complexes and the characteristics of the coatings obtained by MOCVD using these precursors. The complexes with Cp^{X} = Cp^{Pr}, Cp^{Bu} are new ones and the others (Cp^{X} = Cp^{Et}, Cp*) are known but their thermal properties are unexplored.



The obtained complexes were characterized by various techniques (XRD, IR, NMR, MS and CHN). Thermal properties of the complexes in condensed phase were investigated by thermogravimetry. For all compounds, mass loss occurs in single step and residual mass is less than 1% indicating the complete evaporation. For some complexes, the temperature dependences of saturated vapor pressure were measured by Knudsen’s effusion method and the thermodynamic parameters of evaporation were calculated. It was shown that increasing length of substituents or their amount led to decrease of the complex saturated vapor pressure. The obtained complexes were also used as precursors in MOCVD process. Metallic iridium coatings were prepared in similar conditions and analysed by SEM, XRD and XPS. The coatings obtained from different precursors have different texture according to XRD.

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Fe^{III}-M^{II}(M=Mn, Ni, Zn, Cd) MOLECULAR METAL COMPLEXES: STRUCTURES, MÖSSBAUER SPECTROSCOPY AND THERMAL PROPERTIES

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Iron(III) ions in the presence of carboxylate ligands from oxocarboxylate complexes with triangle or tetrahedral fragments. An addition of heterometal in the reaction mixture allows to replace some iron ions and formation of metal core analogous to iron(III) compounds as well as new types of metal core. The presence of chelate ligands in reaction mixture could results in formation of new complexes.

Here we presents results of synthesis of new heterometallic compounds based on iron(III) oxocarboxylates. We used different chemical methods and synthesized new complexes of iron and 3d-metal ions in the presence of 1,10-phenantroline or without it with different nuclearity and metal core geometry: *three*-$[Fe_2NiO(Piv)_6(Et_2O)(H_2O)_2]$ (**I**), $[Fe_2NiO(Piv)_6(phen)(H_2O)]$ (**II**, Fig.1a), *tetra*-$[Fe_2Ni_2(OH)_2(Piv)_8(phen)_2]$ (**III**, Fig.1b), *penta*-$[Fe_3Zn_2(O)_2(Piv)_9(phen)]$ (**IV**), *hexa*-$[Fe_2Zn_4(O)_2(Piv)_{10}]$ (**V**), $[Fe_2Mn_4(O)_2(Piv)_{10}(HPiv)_4]$ (**VI**, Fig. 1c), $[Fe_4Mn_2(O)_2(Piv)_{12}(O_2CH_2)(HPiv)_2]$ (**VII**), *hepta*nuclear-$[Fe_4Zn_3(O)_3(Piv)_{12}(H_2O)]$ (**VIII**). The use of cadmium(II) allowed to carried out new type of “iron wheel” complexes, $[Fe_8Cd(\mu\text{-}OH)_8(Piv)_{18}]\cdot Et_2O$ (**IX**, Fig. 1d), with incapsuated $\{Cd(Piv)_2\}$ fragment.

The presentation will focus on the synthesis, structure (according to single crystal X-ray data), as well as, Mössbauer spectroscopy, magnetic measurements and simultaneous thermal analysis(STA).

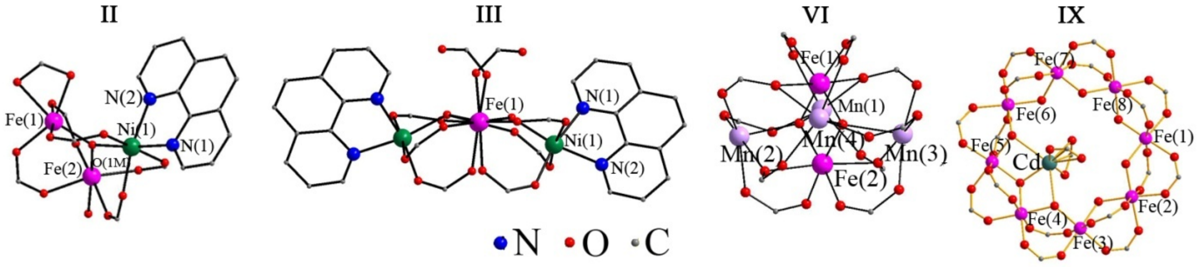

Figure 1 – Molecular structures of **II**, **III**, **VI** and **IX** complexes (^{t}Bu groups are omitted)

The data of Mössbauer spectroscopy allow us to conclude that high-spin Fe^{3+} ions exist in complexes in the octahedral environment of O^{2-} (Table 1). Increased values of isomeric shifts (δ) and quadrupole splittings (Δ) indicate a distortion of the local environment of iron (III), the most pronounced in **III**, **IV**, **VIII**.

Table 1. Parameters of Fe forms(T = 300°C)

	II	III	IV	V	VI	VIII	IX
δ	0.43	0.39/0.44	0.39/0.47	0.36	0.42	0.40	0.35/0.49
Δ	0.85	0.75/1.21	0.85/1.27	0.77	0.67	0.90	0.61/0.80
G	0.35	0.52/0.53	0.54/0.54	0.44	0.44	0.64	0.38/0.40
A	1.00	0.63/0.37	0.79/0.21	1.00	1.00	1.00	0.50/0.50

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TRANSITION METAL BIS(DICARBOLLIDE) COMPLEXES AS STRUCTURAL UNITS IN DESIGN OF MOLECULAR SWITCHES

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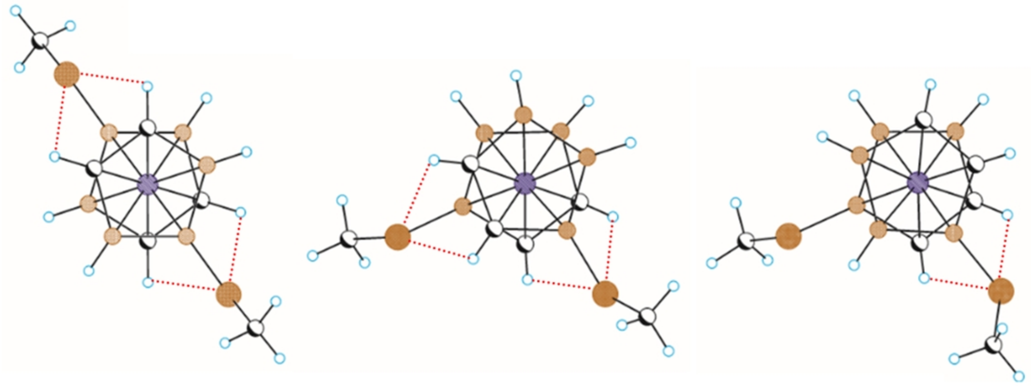
Molecular switches are molecules or supramolecular complexes having bistability, i.e., the ability to exist in two or more stable forms, among which may be reversible transitions under external influence. The design of molecules capable of performing mechanical movement is an important problem of modern chemistry. The interesting example of such molecules are bis(dicarbollide) complexes of transition metals $[3,3'\text{-M}(1,2\text{-C}_2B_9H_{11})_2]^{n-}$. The control of the ligand rotation in these complexes can be reached using substituents which could provide stabilization of certain rotamers due to specific interactions between the ligands, on the one hand, and which can act as Lewis bases to form complexes with external metals resulting in a change in the rotation angle of the ligands, on the other hand. The MeS group was used as the substituent that can stabilize different rotamers due to formation of hydrogen bonds $CH_{carb}...S(Me)B$ between the different ligands. A series of isomeric bis(dicarbollide) complexes $[X,Y\text{-(MeS)}_2\text{-}3,3'\text{-M}(1,2\text{-C}_2B_9H_{10})_2]^{n-}$ (M = Co, Fe, and Ni) was synthesized. It was found that the *transoid*- and *gauche*-conformations of the 8,8'- and 4,4'-isomers are stabilized by four intramolecular CH···S hydrogen bonds each one, whereas *gauche*-conformation of the 4,7'-isomer is stabilized by two CH···S hydrogen bonds.



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CHIRAL BISDIAMIDOPHOSPHITES AS LIGANDS FOR ASYMMETRIC TRANSITION-METAL CATALYSIS

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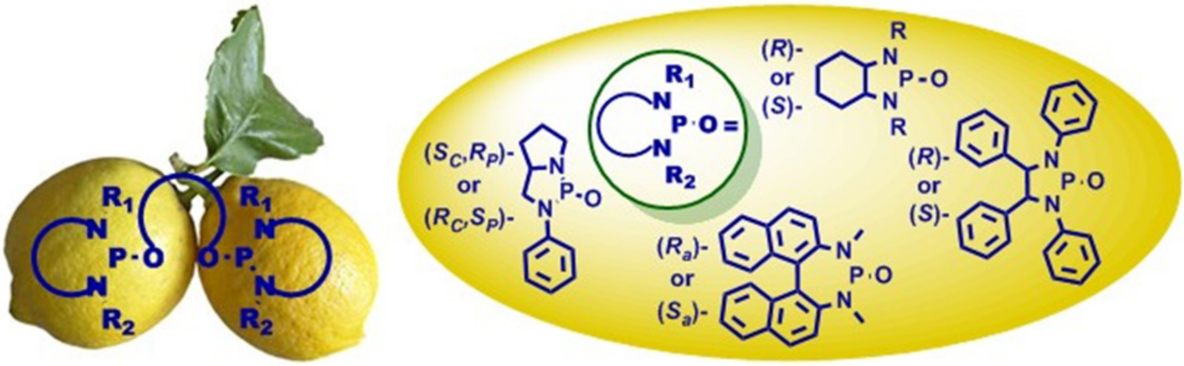
Among the phosphite-type *P,P*-bidentate chiral ligands, bisdiamidophosphites are a relatively small but very promising group. These compounds have different properties from more common bisphosphites or bisphosphoramidites. For example, nitrogen substituents create more steric bulk around the phosphorus than the oxygen atom, since nitrogen substitution may be greater. Furthermore, replacing the oxygen atom in the first coordination sphere of the phosphorus with a nitrogen atom increases the electron density on the phosphorus center, and the possibility of varying the nature of the substituents at the nitrogen and phosphorus atoms allows control over the steric and electronic parameters. If the donor phosphorus atom is asymmetric, this significantly assists in the transfer of chirality in the catalytic cycle, because this atom is directly bonded to the central metal atom (ion) and it is positioned very close to the coordinated substrate. Also, modular nature of the bisdiamidophosphite ligands allows a facile systematic variation of the configuration at the P^*- and C^*-stereocenters.



The exploration of various bisdiamidophosphite chiral inductors in Pd-catalyzed asymmetric allylation, deracemization, desymmetrization and cycloaddition reactions as well as in Rh-catalyzed asymmetric addition, hydrogenation and hydroformylation transformations are discussed. On the one hand, these reactions are the reliable models for the determination of the efficiency of novel chiral ligands. From a functional point of view, the enantiomeric excesses obtained are the simplest indexes for evaluating new stereoselectors. On the other hand, these versatile processes are widely used in the total synthesis of enantiopure natural and unnatural products. For instance, products of alkylation with dimethyl malonate can be readily transformed into esters and amides of chiral unsaturated carboxylic acids under mild conditions. The allylic alkylation of (*E*)-1,3-diphenylallyl acetate with 1-cyclohexenylpyrrolidine has been used as a key step in the synthesis of a selective antimuscarinic agent. Both enantiomers of the desymmetrization product of *N,N'*-ditosyl-*meso*-cyclopent-4-ene-1,3-diol biscarbamate are key precursors of pharmacologically active compounds mannostatin A and (–)-swainsonine.

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TETRYLENES STABILIZED BY POLYDENTATE LIGANDS: SYNTHESIS, STRUCTURE, PROPERTIES AND APPLICATION

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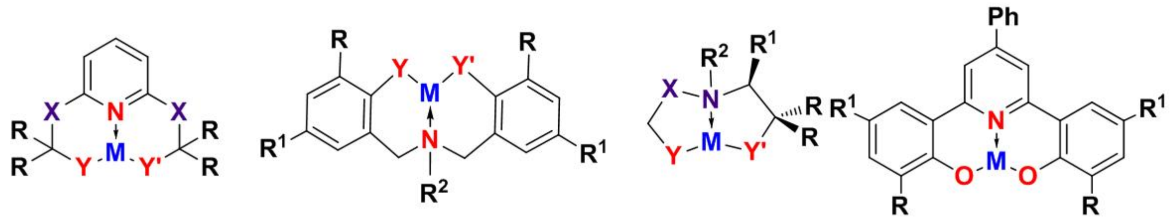
The heavier carbene analogs R_2E (low-valent derivatives of Group 14 elements, E = Si, Ge, Sn, Pb) attract significant attention due to fundamental interest and to possible practical application. Such compounds are very reactive and usually highly unstable. The stabilization may be achieved kinetically (by introduction of sterically voluminous groups R), or thermodynamically (by using of special designed ligands R, possible to electronic interaction with E atom) [1, 2].

In this report the synthesis, investigation of structure, studies of chemical and catalytic properties of a number of tetrylenes based on polydentate ligands are described. The ligands of various nature (differed in electronic and geometric characteristics of the substituents, donor atoms, rigidity) were used [3, 4].



M = Si(II), Ge(II), Sn(II), Pb(II); Y, Y' = O, S, N(Ts), $N(C_6F_5)$;
X = CH_2, CH_2CH_2; R, R^1, R^2 = H, Me, Ph, Bn, 2-Py

It is shown that tetrylenes are effectively stabilized by ligands elaborated in our laboratory; the compounds obtained were used in the synthesis of different organometallic derivatives or as ligands for transition metal complexes. Furthermore, carbenes obtained used as initiators of ring-opening polymerization of lactones and may be characterized as very active catalysts giving target polymers with high control of the process.

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SYNTHESIS OF POLYMETHYLMETHACRYLATE IN THE PRESENCE OF VARIOUS O-IMINOSEMIQUINONE COMPLEXES OF TIN(IV)

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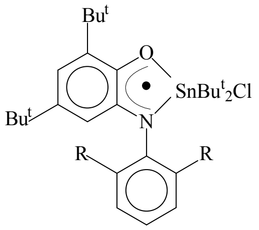
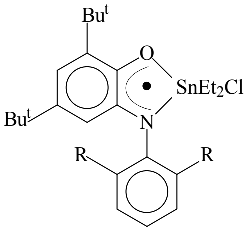
The paramagnetic complexes of tin(IV) based on 4.6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-aminophenol, may be used as regulators of radical polymerizations of methylmethacrylate (**MMA**) initiated by azobis(isobutyronitrile) (**AIBN**) at 70ºC [1]. Complex with *tert*-buthyl substitutions acts as iniferter – the initiator and regulator of radical polymerization of (meth)acrylic monomers and styrene at 70-110°C [1, 2].

The aim of this work was to study and compare the polymerization of MMA with the participation of paramagnetic tin(IV) complexes ***1-2*** on various conditions.



1a-c



2a-c

*R = Me (**a**), Et (**b**), Pr^i (**c**)*

It was found that each of the ***1a-c*** acts as iniferter of MMA polymerization at 50-90°C. Polydispersity indexes (***PDI***) of polyMMA samples obtained using ***1a-c*** are ~ 1.3-1.5 at the initial stage.

It was established that each of compounds ***1-2*** in the range of 70-90°C reduces the polymerization rate of MMA initiated by AIBN in proportion of its concentration. When complexes with *tert*-butyl substituents (***1a-c***) are used, the MMA polymerization proceed more rapidly than with the participation of it's ethyl derivatives analogous (***2a-c***). The size of the alkyl substituent in the aryl fragment of the paramagnetic ligand is significant in series ***1a-c*** (***2a-c***); the larger it is, the slower the polymerization processes.

It is worth noting that the number average molecular weights ($\boldsymbol{M_n}$) of the polyMMA samples obtained with the participation of each of the ***1-2*** increase proportionally with increasing conversion both at 70 and at 90°C. PDI of polyMMA samples obtained using ***1a-c*** are ~ 1.5-1.7 at the initial stage and increase to 3.0-3.5. In the case of complexes ***2a-c*** PDI remain in the range 1.4-2.0 up to the limiting degrees of monomer conversion.

It was found that polymers prepared in the presence of ***1a-c*** at 70-90ºC capable to reinitiation of polymerization various vinyl monomers. PolyMMA prepared in the presence of AIBN and each of the ***1-2*** at 70-90ºC also can act as a macroinitiators. The effectiveness of re-initiation depends on the composition of the complex and the conditions of the processes.

Thus, complexes of tin(IV) with various redox-active *o*-iminosemiquinone ligand can act as regulators of chain growth in polymerization of MMA initiated by AIBN and without it. The regulating capacity of complexes depends on the composition of the aryl fragment of the ligand, and the alkyl substituent at the tin atom.

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HYBRID NANOPARTICLE BASED ON WATER-SOLUBLE MACROCYCLIC SULFO DERIVATIVES AND SILICON DIOXIDE: SYNTHESIS AND SELF-ASSEMBLE

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Self-assembly / self-organization of supramolecular materials through weak non-covalent interactions opens up new opportunities for their successful application in the design of sensors, catalysts, biomimetic systems, selective extractants, drug delivery systems and programmable materials. Compounds that can both selectively and reversibly bind to biologically important macromolecules are promising as therapeutic and diagnostic tools. Such potential objects capable to recognizing / isolating biologically important compounds are hybrid organo-inorganic materials based on silicon dioxide and water-soluble macrocycles.

In this paper, the synthesis and non-covalent self-assembly of macrocycles, functionalized by various binding sites ((poly)amino, ammonium, sulfonic acid fragments) and hybrid surface modified nanoscale silica particles are presented. These self-assembled particles have been successfully applied to the recognition of various types of macromolecules (proteins and DNA).

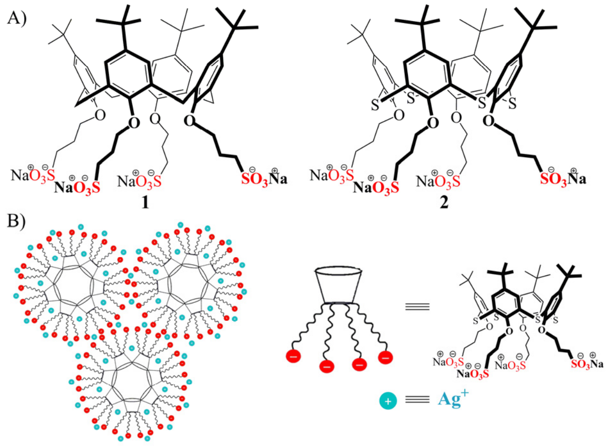

Fig. A) Structures of the (thia)calix[4]arenes **1** and **2**; B) Outline representation of the water-soluble thiacalix[4]arene **2** and of the formation of the thiacalix[4]arene stabilized silver nanoparticles

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RHODIUM AND IRIDIUM INDENYL COMPLEXES IN REDUCTIVE AMINATION OF ALDEHYDES AND KETONES

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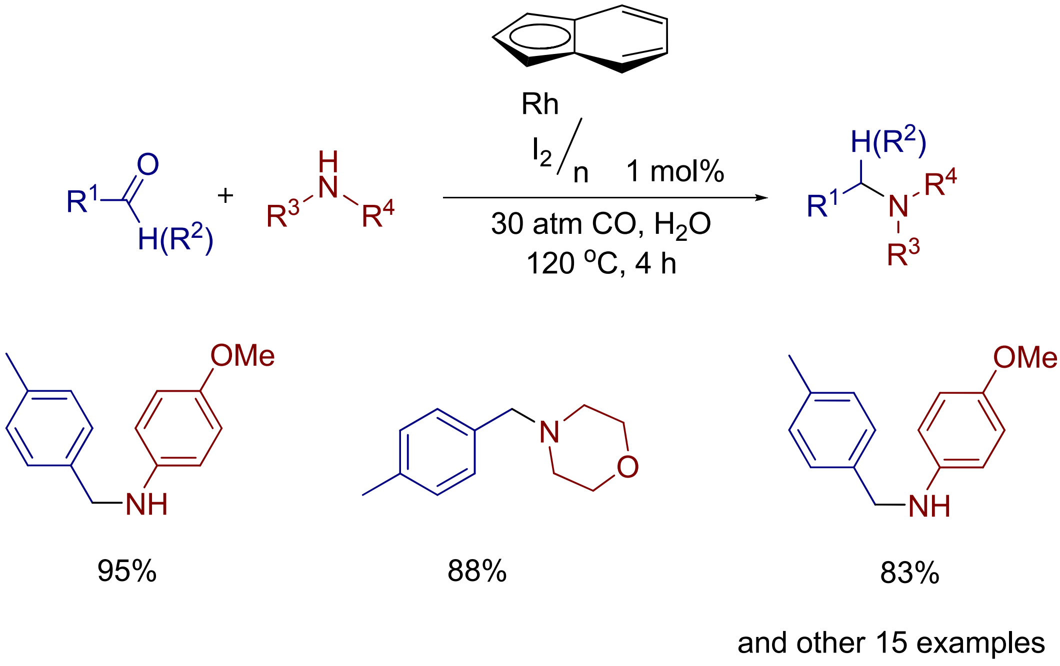
Among the transformations which are conventionally classified as reductions, reductive amination is notable for particularly high preparative significance, being one of the most convenient and versatile methods of the C-N bond formation [1]. We have recently discovered a catalytic reductive methodology which takes advantage of the deoxygenative potential of carbon monoxide and does not require an external hydrogen source unlike the conventional approaches [2].

In the present work we developed general methods for the synthesis of rhodium and iridium indenyl complexes and demonstrated its efficiency as catalysts for reductive amination of aldehydes and ketones. For example, the iodide derivatives $[(\eta^5\text{-indenyl})MI_2]_n$ (M = Rh, Ir) revealed higher catalytic activity than cyclopentadienyl analogs. Solvent screening shown that protonic solvents (e.g. water and alcohols) are the best choice for the reaction. Both aromatic and aliphatic amines are suitable, and both primary and secondary amines can be used.



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Dedication – This work is dedicated to the memory of Prof. Alexander R. Kudinov who contributed much to the development of organometallic chemistry.

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REACTIONS OF TRANSITION METAL-PNICTOGEN COMPLEXES WITH DIVALENT SAMAROCEN AND YTTERBOCEN.

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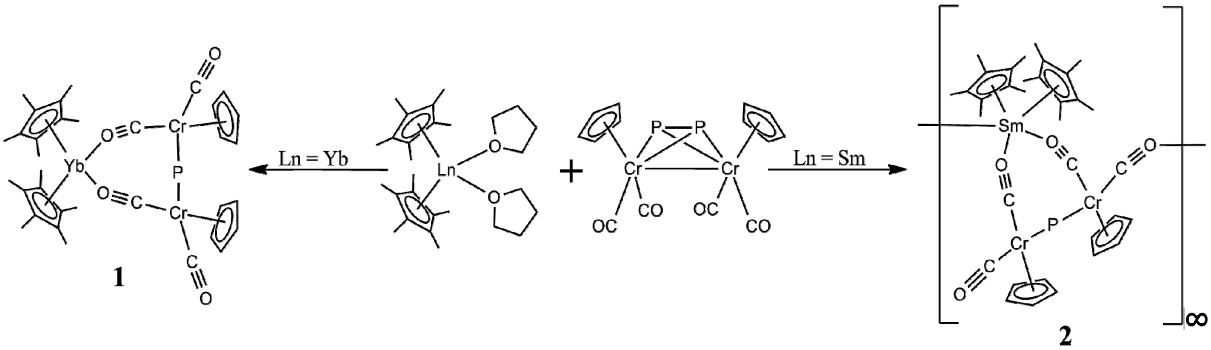
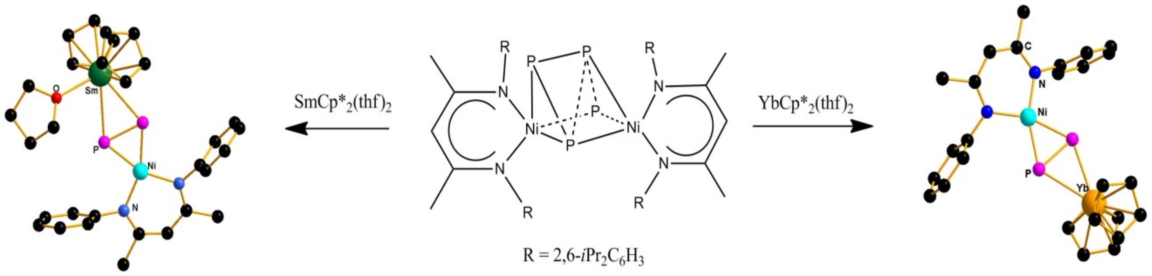
In contrast to *d*-metal (TM) polyphosphide (P_n) complexes the lanthanide (Ln) ones are far less common. Their story starts from [$(Cp^*_2Sm)_4P_8$] obtained by reduction of P_4 with [Cp^*_2Sm] [1]. This "reductive approach" is found to be really useful for preparation of mixed TM/Ln P_n-complexes. For instance, the reaction of [$Cp^*_2Sm(thf)_2$] ($Cp^* = \eta^5$-C_5Me_5) with [$\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}$-$P_2)$] was found to lead to the compounds containing Sm-P bonds [$(Cp^*_2Sm)_2P_4(CpMo(CO)_2)_2$] and [$(Cp^*_2Sm)_3P_5(CpMo(CO)_2)_3$] [2]. Herewith we report about the reaction of the chromium analogue [$\{CpCr(CO)_2\}_2(\mu,\eta^{2:2}$-$P_2)$] with [$Cp^*_2Ln(thf)_2$] (Ln = Sm, Yb), which results in different products containing the chromium $\{(\mu$-$P)(CrCp(CO)_2)_2\}$ and $\{Cp^*_2Ln\}$ moieties bonded only *via iso*-CO ligands (Scheme 1). The Cr-P bonds in the compounds thus obtained are the shortest among the known ones 2.0984(9) (for Yb) Å and 2.0879(8) (for Sm).



In contrast to [$\{CpCr(CO)_2\}_2(\mu,\eta^{2:2}$-$P_2)$] the complex [$(L^{iPr}Ni)_2P_4$] ($L^{iPr}$=CH[CMeN(2,6-$^iPr_2C_6H_3$)]$_2$) does not have CO-ligands, and its reaction with [$Cp^*_2Ln(thf)_2$] (Ln = Sm, Yb) lead to the reductive cleavage of P-P bond and formation of heterometallic complexes $\{Ln(\mu,\eta^{2:2}$-$P_2)Ni\}$ containing the Ln-P bonds.



CH_3-groups of Cp* and ^{i}Pr-groups of 2,6-$^iPr_2C_6H_3$ ligands are omitted for clarity.

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SOLVATION PROPERTIES OF COPPER(II) AMINO ACIDS COMPLEXES

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Coordination number of copper(II) in water solution is still questionable. Many investigators have done different experimental and theoretical works to define the number of solvent molecules in coordination spheres of copper(II) aqua ion, but the question is opened so far. In our previous researches [1, 2] some solvation properties of copper(II) complexes with amino acids and oligopeptides in water solutions have been found by joined usage of EPR, NMR relaxation methods and quantum chemical calculations. Such complexes are of very interest for bioinorganic chemistry. It was proposed that higher donor ability of ligands results in pentacoordination of copper(II) in complexes. The goal of present work was the verification by molecular dynamic calculations (MD) of main conclusions of that researches, namely pentacoordination of copper(II), obtained distances for the inner and second coordination spheres water molecules, their numbers and lifetimes.

MD simulations were performed by Gromacs 5.1.4 package [3] for the copper(II) *bis*-amino acids complexes with glycine, alanine, serine, lysine, arginine, asparagine, glutamine, aspartic and glutamic acids. Each complex was solvated in periodic rectangular cell [4 nm x 4 nm x 4 nm] and MD simulations for 10 ns were carried out under constant temperature and pressure. The FFWa-SPCE [4] force field parameters were used under simulation, but parameters of Lennard-Jones potential for Cu(II) were taken from GROMOS96 (ver. 54a7) force field [5]. From trajectories simulated the Cu(II)-O_{water} and Cu(II)-H_{water} radial distribution functions, numbers and mean lifetimes of water molecules in the inner and second coordination spheres were calculated and analysed.

It was obtained that MD simulation results agree well with those found experimentally by EPR and NMR relaxation methods. It was shown that the number and lifetimes of water molecules in coordination spheres depend on the side chain of amino acids. The presence of charged side chain groups results in increasing the water molecules lifetimes in the 2nd coordination sphere and in the same time leads to a decrease of lifetime of the 1st coordination sphere water molecules. MD simulation results also support the conclusion about existence of pentacoordinated copper(II) in complexes studied with coordination of only one water molecule in axial position.

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SYNTHESIS OF TRINUCLEAR COMPLEXES ON THE BASE OF HEMIHEXAPHYRAZINES

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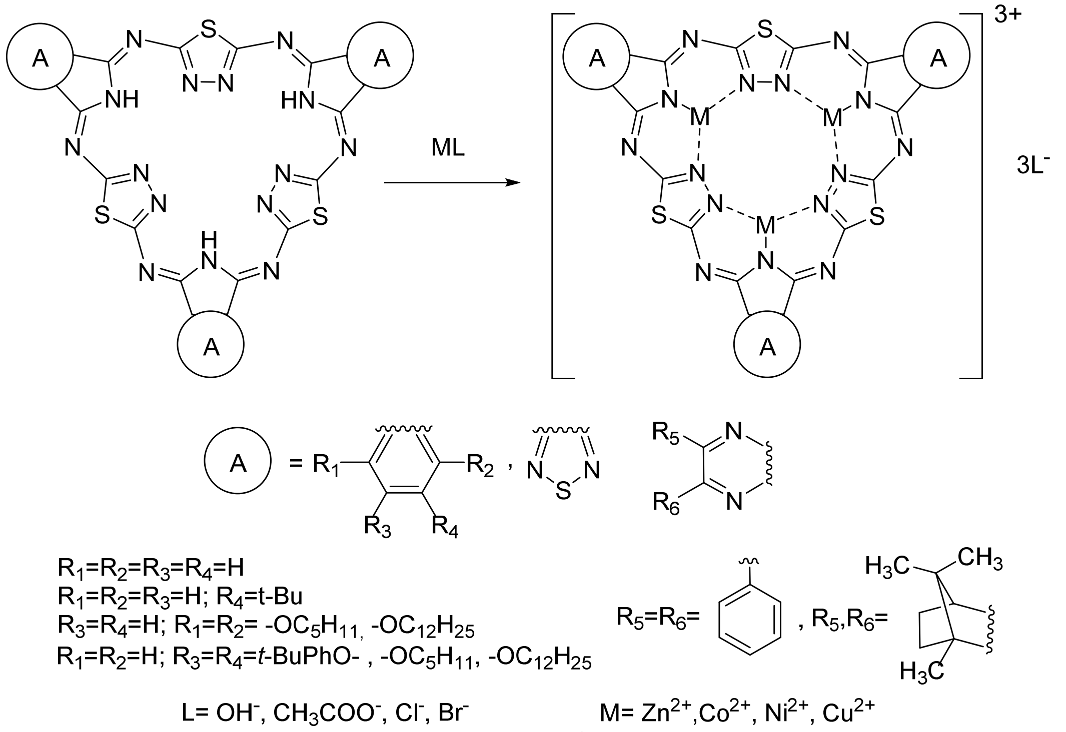
Hemihexaphyrazines are macroheterocyclic compounds of ABABAB-type with an expanded coordination cavity, which is able to coordinate 3 atoms of transition metal [1, 2] to form stable complexes. The homotrinuclear complexes were synthesized by metallation of hemihexaphyrazines [3] with salts of Co (II), Ni (II), Cu (II) and Zn (II) in DMF or phenol.



R_1=R_2=R_3=R_4=H
R_1=R_2=R_3=H; R_4=t-Bu
R_3=R_4=H; R_1=R_2= -OC_5H_{11}, -$OC_{12}H_{25}$
R_1=R_2=H; R_3=R_4=*t*-BuPhO- , -OC_5H_{11}, -$OC_{12}H_{25}$

L= OH^-, CH_3COO^-, Cl^-, Br^- M= Zn^{2+},Co^{2+}, Ni^{2+}, Cu^{2+}

The complexes were characterized by UV-vis, IR, ^{1}H NMR spectroscopy, mass-spectrometry, elemental and thermogravimetric analysis, X-ray data. Their structure particularities were discussed using quantum chemistry methods.

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NEW ACYCLIC DIAMINOCARBENE PALLADIUM(II) COMPLEXES BY METAL-MEDIATED ADDITION OF BIFUNCTIONAL *N,N*-NUCLEOPHILES TO ISOCYANIDES

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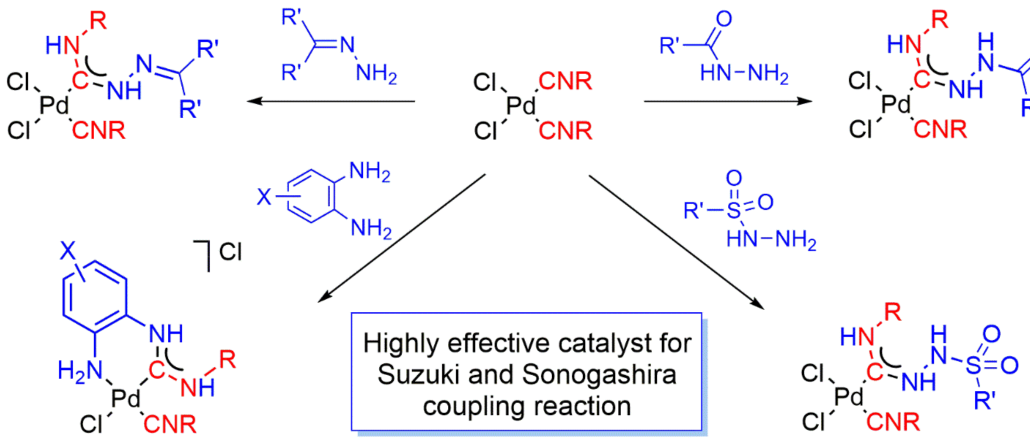
In the last decade, palladium(II) complexes with acyclic diaminocarbene ligands (ADCs) gained prominence as catalysts for various organic transformations [1]. Generation of high-performance catalysts based upon [Pd]–(ADC)s complexes for application in cross-coupling processes can be achieved via several distinct routes when most promising approach involves a metal-mediated addition of *N*-nucleophiles to Pd-bound isocyanides. Coordination to a metal center increases the reactivity of isocyanides and enables their coupling with various *NH*-species [2]. We studied the coupling of symmetrical and unsymmetrical (i.e., containing two different nucleophilic centers in one molecule) bifunctional *N,N*-nucleophiles to Pd-bound isocyanides. In the framework of this project, it was found that the direction of the reaction between the isocyanide-palladium species and *N,N*-nucleophiles depends on the position of the nucleophilic centers and led to different types [Pd]–(ADC)s species. The latter are useful as acyclic diaminocarbene-based catalysts for various cross-coupling reactions. In particular, we developed the first [Pd]–(ADC)s involved catalytic system for conductance of Suzuki reaction in an aqueous medium. Aminocarbene catalysts that allow the synthesis of substituted alkynes by Sonogashira reaction at room temperature have also been studied


Highly effective catalyst for Suzuki and Sonogashira coupling reaction

In this talk, the reactivity *N,N*-nucleophiles in metal-mediated coupling with Pd^{II}-bound isocyanides and major chemical dependence between structures of bifunctional *N,N*-nucleophiles and structures of thus generated [Pd]–(ADC)s complexes will be analyzed.

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COORDINATION LIGAND REACTIONS AS A METHOD OF NEW IRON(II) MACROBICYCLIC TRIS-DIOXIMATES PREPARING

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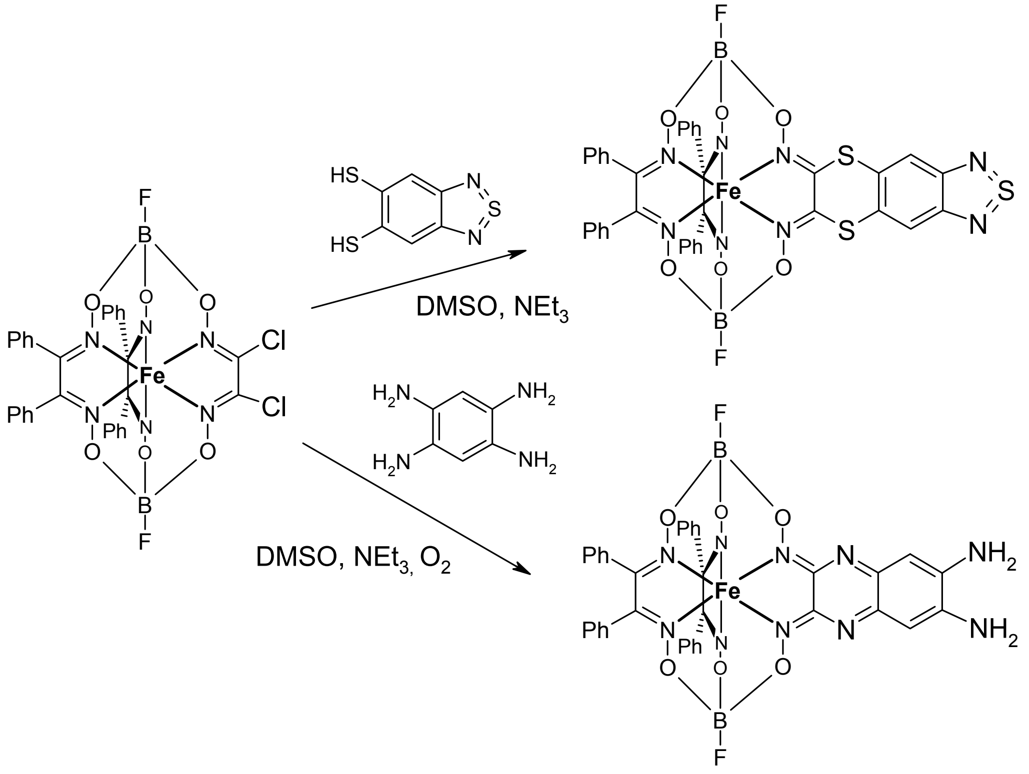
Macrobicyclic tris-dioximates of metals belong to the class of cage coordination compounds containing metal ion encapsulated in the cavity of the ligand. In the case of iron(II) clathrochelates high stability of the cage and the encapsulated metal ion strongly stabilized in the oxidation state +2 essentially limit the chemistry of these compounds to reactions in the ligand sphere. The possibility of ligand modification makes tris-dioximate clathrochelates a promising molecular platforms for design of polyfunctional compounds.

In our work we are developing several synthetic approaches to the modification of the clathrochelate dioximate cage using complexes with different substituents at dioxime ribs as precursors. The main purpose of our research is the synthesis of the new clathrochelates possessing reversible ligand-centered redox chemistry and/or ability to bind metal ions.



The clathrochelates obtained were characterized with a number of methods including single crystal X-ray crystallography and multinuclear NMR spectroscopy. Redox properties have been investigated using CVA and other methods.

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WATER-SOLUBLE POLYNUCLEAR METALLAMACROCYCLIC 3d-4f COMPLEXES: TOWARDS NEW APPLICATIONS

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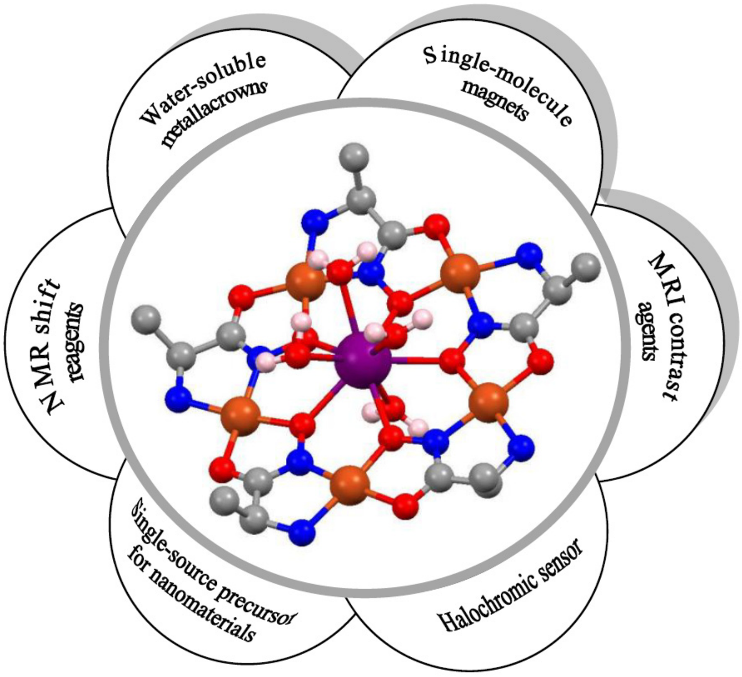
Nowadays, major efforts have been made in searching for water-soluble transition metal complexes toward the development of new functionalized materials. The polynuclear metallamacrocyclic 15-MC-5 copper(II) - lanthanide(III) complexes presented the unique supramolecular complexes with a metallamacrocyclic motif that structurally resembles crown ethers. Their scaffold consists of cyclic molecular entities in which bridging ligands are coordinated to ring metal ions to form cyclic structures with five oxygen cavity in the middle. With an idea to explore the unique structure of these complexes herein we presented their potential applications as MRI contrast agents, NMR shift reagents, halochromic sensors, single-molecular magnets and single-source precursor for nanomaterials [1-4].



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QUANTUM-CHEMICAL MODELING OF MOLECULAR STRUCTURES OF ISOMERIC MACROTRICYCLIC CHELATES OF 4*d*-ELEMENT M(II) IONS WITH AMBIDENTATE (NNNN)-DONOR LIGAND

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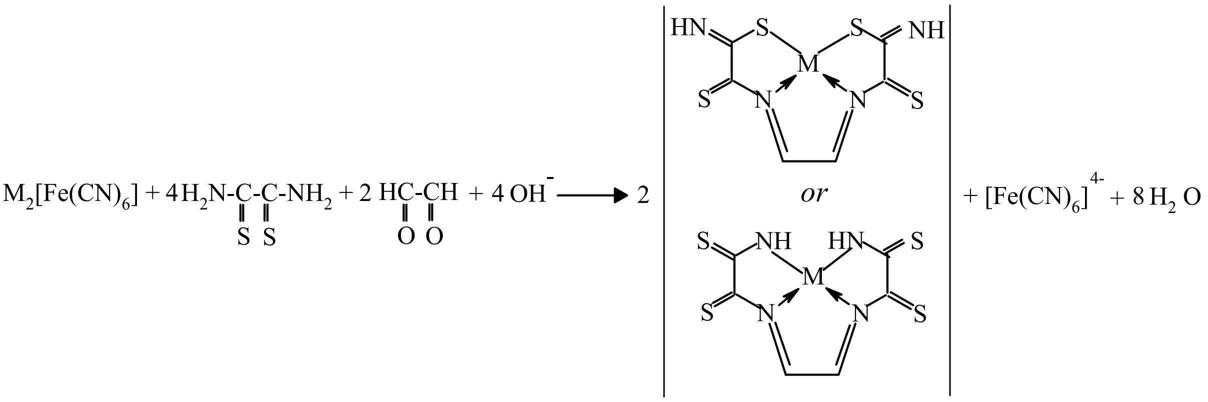
The geometric parameters of the molecular structures of Mo(II), Tc(II), Ru(II), Rh(II), Pd(II), Ag(II), and Cd(II) (555)macrocyclic chelates with the (NSSN)- and (NNNN)-coordination of the ambidentate ligand – 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1,8 formed as a result of complexing ("self-assembly") with participation of the corresponding M(II) ions with ethanedithioamide $H_2N–C(=S)–C(=S)–NH_2$ and ethanedial HC(=O)–CH(=O) according to general scheme



have been calculated by means of the OPBE/TZVP//QZP hybrid density functional theory method with the use of the Gaussian09 program package. It has been noted that in the case of 4*d*-element ions Mo(II), Tc(II), Ru(II), Rh(II) and Pd(II), are chelates with (NSSN) coordination are more stable that chelates with (NNNN) coordination whereas in the case of Ag(II) and Cd(II), the reverse situation takes place. The bond lengths, bond angles and torsion (dihedral) angles in these complexes and in the corresponding chelate ambidentate ligand (2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1,8) have been calculated. It has been stated that the Rh(II), Ag(II) and Cd(II) chelates are ideally planar, Tc(II) and Cd(II) chelates are slightly nonplanar, whereas Mo(II) and Ru(II) chelates exhibit a rather considerable deviation from coplanarity. The additional five-membered chelate ring resulting from template cross-linking is either strictly planar [in the Mo(II), Tc(II), Rh(II), Pd(II), Ag(II) and Cd(II) chelates] or nearly planar [in the Ru(II) chelate].

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CROSS-COUPLING REACTIONS OF HALOGEN-*CLOSO*-DECABORATES - THE APPROACH TO THE SELECTIVE SYNTHESIS OF BIOLOGICAL ACTIVE SUBSTANCES

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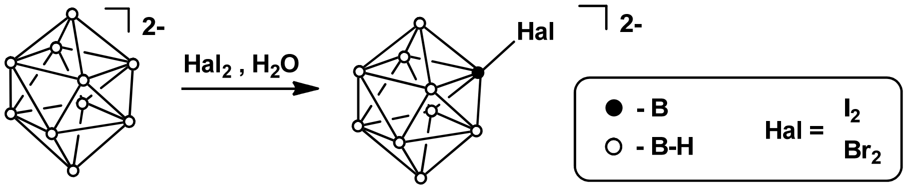
One of the most important applications of boron clusters is the use as drugs for BNCT. The main attention of researchers is focused on finding efficient transport groups for selective delivery of carboranes, carbolides of metals, and *closo*-anion $[B_{12}H_{12}]^{2-}$ to cancer cells. The formation of molecular assemblies and bioinorganic systems based on boron cluster with *exo*-polyhedral bonds B-C, B-N, B-O requires the development of methods for their targeted functionalization

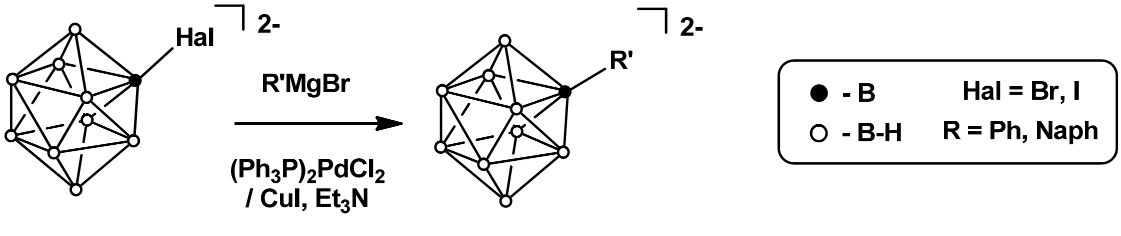
The formation of substituted anion derivatives of $[B_{10}H_{10}]^{2-}$ with *exo*-polyhedral B-C bonds is an important and urgent problem, and cross-coupling reactions provides great opportunities for solving it. This study is devoted to the development of new methods of modification of the *closo*-decaborate anion, in particular to the preparation of substituted derivatives with the *exo*-polyhedral boron-carbon bond.

A new method for the selective preparation of bromo- and iodo-substituted *closo*-decaborate substrates for the subsequent palladium-catalyzed cross-coupling was also proposed. To increase the selectivity of the halogenation process, reaction was carried out under controlling of the pH of the reaction medium:



It was found that as the pH of the medium increases, the amount of by-products decreases, and at pH 14 it is possible to obtain exceptionally substituted derivatives with an equatorial position of the substituent. Investigated processes are characterized by high yields and ease of isolation of the target product.

Cross-coupling reactions of halogen-*closo*-decaborate were studied. Grignard's reagents were selected as
nucleophiles:



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LUMINESCENT, MECANO- AND CHEMOSENSORIC PROPERTIES OF RARE-EARTH AND BORON COORDINATION COMPOUNDS AND FUNCTIONAL MATERIALS ON THEIR BASE

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The report presents the data on interconnection between geometrical and electron structure of the rare-earth and p-element complexes and their luminescent, triboluminescent, thermochromic, optic chemosensoric and photochemical properties.

A special attention given to the synthesis and study of new lanthanides triboluminophors and "switching-on" luminescent chemosensors based on boron, europium and terbium compounds inducing their own luminescence under mechanical impact (triboluminophors) or by binding of substrate (analyte) due to intra- and intermolecular processes of charge transfer (optical chemosensors).

The examples of nano- and microstructured functional optical materials on the basis of complex compounds of lanthanides and boron were demonstrated. The examples of optical materials prospective for development of the devices to be used in transformation and processing of optical signals were also demonstrated. The obtained data can be used in development of sensor materials for detecting vapors of harmful chemical compounds, in particular, those of polar solvents and monocyclic aromatic hydrocarbons, ammonia, amines, acetone.

The prospects of finding new multifunctional polymeric systems for optical sensing, environmental monitoring and optoelectronics are given.

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LANTHANIDE-DOPED NANOPARTICLES FOR SENSING AND IMAGING

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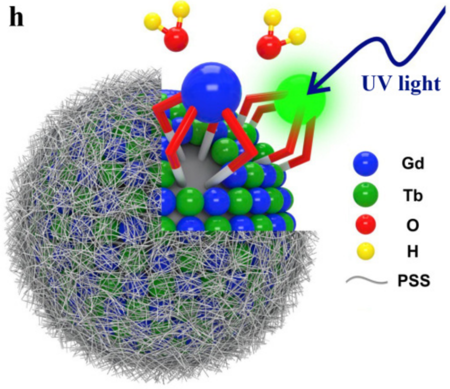
The report introduces three synthetic approaches of conversion Tb(III) and Gd(III) complexes to hydrophilic nanosized colloids with high Tb(III)-centered luminescence and efficient magnetic relaxation properties correspondingly. The first synthetic approach is based on doping of the complexes into silica nanoparticles through a sol-gel technique. Deposition of a hydrophilic shell onto hard templates built from nanosized species of lanthanide complexes is an alternative route of getting hydrophilic lanthanide-based nanoparticles. The obtained results and literature data reveal significant difference in the factors responsible for most enhanced luminescence of the Tb(III)-based colloids and high relaxivity of the Gd(III)-based colloids. For example, high inner-sphere hydration of the lanthanide centers is the reason for high relaxivity, while both low inner-sphere hydration and specific ligand environment are required for high relaxivity. Both nature and thickness of the hydrophilic exterior layer are also highlighted as significant reasons for a tuning of luminescent or magnetic relaxation properties.



Cytotoxicity and cellular uptake behaviour of the differently synthesized nanoparticles are discussed in the correlation with a structure of lanthanide complexes and a nature of hydrophilic exterior layer.

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PECULIARITIES OF DIHYDROGEN BONDING AND PROTON TRANSFER FROM MH vs OH ACIDS TO GROUP 10 METAL HYDRIDES

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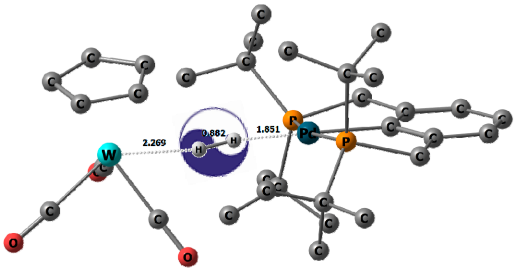
The reactivity of neutral transition metal hydrides being formally the sources of hydride ion H^- or proton H^+ is well appreciated. It can be attenuated at the early stage of an intermolecular complex of reactants.[1] The hydride ligands possessing a partly negative charge are *proton accepting sites* forming a dihydrogen bond (DHB), $M{-}H^{\delta-}\cdots{}^{\delta+}HA$, whereas those serving as a *proton source* give hydrogen bond of $M{-}H^{\delta+}\cdots B$ type (B = organic base).[2] Recently, while studying the reaction between the acidic $(\eta^5\text{-}C_5H_5)WH(CO)_3$ and the basic $(^{t\mathrm{Bu}}PCP)NiH$ $[^{t\mathrm{Bu}}PCP = \kappa^3\text{-}2,6\text{-}(t\mathrm{Bu}_2PCH_2)_2C_6H_3]$, we have established for the first time that the acid–base interaction between the two hydrides is mediated by a dihydrogen bonded complex.[3] In this talk we report the results of the detailed spectral and quantum chemical studies of dihydrogen bonding and proton transfer to $(^{t\mathrm{Bu}}PCP)MH$ hydrides (**1**; M = Ni (**a**), Pd (**b**)) from $CpW(CO)_3H$ [4] and its analogue $TpW(CO)_3H$ (Tp = κ^3-*N*-hydridotris(pyrazolyl)borate) as well as traditional OH acids. The $M{-}H^{\delta-}\cdots{}^{\delta+}HW$ bonds are much weaker than those of **1** with NH or OH acids, but the former complexes are more reactive. Kinetic and thermodynamic parameters of proton transfer accompanied by H_2 evolution were obtained by IR (ν_{MH}, ν_{CO}) and NMR spectroscopy (^1H, ^{31}P) in a wide temperature range (190-300 K). The peculiarities of products and intermediates structure were assessed by DFT calculations. The influence of the metal and ligands nature on the thermodynamic and kinetic parameters of the various stages of the process will be discussed.



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PROTECTIVE EFFECT OF 2,6-DI-*TERT*-BUTYLPHENOL DERIVATIVES AGAINST TOXIC IMPACT OF HEAVY METAL COMPOUNDS

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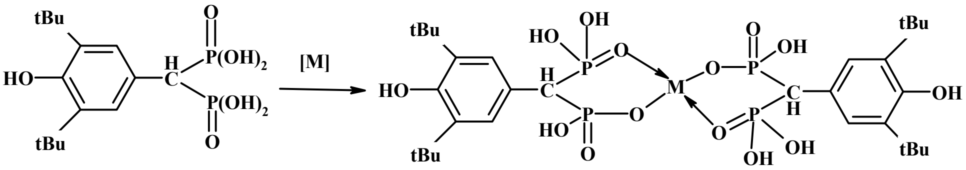
The toxicity of organic derivatives of Hg and Sn is associated not only with the binding with proteins, but also with the homolytic cleavage of the C-M bond, which leads to the generation of reactive organic radicals R°, which are promoters of oxidative stress. In order to inhibit effectively the oxidative damage of biomolecules induced by toxic heavy metal compounds the protectors that combine in one molecule both chelating fragment and antioxidant group of 2,6-di-tert-butylphenol might be used. The antioxidant effect of 2,6-di-tert-butylphenol derivatives containing a fragment of bicyclic pyrrolidines, phosphonic acids and porphyrins was studied under the conditions of promoting the long-flowing process of lipid peroxidation of liver and sperm of Russian sturgeon, and of fish feed. Sn and Hg compounds present in the aqueous medium due to their use as biocides or formed as a result of biochemical methylation have been studied as promoters. It was ~~is~~ shown that in the presence of Sn and Hg compounds, the level of lipid peroxidation of feed, liver and sperm of Russian sturgeon in experiments in vitro and in vivo increases significantly with respect to control, which confirms the prooxidant effect of organometallic compounds. After the addition of of 2,6-di-tert-butylphenol derivatives, the prooxidant effect of tin and mercury compounds ~~was~~ reduced significantly, which can be ~~is~~ explained by the ability of protectors to bind metal ions according to the scheme.



The prolonged antioxidant effect of polyfunctional derivatives of 2,6-di-*tert*-butylphenol is due to the presence of hindered phenolic fragments that are scavengers of reactive radicals participating in oxidative processes. The highest antioxidant activity was found for (4-hydroxy-3,5-di-*tert*-butylphenyl)methylenediphosphonic acid, which is presumably due to the intramolecular synergistic effect of the phenolic and phosphorus-containing groups. That makes it possible to propose this compound as detoxifying additive~~s~~, for example, in fish feeds. It has been shown that the administration of (4-hydroxy-3,5-di-*tert*-butylphenyl)methylenediphosphonic acid at a concentration of 150 mg/kg in feed together with $(CH_3)_3SnCl$ contributes to reducing the toxicity of the organotin compound by enhancing the activity of the organism natural antioxidant defense system. The study of the antioxidant activity of new hybrid molecules based on 2,6-di-*tert*-butylphenol showed their high antioxidant potency in comparison with the known phenols due to the multifunctional mechanism of their mode of action. It has been established that the anti/prooxidant properties depend significantly on the structure of the molecule and the presence of the phenolic fragment, as well as on the oxidation conditions and the nature of the substrate.

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27th International Chugaev Conference on Coordination Chemistry
4th Conference-School for Young Researchers "Physicochemical Methods in Coordination Chemistry"
October 2-6, 2017, N. Novgorod, Russia

ARYL-SUBSTITUTED METALLOPORPHYRINS AND METALLOCORROLES: ELECTROCHEMICAL CHARACTERISTICS AND MOLECULAR OXYGEN ELECTROREDUCTION

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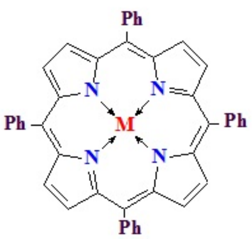
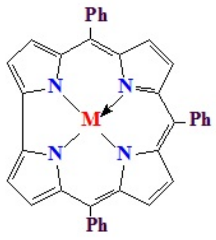
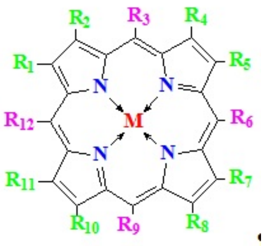
Among of macrocyclic complexes of transition metals N_4-macrocyclic complexes are of particular interest on account of their high stability, possibilities of varying their structures in a wide range by targeted synthesis and their lower cost compare to noble metals as an electrocatalysts. One of the most important properties of porphyrins and their analogs are redox ones. It was shown that metalloporphyrins and metallophtalocyanines generally exhibit a good activity in the oxygen reduction reaction (ORR) [1-3]. Electrocatalytic properties are different as differ individual structural features for porphyrins of various classes.

The aim of this work is to compare electrochemical behavior and electrocatalytic abilities of ORR of MCor with MP of closely related structures. *ms*-Tetraphenylporphyrin $\{H_2(Ph)_4P\}$, pyridylporhyrins with different numbers of *ms*-pyridyl groups, their isomerism (4-, 3-, 2-), β-alkyl substituents $\{H_2(Py)_4P\}$ and corroles $\{H_3Cor\}$ as a porphyrin analogs bearing *ms*-aryl substituents are considered.







The electrochemical behavior of pyridyl-substituted porphyrins in aqueous alkaline medium has been characterized in the course of electroreduction (electrooxidation) processes not only on the metal (Co(II), Cu(II), Fe(III)) or the π-conjugated system of the macrocycle, but also on the electron-withdrawing (pyridyl) substituents, which are reduced in the potential range -0.7÷-0.8 V (*vs.* Ag/AgCl electrode), compared to the complexes of *ms*-tetraphenylporphyrin. Moreover, it was found that the introduction of a pyridyl substituent in porphyrins leads to an increase in the rate of ORR.

The electrochemical behavior of corroles in aqueous alkaline medium has been characterized in the course of electroreduction (electrooxidation) processes on the metal (Cu(II and III), Co(III), Fe(III), Mn(III and IV)) and one on the π-conjugated system of the macrocycle.

In these studies we have demonstrated the possibility of evaluating the electrocatalytic properties in ORR on the fixed electrodes with active layers containing porphyrins or corroles in active mass. In our view, these investigations increasingly model of actual use of hydrophobized cathodes in power sources with oxygen (air) depolarization.

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DIPHOSPHIOXIDE BEARING PYRIDINES AS CHELATING LIGANDS FOR F-ELEMENTS

N.E. Borisova, G.G. Zakirova, S. Bakaev, A.V. Kharcheva, P.I. Matveev, S.V. Patsaeva and S.N. Kalmykov

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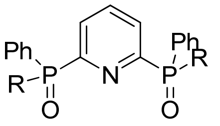
A new type of heterocyclic "hard-and-soft" ligands (1-3) for f-elements binding was proposed from the basis of DFT simulation (PBE, B3LYP, cc-pVDZ and cc-pVTZ basis sets). The efficient methods (Pd-catalysed cross-coupling reaction and nucleophilic substitution) for the scalable preparation of the reagents starting from corresponding heterocyclic halides were developed. Water soluble reagents (R=3-HSO3C6H4) were be obtained by sulfation of the corresponding phosphinoxides with moderate yields. The structure of the ligands was estimated by X-Ray. All of the synthesized reagents show americium over europium selectivity on extraction from 3M nitric acid to polar diluents. Phosphinoxides of type 1 possess the better among them efficiency and Am/Eu selectivity. For the first time the significant affect of P,P-diasteriomers on extraction was observed.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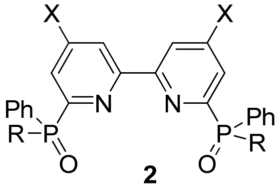
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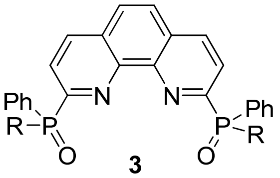
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R = Ph(a), 3-HSO$_3$C$_6$H$_4$ (b), ^{t}Bu(c)

A series of complexes of ligands 2 and 3 with f-elements were received and their structure studied in solid and in solution by X-Ray and NMR. The europium complexes with 2a, 2b and 3a in solid state and in solution demonstrate ion-centered luminescence. The europium complexes of ligands 2a and 3a bearing nitrate and trifluoroacetate (TFA) counterions show counterion-dependent life-times: 1.20 ms for 2a Eu$(NO_3)_3$ and 1.01 ms for 3a Eu$(NO_3)_3$ but twice higher values were observed for TFA-complexes 2.16 ms for 2a Eu(TFA)$_3$ and 1.84 ms for 3a Eu(TFA)$_3$. The quantum yields (QY) are ligand-dependent: both complexes of 2a possess about 85% QY, but a concentrations quenching was observed at concentrations of more than 8.0×10^{-6} M, and complexes of 3a show low 10-20% QY in all concentration range. Water soluble ligand 2b readily form complex with europium nitrate, its structure in DMSO solutions was studied by NMR techniques. The complex possess high (68%) QY which is quenched by water addition to 13% and keep on this level up to 50% DMSO solution. After addition of the complex to a solution of human serum albumin (HSA) in acetate buffer the emission of albumin fluorescence does not change, but HSA fluorescence excitation at 227 nm is disappeared and at 284 nm greatly decreased. Thus we can expect the europium complex enters the first binding site of albumin from the basis of decrease in the intensity of the tyrosine fluorescence excitation. The quantum yield of europium luminescence has value of 1.3%.

Acknowledgements - The results have been obtained under support of the RSF grant no. 16-13-10451.

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REDUCTION BY LANTHANIDE 2+ COMPLEXES AS A WAY TO PNICTOGENIDE AND CHALCOGENIDE DERIVATIVES: AN EFFECT OF LIGAND, METAL, AND PRECURSOR TYPE

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Complexes with ligands featuring heavy group 15 and 16 donor atoms (E = P, As, Sb, S, Se, Te) are quite rare in the lanthanide (Ln) chemistry and their synthesis is usually combined with definite challenges. Nevertheless, representative examples of such compounds show interesting structural properties, luminescent, magnetic, and catalytic behavior [1], so this area of chemistry is rapidly expanding nowadays. Synthesis of such compounds by reduction of proper precursors with Ln(II) complexes is a good alternative to salt metathesis and protonolysis reactions. Potentially, only one compound is formed during reduction process, and there is no by-products, such as ate-complexes or protonated leaving groups, as in the case of other approaches.

We investigated the reduction of precursors containing an E–E bond by Ln^{2+} complexes of different types with sterically demanding ligands. Reduction of P_2Ph_4 by samarocenes $[Sm^{II}Cp^x(thf)_n]$ leads to different products depending on the Cp^x ligand ($Cp^* = \eta^5\text{-}C_5Me_5$ or $Cp'' = \eta^5\text{-}C_5H_3Bu^t{}_2$) and reaction conditions (Fig. 1*a,b*). Structures of the products allowed the reaction routes to be proposed [2]. Reduction of diaryldichalcogenides Ar_2E_2 (E = S, Se, Te) by formamidinate complexes of Sm and Yb, $[Ln^{II}(Dippform)_2(thf)_2]$, leads to nearly quantitative formation of chalcogenolate complexes $[Ln^{III}(Dippform)_2(EAr)(thf)_n]$ (n = 1, 0, Fig. 1*c*), whose structure depends on the size of Ln cation and type of aryl substituent.

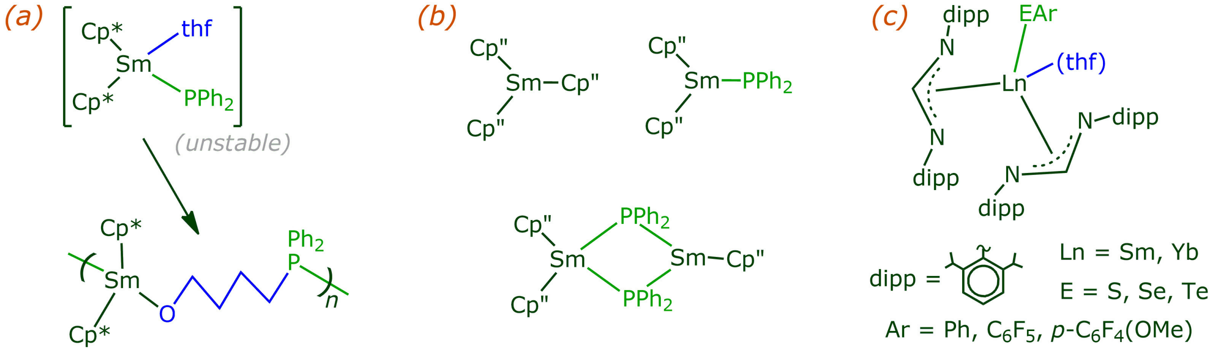

Fig. 1. Mixtures of products formed in the reaction of P_2Ph_4 with *(a)* $[SmCp^*_2(thf)_n]$ or *(b)* $[SmCp''_2(thf)_n]$; *(c)* products of the reactions of $[Ln(Dippform)_2(thf)_2]$ complexes with Ar_2E_2

[1] T. Li, S. Kaercher and P. Roesky, *Chem. Soc. Rev.*, **2014**, *43*, 42–57; T. Pugh, F. Tuna, L. Ungur, D. Collison, E. J. L. McInnes, L. F. Chibotaru, R. A. Layfield, *Nat. Commun.*, **2015**, *6*, 7492.
[2] N. A. Pushkarevsky, I. Yu. Ilyin, P. A. Petrov, D. G. Samsonenko, M. R. Ryzhikov, P. W. Roesky and S. N. Konchenko, *Organometallics*, **2017**, *36*, 1287–1295.

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NEW «CENTAUR» $[Re_3Mo_3Q_8(CN)_6]$ CLUSTERS: SYNTHESIS AND DETAILED STUDY

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The chemistry of chalcogenide Mo_6 and Re_6 metal atom clusters is widely developed and very rich since it ranges from the solid state chemistry for the synthesis of pure inorganic compounds to the solution and coordination chemistry for the elaboration of hybrid molecular assemblies and nanomaterials [1, 2]. These metal clusters are associated with ligands to form face-capped $[M_6L^i_8L^a_6]^{n-}$ units that exhibit unique physico-structural properties: red luminescence with a large Stockes shift, catalysis & photocatalysis, singlet oxygen generation, luminescence sensitizing.

Electrochemical measurements showed that $[Re_6Q_8(CN)_6]$ cluster complexes reveal electron-rich states, namely 23 and 24 cluster valence electrons (CVE) per cluster with Re-Re bonds of 2.60-2.63 Å, while cluster complexes $[Mo_6Q_8(CN)_6]$ reveal electron-poor states, namely, 20/21/22 cluster valence electrons with Mo-Mo bonds of 2.70-2.73 Å.

Recently we have prepared unique heterometallic cluster complexes $[Re_3Mo_3Q_8(CN)_6]$, Q=S, Se [3]. Mixed-metal cluster species were prepared by high-temperature synthesis using ReQ_2, MoQ_2 and KCN as precursors. Long-term reaction resulted in formation of chain-like polymeric compound having the composition of $K_6[Re_3Mo_3Q_8(CN)_5]$. The reaction of depolymerisation allowed us to obtain the water-soluble molecular complexes with the composition of $K_5[Re_3Mo_3Q_8(CN)_6]\cdot nH_2O$, comprising cluster anion $[Re_3Mo_3Q_8(CN)_6]^{5-}$. These clusters exist as two isomers of $\{Re_3Mo_3\}$ with different metal arrangements, namely, *fac-* and *mer-*.

Detailed study of this class of compounds by X-Ray structural analysis, cyclovoltammetry, DFT calculations and EXAFS analysis revealed that these «Centaur» complexes demonstrate properties characteristic both to Re_6 and to Mo_6 clusters. For example, these complexes undergo multiple redox processes giving clusters with number of CVE from 24 to 21. Analysis showed that metal cluster in $[Re_3Mo_3Q_8(CN)_6]^n$ complexes are distorted, the degree of distortion raises with decrease of number of CVE with Re-Re bonds being of ~2.64 Å and Mo-Mo bonds ~2.75 Å. Ambidentate nature of CN-ligands bounded to metal cluster favors to formation of numerous “Prussian Blue” related coordination polymers [4].

[1] M. N. Sokolov, N. G. Naumov, P. P. Samoylov and V. P. Fedin, *Compr. Inorg. Chem. II*, **2013**, 271-310.
[2] J.-C. P. Gabriel, K. Boubekeur, S. Uriel and P. Batail, *Chem. Rev.* **2001**, *101*, 2037-2066.
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[4] A. V. Virovets, Y. M. Gayfulin, E. V. Peresypkina, Y. V. Mironov and N. G. Naumov, *Crystengcomm*, **2015**, *17*, 1477-1482.

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GROUP 13 METAL COMPLEXES SUPPORTED BY DPP-BIAN LIGAND AS EFFECTIVE CATALYSTS FOR THE PRODUCTION OF BIODEGRADABLE POLYMERS IN CONTROLLABLE MANNER

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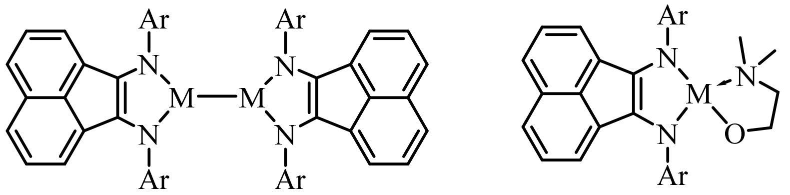
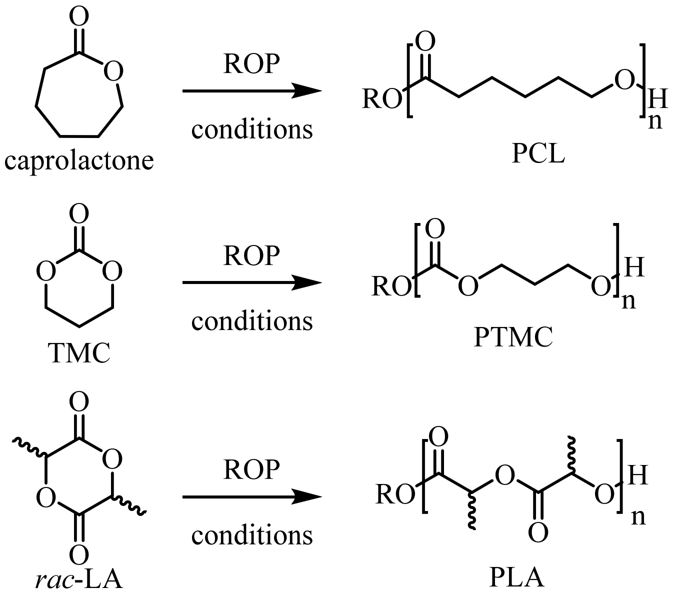
Nowadays biodegradable polymers are widely used in different fields such as medicine (temporary implants, soluble sutures), food processing industry (packing, disposable containers) etc.. The most commonly used monomers for producing biodegradable materials are cyclic esters and carbonates. The physical properties of resulting materials can be tuned by chain length control and the stereoregularity of polymer. Thus the importance of an approach for the preparation biodegradable polymers in controllable manner has been arising in recent years. In the present study the ability of gallium and aluminium compounds supported by 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphtene (dpp-bian) are shown to act as polymerization catalysts of trimethylene carbonate (TMC), ε-caprolactone (ε-CL) and lactide.



M = Al, Ga   Ar = 2,6-diisopropylphenyl



Catalytic conditions were optimized and kinetic studies were carried out demonstrating the controlled nature of the ring-opening polymerization (ROP) process. A range of polymers with predictable molecular weight and narrow polydispersity were prepared and characterized. Novel complexes of dialuminum compound with coordinated monomers trimethylene carbonate and ε-caprolactone were synthesized.

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SIMULTANEOUS INTRODUCTION OF TWO NITROXIDES AS A NEW APPROACH TO THE SYNTHESIS OF HETEROSPIN COMPLEXES

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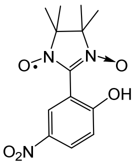
We have developed a new approach to the synthesis of multispin compounds suggested a simultaneous introduction of two different stable nitroxides (nitronyl nitroxid and imino niroxide) in the reaction with the metal ion. Noteworthy, nitronyl nitroxyl and imino niroxide can be products of different derivative series. Chemical possibilities of the approach were demonstrated by the synthesis of multispin mixed-paramagnetic-ligand complexes $[Ni_2(A^1)(L^2)_2(Piv)(MeOH)]$, $[Ni_2(L^1)(A^2)_2(Piv)(H_2O)]$, $[Co_2(A^1)(L^2)_2(Piv)(MeOH)]$ and $[Co_3(L^1)_2(A^2)_2(Piv)_2]$. The figure given below shows the different molecular structures of L^n and A^n. There are examples of mixed-paramagnetic-ligand complexes with nontrivial magnetic properties, e. g. $[Co_2(A^1)(L^2)_2(Piv)(MeOH)]$ showing bulk magnetic ordering below 3.5 K, among these compouds. We would like to draw attention to the following fact: potentially, a number of multispin compounds that could be synthesized using the proposed approach is practically unlimited.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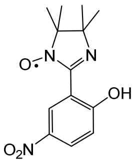
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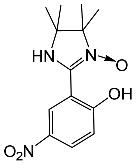
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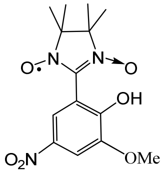
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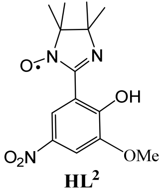
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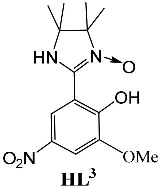
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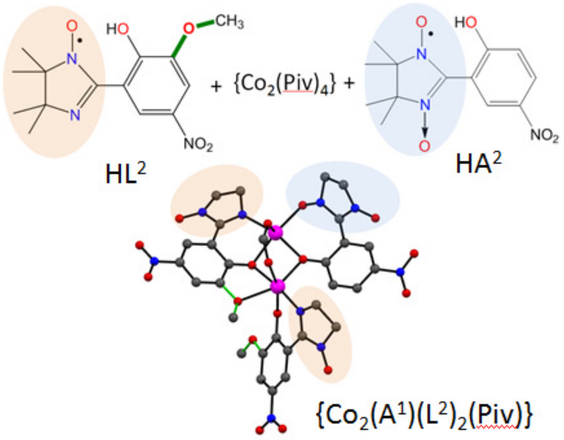

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NEW ASPECTS OF THE CHEMISTRY OF THE EARLY TRANSITION METALS: CATECHOLATES AND COMPLEXES WITH N-HETEROCYCLIC CARBENES

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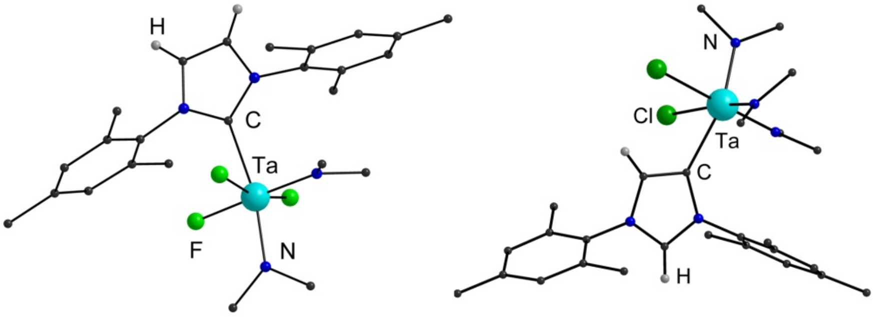
Complexes of the late transition metals with N-heterocyclic carbenes (NHC) have found applications mostly as homogeneous catalysts. In contrast, those of the early transition metals (especially of the group 5) still remain extremely rare. We have found that reaction of $Ta(NMe_2)_5$ with common NHC precursors, the imidazoline salts $NHC{\cdot}HBF_4$, gives new NHC complexes of tantalum amidofluorides, $(NHC)TaF_3(NMe_2)_2$. The chloride NHC precursor NHC·HCl reacts differently, to give $(a\mathrm{NHC})TaCl_2(NMe_2)_3$, the first example of abnormally (i.e. via C-4 atom) coordinated NHC complex of an early transition metal [1].



New cluster catecholate $[Mo_3S_7(O_2C_6Br_4)_3]^{2-}$ has been obtained by reaction of $[Mo_3S_7Br_6]^{2-}$, tetrabromocatechole and Et_3N. Sulphur elimination from the cluster core gives $[Mo_3S_4(O_2C_6Br_4)_3(thf)_2]^{2-}$, which features only two coordinated thf molecules core, and subsequently, different coordination numbers of Mo atoms (5, 6 and 6). Similar cluster $[Mo_3S_7(Cat^{36})_3]^{2-}$ (Cat^{36} = 3,6-di-*tert*-butyl-catecholate) containing catecholate with donor substituents readily oxidizes into paramagnetic $[Mo_3S_7(Cat^{36})_3]^{-}$, which, according to bond lengths in dioxolene ligands, appears to be a metal-centred anion-radical. Catecholate derivatives of titanocene were also investigated. The products in the reactions with Cp_2TiCl_2 depend on the catecholate: use of Na_2Cat^{36} results in ligand exchange and formation of $[Cp_2Ti(Cat^{36})]$, while isomeric 3,5-di-*tert*-butyl-catecholate (Cat^{35}) unexpectedly leads to partial Ti reduction and the formation of mixed-valent paramagnetic $[Cp_2Ti^{IV}(\mu\text{-}Cat^{35})_2Ti^{III}Cp]$.

[1] P.A. Petrov, T.S. Sukhikh, M.N. Sokolov, *Dalton Trans.*, **2017**, *46*, 4902–4906.

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NEW METHODS FOR SOLUTION STUDIES OF GROUP 5 AND 6 POLYOXOMETALATES

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Polyoxometalates (POMs) present an important class of inorganic compounds widely used as catalysts in the processes of homogeneous and heterogeneous catalysis, photochemistry, electronic microscopy, as the contrast agents for tomography and as the components of pharmaceutical preparations. The chemistry of POMs is very complicated as they form a variety of the species in aqueous and organic solutions which are difficult to identify due to the identity of their chemical behavior and the absence of individual signatures in different kind of spectra such as NMR, UV-VIS etc. The composition and the structure of these compounds are the fundamental features to characterize their properties and stability in solutions. For this purpose NMR spectroscopy, X-ray structural analysis and mass spectrometry are currently used. The methods of cyclic voltammetry, potentiometry, IR spectroscopy, photoluminescence and electroluminescence are also applied but much less. One of the most serious problems in the study of POMs refers to their instability resulting in the presence of the different equilibrated chemical species in solutions. On the other hand POMs demonstrate the different trends in changing of the structures in solution, depending on the medium conditions. The observation of such processes requires special direct techniques and approaches, so the data interpretation is often obstructed. As for high performance liquid chromatography (HPLC) there are only a few examples of the method application. A serious difficulty to identify the complexes forming in solution during self-assembly reactions is the inaccessibility of the individual compounds of a predetermined composition. In this regard, a special attention should be paid to hyphenated techniques such as combination of HPLC or capillary zone electrophoresis with the element-selective detector, for example, inductively coupled plasma atomic emission spectrometry (ICP-AES), which is the most appropriate for estimating the stoichiometry of the components forming during the process.

In this work we found and optimized conditions for the analysis of acidic and basic solutions of different POMs by such coupled methods. In acidic conditions we studied self-assembly reactions of molybdate, niobium source and phosphoric acid producing mixed Keggin-type anions $[PMo_{12-x}Nb_xO_{40}]^{n-}$ (x = 1 - 3). Moreover stability of mixed heteropoly anions $[(AsW_9O_{33})_2(NbO)_3(H_2O)]^{9-}$ and $[(SbW_9O_{33})_2(Nb(C_2O_4)_3]^{12-}$ in acidic media was investigated. In basic solutions we scanned reaction products after thermolysis of hexaniobates and different sources of heteroelements (W, Sb). Two types of heteroanions were observed by chromatography and accordingly to ICP-AES measurements they refer to mono and disubstituted Lindqvist anions.

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BORON(III) COMPLEXES OF HETEROCYCLIC (SUB)PHTHALOCYANINE ANALOGUES: 1,2,5-THIADIAZOLE FUSED (SUB)PORPHYRAZINES

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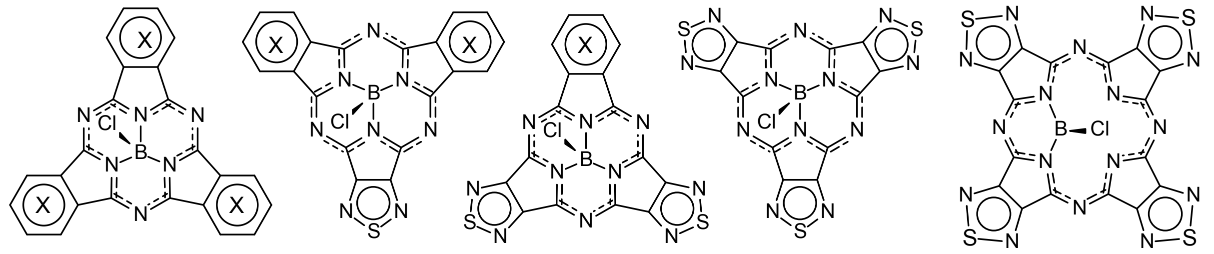
Boron(III) subphthalocyanines (**1a**) are widely investigated as perspective materials for organic electronics [1]. Usually they behave as *p*-type materials; their perfluorinated derivatives (**1b**) exhibit the *n*-type conductivity. Another way to enhance the electron acceptor properties of subporphyrazine core is annulation of π-deficient heterocycles instead of benzene rings. Thus, fusion of 1,2,5-thiadiazole rings strongly increases π-electron-deficiency of porphyrazine core [2] and tetra(1,2,5-thiadiazolo)porphyrazines were used as *n*-type layers in the prototypes of photovoltaic cells and other electronic devices [3]. Recently, we have prepared the first heterocyclic subphthalocyanine analogue with strongly electron deficient 1,2,5-thadiazole rings (**4**) [4]. In order to reveal the influence of these heterocycles on the electronic properties of boron(III) subporphyrazines we have synthesized the series of macrocycles combining 1,2,5-thiadiazole and benzene rings (**2a**, **3a**) and their perfluorinated derivatives (**2b**, **3b**).



X = H or F

The electronic absorption and emission spectra, electrochemical properties, conductivity of the sublimed thin films have been studied and the results are compared with the properties of boron(III) subphthalocyanine **1a** and perfluorosubphthalocyanine **1b**.

The evidence have been obtained that reaction of 1,2,5-thiadiazole-3,4-dicarbonitrile with BCl_3 along with boron(III) subporphyrazine **4** affords also boron(III) porphyrazine complex **5** as a cyclotetramerization by-product.

The influence of the 1,2,5-thiadiazole annulation on the electronic properties and geometrical features of subporphyrazine complexes as well as possible structures of boron(III) porphyrazines is discussed an the basis of DFT calculations results.

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[2] M.P. Donzello, C. Ercolani, P.A. Stuzhin, *Coord. Chem. Rev.***2006**, *250*, 1530–1561.
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[4]M. Hamdoush, S. Ivanova, G. Pakhomov, P.A. Stuzhin, *Macroheterocycles*, **2016**, *9*, 230-233

Acknowledgements. This work was supported by Russian Science Foundation (grant17-13-01522).

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POLYDENTATE AZOLE DERIVATIVES IN THE SYNTHESIS OF COORDINATION AND ORGANOMETALLIC COMPOUNDS

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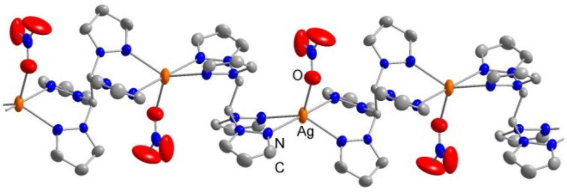
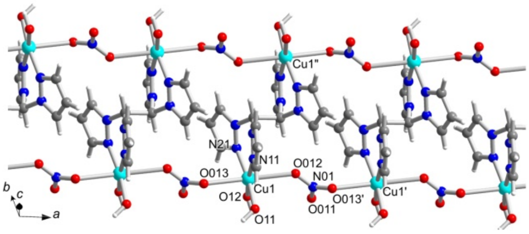
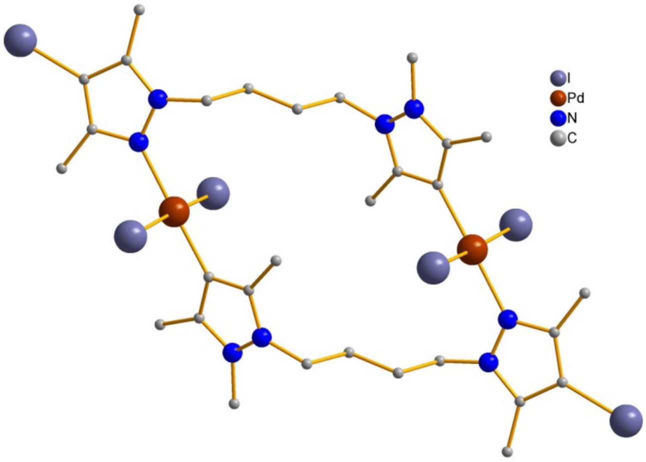
Poly(azolyl)alkanes are flexible neutral nitrogen ligands capable of forming both molecular coordination compounds and coordination polymers. We have developed facile procedures for the preparation of a wide range of bidentate bis(azol-1-yl)alkanes, as well as bitopic tetra(azol-1-yl)derivatives and studied their coordination behavior. The first examples of discrete molecular complexes and linear coordination polymers from a bitopic 1,1,2,2-tetrakis(pyrazol-1-yl)ethane (Pz_4) ligand and transition metal ions were prepared and structurally characterized. Depending on metal-to-ligand ratio and reaction conditions copper(II) nitrate formed dinuclear molecular complexes or two types or linear coordination polymers – 1D metal-ligand chains or ladder-type copper-nitrate double chains with bridging Pz_4 ligands. Silver(I) formed only 1D coordination polymers of different structures.





Pyrazolium salts based on bis(4-iodopyrazol-1-yl)alkanes were used to prepare new types of mesoionic N-heterocyclic carbene palladium(II) complexes, in which palladium ions are coordinate bis(pyrazol-1-yl)alkane ligands through carbene center of on pyrazole cycle and nitrogen atom of another cycle forming a bimetallomacrocycle. Coordination sphere of palladium is completed to square planar by two additional iodine atoms. As far as we are aware, structures of this type has never been observed before for mesoionic carbene complexes.



Acknowledgements – Russian Science Foundation, Grant No. 15-13-10023.

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POLYHALIDE COMPLEXES OF GROUP 15 AND 16 ELEMENTS: STRUCTURAL AND PHYSICAL FEATURES

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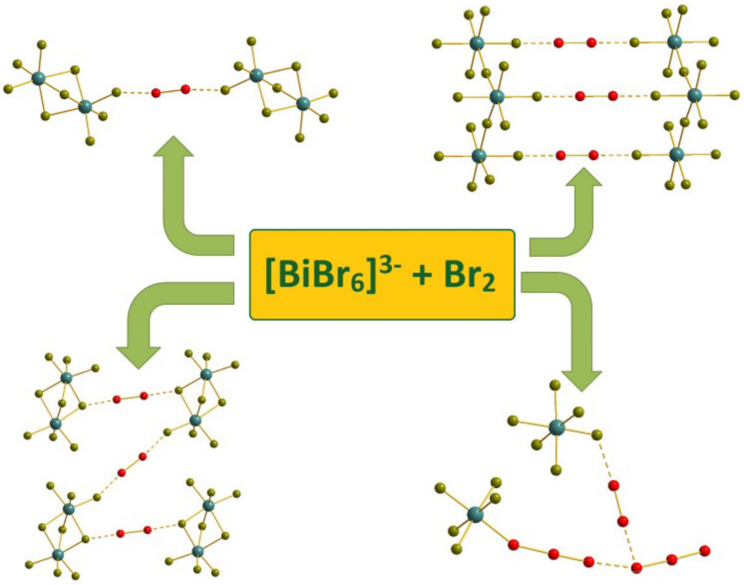
[a]*Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA.*
[b]*Novosibirsk State University, Novosibirsk, RUSSIA.*

Halide complexes of post-transition metals attract an interest due to their optical properties and possible applications in phorovoltaics. During our studies of bromobismuthates (III), we have found that reactions "

$$[BiBr_6]^{3-} + Br_2 + (cation)Br_x$$

in HBr solutions may result in anionic polybromide Bi(III) complexes where $\{Br_2\}$ units are connected with bromide lidands of Bi(III) coordination sphere by specific supramolecular contacts, yielding in $\{Br_x\}^{y-}$type polymeric ligands. In some cases, there also form tribromide $\{Br_3\}^-$ ligands coordinated to bismuth atoms. The structure of anionic part strongly depends on the nature of cation used in reaction.



The complexes demonstrate remarkable thermal stability (typically decomposition does not occur up to 120-150°C). At the same time, the "captured" $\{Br_2\}$ units preserve their ability to react with unsaturated hydrocarbons; selectivity of these reactions towards various alkenes was studied [1-3]. Mixed-halide complexes – polybromide-chlorobismuthates and polyodide-bromobismuthates – may be obtained by similar strategy. Besides, it was found that polyiodo-bromoantimonates (III) may be obtained in similar way, revealing several additional structural types, including those where Sb atom is 5-coordinated (pyramidal environment).

[1] S.A. Adonin et al., *Dalton Trans.*, **2016**, *45*, 3691.
[2] S.A. Adonin et al., *Chem. Commun.*, **2016**, *52*, 5061.
[3] S.A. Adonin et al., *RSC Adv.*, **2016**, *6*, 62011.

Acknowledgements - Russian Science Foundation (14-23-00013), Novosibirsk State University

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HIGH-RESOLUTION PHOTOIONIZATION SPECTROSCOPY OF SANDWICH COMPOUNDS: NEW APPROACHES TO STRUCTURE-PROPERTY RELATIONSHIPS IN METAL COMPLEXES

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Since discovery of ferrocene and bis(benzene)chromium over 60 years ago transition metal sandwich complexes have become one of the most important classes of organometallic compounds. They represent model molecular systems studying the nature and fundamental properties of the metal-ligand delocalized chemical bonds. On the other hand, intense chemical interest has been focused on these compounds during last decades because of their relevance to organic synthesis, catalysis, bio-organometallic chemistry and material science.

Qualitatively new opportunities for studying electronic structures of sandwich compounds appeared as modern variants of laser photoionization spectroscopy of molecules cooled in a supersonic jet have been developed. The resonance enhanced multiphoton ionization (REMPI), zero kinetic energy (ZEKE) and mass-analyzed threshold ionization (MATI) techniques provide unprecedented resolution in measuring energies of electronic excited states and vibrational frequencies of polyatomic molecules. The REMPI spectra of ferrocene as well as of $(C_6H_6)_2Cr$ and its deuterated analogues appeared to give unique information on the excited states of sandwich molecules [1, 2]. The MATI experiments provided new insights into the properties of individual rotational isomers of bis(toluene)chromium [3] and vibronic interactions in cobaltocene [4]. The threshold ionization study of monosubstituted derivatives of bis(benzene)chromium revealed accurate contributions of a single methyl or phenyl group to the ionization energy changes [5].

In this work we report recent results on the REMPI and MATI studies of metallocenes, bisarene and mixed sandwich systems. The high-resolution laser ionization spectroscopy makes it possible to analyze fine effects of the metal atom, carbocycle and substituents on the electronic structures of sandwich molecules. The spectroscopic data are supported by extended DFT calculations unveiling the mechanisms of the molecular structure influence on properties of metal complexes. The computations include analysis of both orbital interactions and electron density distributions.

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LANTHANIDE COMPLEXES BASED ON O-IMINOQUINONE LIGANDS

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A number of synthetic approaches for the preparation of rare earths (RE) complexes based on 4,6-di-tert-butyl-N-(2,6-diisopropylphenyl)-o-iminobenzoquinone (IQ) in various reduction states were developed:

1. To obtain homoligand complexes the direct reduction of o-iminobenzoquinone using metallic lanthanides exhibiting a stable oxidation state of +2 (Eu, Sm, Yb) were used. This simple atom-economical method will make it possible to obtain the target compounds in high yield without any by-products. By this method new homoligand o-amidophenolate complexes of divalent lanthanides were obtained.

2. The exchange interactions of europium, ytterbium and samarium diiodides with o-iminosemiquinolates and o-amidophenolates of alkali metals were investigated in order to obtain the corresponding complexes of divalent lanthanides.

The reactivity of the resulting o-amidophenolate complexes containing two redox-active centers - divalent lanthanide and dianionic redox active ligand - were investigated with respect to the oxidants. The interaction of lanthanide o-amidophenolates with a quantitative amount of initial o-iminoquinones afforded symmetric bis-iminosemiquinolates of the lanthanides. The products of the interaction of lanthanide o-amidophenolates with iodine in various reagent ratios were also investigated and led to the subsequent oxidation of divalent metal and redox-active ligand.

3. An effective synthetic method for the preparation of heteroligand complexes of trivalent rare earths (Y, Dy, Er) based on the salt metathesis reactions of dichlorides L^iLnCl_2 ligated by spectator β-diketiminate ligands with different steric hindrance (L^1 - 2,6-$^iPr_2C_6H_3$-NC(Me)CHC(Me)N-2,6-$^iPr_2C_6H_3$, L^2 - 2,4,6-$Me_3C_6H_2$-NC(Me)CHC(Me)N-2,4,6-$Me_3C_6H_2$) with the corresponding amidophenolates of alkali metals was successfully used as the main synthetic approach to the RE complexes of the common formula L^iLnAP (AP – amidophenolate). Such a combination of sterically hindered redox-active ligand and spectator monoanionic β-diketiminates with various substituents at nitrogen atoms allow the creation of a diverse steric environment of the central RE atom.

The molecular structures of all new lanthanide complexes were determined by single-crystal X-ray diffraction analysis. The processes of electrochemical oxidation of homo- and heteroligand o-amidophenolate complexes of RE were investigated by means of cyclic voltammetry. The magnetic properties of some prepared complexes were studied in detail.

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SYNTHETIC APPROACHES TO FORMATION OF 3D-4F HETEROMETALLIC COORDINATION COMPOUNDS POSESSING LUMINESCENCE AND MAGNETIC PROPERTIES

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Search for new and original synthetic approaches for simple preparation of heterometallic coordination compounds is one of the most interesting tasks of the modern inorganic chemistry. Complexes, containing two and more metals of different electronic structure are especially interesting because they can be directly used for creation of new functional materials with unique magnetic, luminescence, and/or catalytic properties, as well as they are considered as promising stoichiometric precursors for the preparation of heterometallic compounds by thermal decomposition.

Recently [1] we carried out direct synthesis of heterometallic compound $[Zn_2Eu(NO_3)(Piv)_6(MeCN)_2]$ (Piv is pivalate) starting from coordination polymer $[Zn(Piv)_2]_n$ and $Eu(NO_3)_3$. The title trinuclear complex is suitable staring material for further chemical modifications because labile acetonitrile ligands can be easily replaced by another mono- or binuclear N-donor ligands. Using this approach we have synthesized and characterized series of complexes $[Zn_2Ln(NO_3)(Piv)_6(Ph\text{-}Py)_2]$ (Ln = Y, from La to Lu, Ph-Py is 2-phenylpyridine). Introduction of Ph-Py caused noticeable enhancing of luminescence quantum yield of complexes (Ln = Eu, Tb) in comparison with starting material. The majority of compounds from this systematic series demonstrate thermally induced structural phase transitions that are accompanied by change of unit cell symmetry. It is worth to note that replacement of 3d-metal from Zn(II) to Co(II) allowed to isolate series of isostructural heterometallic coordination compounds and some of them possess behaviour like Single Molecule Magnets.

On the other hand, replacement of pivatale anion in compounds $[Zn_2Ln(NO_3)(Piv)_6(L)_2]$ to 1-naphthoate (naph) [2] or 1-naphthylacetate (1-naphac) led to rearrangement of the initial trinuclear metal core and formation of tetranuclear $[Zn_2Ln_2(NO_3)_2(A)_8(L)_2]$ (A = naph, naphac) complexes. The same tetranuclear compounds could be obtained by direct reactions of HA, KOH, $Zn(NO_3)_2$, $Ln(NO_3)_3$ and L in MeCN – EtOH media. Yields in these two cases were commensurable (about 80%). Using pyridine simultaneously as organic base and as the ligand in direct reactions allowed to isolatete trinuclear compounds $[Zn_2Ln_2(A)_{10}(Py)_2]$ without nitrate anions that is significant for avoiding of luminescence quenching [2].

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UNUSUAL REDOX ISOMERISM IN MONOLAYERS AND LANGMUIR-BLODGETT FILMS OF LANTHANIDE CROWN-SUBSTITUTED BISPHTHALOCYANINATES

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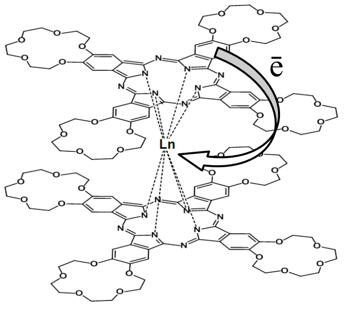
The present work is devoted to investigation of unusual process of redox isomerization in sandwich phthalocyaninates of lanthanides Pc$_2$Ln (Fig.) at air/water and air/solid interfaces. It was previously discovered for the case of Pc$_2$Ce [1] that upon formation of a monolayer of Pc$_2$Ce from chloroform solution, the tetra-valent cerium cation transforms to the three-valence state in the monolayer. The inverse transition takes place upon monolayer compression to high surface pressure and this orientation-induced pressure controlled process is reversible. Both these redox-isomeric transformations are possible due to phthalocyanine environment around the metal center, orientation factor at air/water interface and 2D compression. Actual change of cerium valence state was proved by UV-Vis spectroscopy of monolayer and X-ray photoelectron spectroscopy of Langmuir-Blodgett (LB) films deposited at different pressures. Thermodynamic estimation demonstrates that compression indeed can serve as the driving force for such isomerization. Unexpectedly, the study of the behavior of a monolayer of bisphthalocyaninates of other lanthanides – ytterbium and europium, which can be found in two stable valence states: II and III, showed similar transformations. The spectral measurements have shown that just after spreading of the complex solution onto water subphase the UV-Vis spectrum of Yb and Eu bisphthalocyaninates change. They both become similar to spectra of complexes with divalent metal centers. It is established that reversible transformations $Pc_2Eu^{2+} \leftrightarrow Pc_2Eu^{3+}$ and $Pc_2Yb^{2+} \leftrightarrow Pc_2Yb^{3+}$ can be performed upon cyclical compression and expansion of the monolayer. Existence of two redox-isomeric forms of both complexes is confirmed by spectral and electrochemical studies of monolayers and LB films. Particularly, such redox isomerization of course plays an important role in electrochemical multistability of the system, which is reflected in the form of an additional, third peak on CVA in the range of potentials from -1 to +1 V. Correlations between reduction and oxidation peaks positions of Pc$_2$Ln on the ionic radius of the metal center were demonstrated. Thus, we first discovered orientation-induced and surface pressure controlled Red/Ox isomerization - mechanochemical transformation, changing the electronic system of a single molecule in lanthanide phthalocyaninates complexes. This effect can open up new possibilities for application of ultrathin films based on such compounds in development of nanosized informational devices.



$Pc^{2-}Ln^{3+}Pc^{-} \leftrightarrow Pc^{-}Ln^{2+}Pc^{-}$

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HETEROMETALLIC CHALGENIDE IRON COMPLEXES: SYNTHESIS, STRUCTURE AND REACTIVITY

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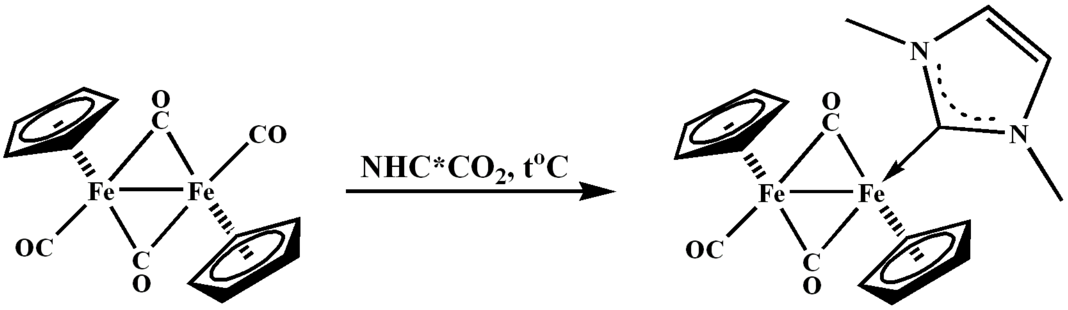
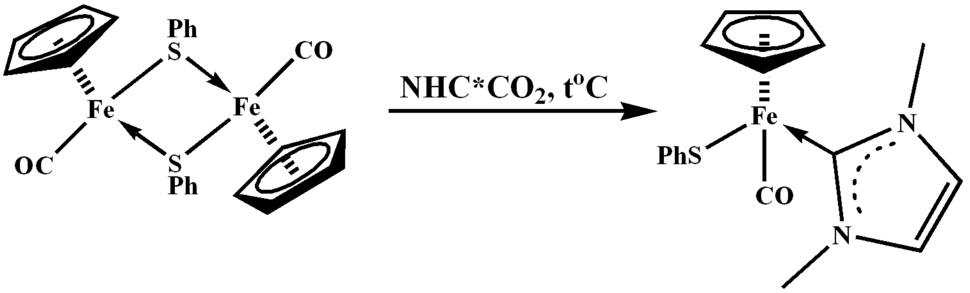
N-heterocyclic carbene complexes have been reported with large namber of metals, including actinides and lanthanides, (alkali) earth metals, main group metals, and all types of d-block transition metals. However, the organometallic chemistry of NHC ligands has been largely dominated by platinum group metal complexes (Ru, Rh, Ir, and Pd) [1]. So the main aim of this work is synthesis of iron carbene complexes with 1,3-dimethylimidazol-2-ylidene and comparison of theirs structure and reactivity with isolobal complexes.

The reaction of $[CpFe(CO)_2]_2$ with $NHC*CO_2$ (NHC = 1,3-dimethylimidazol-2-ylidene) gives us new carbene complex $Cp_2Fe_2(CO)_3(NHC)$. By X-ray data the Fe-Fe bond did not change in comparison with the initial complex and the bond between iron and terminal CO group was slightly shortened (0.012 Å). A change in the geometry of bridged CO groups was also observed: on average, the Fe-C bond was shortened by 0.046Å for the iron atom containing NHC and extended by 0.022 Å for the iron atom containing any carbene ligand.



The formation of carbene complex CpFeCO(NHC)SPh in the reaction of the dimeric complex [CpFe(CO)SPh]2 with dimethylimidazolium carboxylate takes place. An insignificant shortening of the Fe-C6 bond (0.03 Å) and an elongation of the Fe-S bond (0.015 Å) are observed by X-ray data compared with the analogous bond in the $CpFe(CO)_2SPh$ complex.



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DESIGN AND PHOTOCHEMICAL PROPERTIES OF NOVEL BORON CLUSTER CHROMENE CONJUGATES

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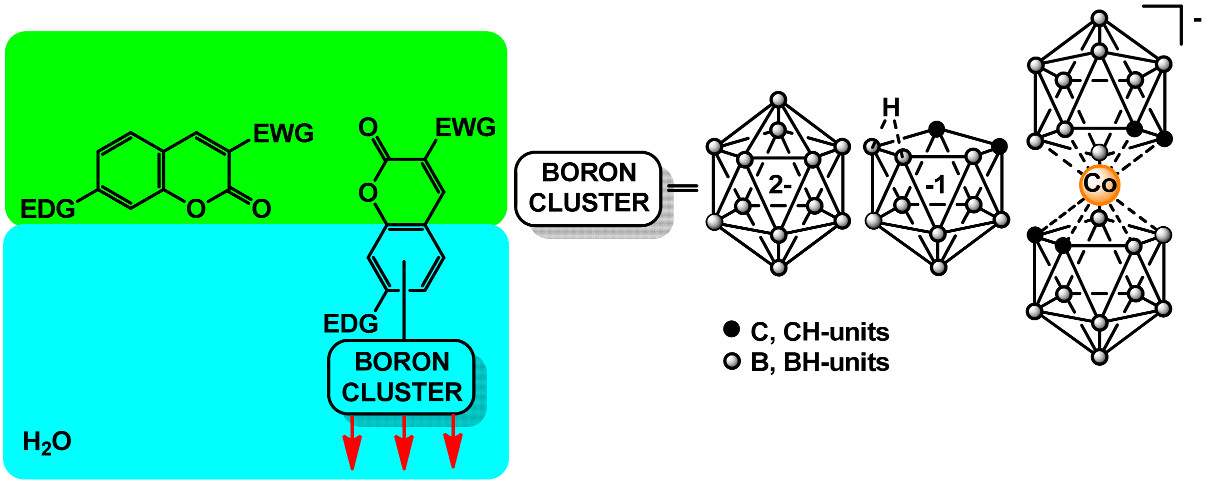
Coumarins represent an important class of natural and non-natural organic compounds witch find use as antineoplactic, antiviral and anticoagulant drugs. Furthermore, materials with a coumarin ring have been used as non-linear optical materials, fluorescent labels etc. Coumarins, substituted with electron donating group (EDG) at the C-7 position and electron withdrawing group (EWG) at C-3 position are of great interest since they exhibit unique fluorescent properties [1]. These compounds are practically insoluble in water, but this property is highly desirable for their uses as fluorescent probes [2]. Na and K salts of anionic boron clusters ($[closo\text{-}B_{12}H_{12}]^{2-}$, $[nido\text{-}C_2B_9H_{11}]^{-}$, $[8,8'\text{-}\mu\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^{-}$) are soluble in water. Thus modification of coumarins with these boron clusters may improve their solubility in water. In this contribution we will present synthesis and photochemical investigation of a series of novel coumarins modified with anionic boron clusters.



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CIS- AND TRANS-INFLUENCE OF THE BIDENTATE LIGANDS IN COORDINATION COMPOUNDS OF 10 AND 11 GROUPS d-METALS

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Cis- and trans-influence of the ligands in the coordination compounds of transition metal ions with monodentate ligands and related dynamic effects occurring in the metal’s coordination sphere where for a long time in the focus of the experimental and theoretical study and the resulting generalizations, rules and theories are forming the solid basis of the coordination chemistry as a science. But the same questions regarding the bi- and polydentate ligands were studied in much lesser extent and systematic manner due to the lack (or very limited number) of experimental information on the structure and thermochemistry of both cis- and trans-isomeric forms of the compounds. The pioneering role in this area can be attributed to the work of V. A. Kogan and N. N. Kharabaev [1, 2], who formulated the regularity of cis-planar structure of bis-chelate transition metal complexes with [2N, 2S] coordination environment and proposed the geometric model for the explanation of the phenomenon.

In this presentation the experimental XRD data about the stereostructure of homoleptic bis-chelates of the tetracoordinated Cu^{II}, Ni^{II}, Pd^{II}, Pt^{II} ions with different donor environment, size of chelate cycles, number of substituents on the donor atoms, *etc* accumulated in the CSD (Cambridge Structure Database) will be analyzed, compared and complemented with the results of quantum-chemical modelling of the relative stability of the stereoisomers. The various types of interaction between ligands – translated through metal (electronic influence) and translated through space (steric repulsion, π-π stacking, dispersion interaction) and their contribution to the relative stability of the isomers will be considered.

It will be shown that for bis-chelates compounds of Cu^{II}, Ni^{II}, Pd^{II}, Pt^{II} with (O,S)-type ligands (so, in absence of the steric repulsion between the ligands) difference in the total energy of the cis- and trans-isomers is determined by the non-bonding σ-type group molecular orbital, which is stabilized in cis- and destabilized in trans-isomers. The value of the effect is getting more pronounced when the σ-HOMO of the ligand becomes more diffuse and asymmetric (regarding the contribution of the donor atoms atomic orbitals). For Ni^{II}, Pd^{II}, Pt^{II} complexes with (O,S)-type ligands a linear correlation between the relative stabilities of planar isomers and the change in the metal-sulphur bond length in the trans-isomer compared with cis-one (Δd(M-S) – measure of the static trans-influence) is found. Growth of the static trans-influence of sulphur donor atom Δd(M-S) results in the growth of the relative stability of the cis-isomeric form. Effectiveness of electronic trans-influence translation is growing in the row Cu^{II}, Ni^{II}, Pd^{II}, Pt^{II}. It is shown that the value of the trans-influence is determined not only by the nature of the donor atoms, but, also on the tautomeric form of the ligand.

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OCTAHEDRAL METAL CLUSTER COMPLEXES FOR BIOMEDICAL APPLICATIONS

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Octahedral metal cluster complexes of molybdenum, tungsten and rhenium of general formula $[\{M_6X_8\}L_6]^n$ and $[\{Re_6Q_8\}L_6]^m$ (where M is either Mo or W, X are halogens, Q are chalcogens and L are terminal ligands) are characterized by high chemical stability of the cluster core as well as by modifiability of an outer ligand environment, by bright long-lived luminescence in the red and near-infrared regions of the spectrum, by ability to generate singlet oxygen, and by high X-ray contrast. Consequently, such a combination of photophysical properties makes the octahedral metal cluster complexes highly attractive for many biological and medical applications, such as bioimaging systems as radiocontrast and fluorescent agents, photodynamic therapy, oxygen sensing and antibacterial surfaces.

However, naked clusters are not ideally suited for these applications due to their poor water solubility. Introducing of inorganic Mo/W/Re cluster complexes with organic biocompatible ligands or organic and inorganic matrices offers great opportunities in terms of integrating the excellent photophysical properties of metal clusters with the bespoke properties of various organic and inorganic polymer matrices and thus to create designer materials tailored to specific applications.

The presentation will describe recently developed approaches to modify cluster complexes to facilitate their incubation into conventional matrices and the effect this incubation has on the photoluminescent properties of the materials as well as biological properties of such hybrid materials.

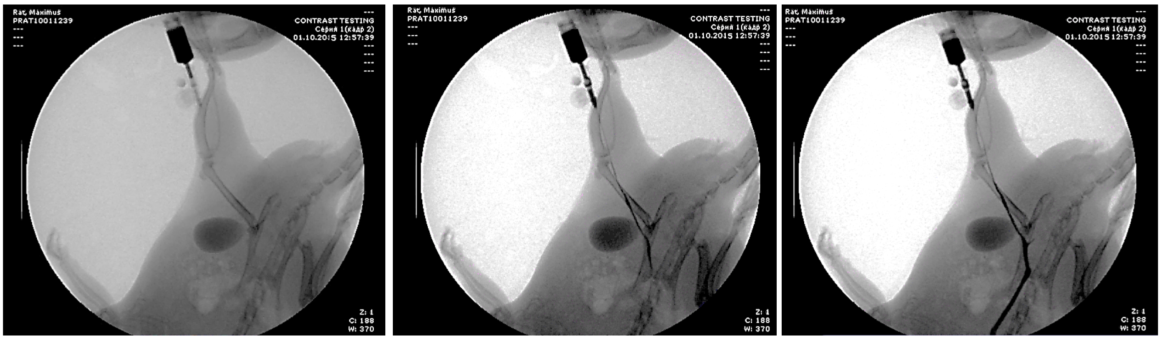

Figure. Angiography of the mouse blood vessels with cluster compound $Na_4[\{Re_6Te_8\}(CN)_6]$

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COMPLEX FORMATION IN HYDROMETALLURGY OF PLATINUM AND RARE EARTH ELEMENTS: MODERN TRENDS

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One of the main applications of coordination compounds is their use in processes of extraction, separation and concentration of various metal ions from complex solutions. Traditionally two main approaches were employed – liquid extraction and sorption, the first being dominating for several decades. The modern trend in hydrometallurgy is widespread replacement of liquid extraction by sorption processes, which are more effective, universal and eco-friendly. In this report we analyze the achievements in the sorption separation within two groups of elements possessing very similar properties – platinum metals and rare earths.

Coordination chemistry forms the basis for technologies discussed. Firstly, the effectivity and selectivity of metal ions sorption by modern sorbents are provided by the use of specific ligands which are chemically attached to solid support. Among these ligands, a special attention is paid to various macrocycles whose application leads to so-called molecular recognition technologies. Secondly, the selectivity of sorption can be regulated by complex formation of metal ions in liquid phase. For example, the addition of complexing ligands, namely, hydroxyl or amino acids, to solution plays significant role in separations of rare earth elements. Complex forming agents are used also for elution of sorbed ions, which is a crucial stage in the separation of platinum metals.

By now numerous sorbents with attached organic ligands are synthesized and tested. In this report we make an emphasis on silica based sorbents which are widely used in analysis, as well as in some industrial processes. The advantages and limitations of these sorbents are discussed.

Some examples of industrial processes of platinum metals and rare earth elements separation are presented.

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INTERACTIONS BETWEEN 3,4-DIARYL-1H-PYRROL-2,5-DIIMINES AND BISISOCYANIDE COMPLEXES OF PT(II)

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The coupling between N-nucleophiles and isocyanides at a Pt(II) center represents an attractive approach for the synthesis of a variety of acyclic diaminocarbene platinum complexes, which may be used as catalysts for hydrosilylation reactions [1]. The past several years has seen the significant development and utilizations of polynucleophiles that can lead to a novel type of carbene ligands [2]. Highly stable nitrogen-acyclic carbene Pt(II) complexes have been synthesized using amidines, 2,6-diaminopyridines, and 3-iminoisoindolin-1-ones [3–5].

We studied the reactions of 3,4-diphenyl-1*H*-pyrrol-2,5-diimines and $[PtHal_2(CN\text{-}R)_2]$ (where Hal = Cl, Br, I; R = alkyl, aryl) and found that the structure of the reaction product depends on the nature of halogen and isocyanide ligands. The prepared acyclic diaminocarbene platinum complexes were studied by NMR, IR, UV-vis, luminescence spectroscopies, HRMS (ESI), and XRD. The tautomeric equilibriums of the bisdiaminocarbene platinum complexes were investigated by 2D NMR techniques (COSY, NOESY, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC, ^1H-^{15}N HSQC и ^1H-^{15}N HMBC).

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STIMULI RESPONSIVE LUMINESCENCE OF NOVEL Au(I) COMPLEXES WITH CYCLIC PNNP LIGAND

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Stimuli responsive luminescence of Au(I) complexes makes them promising candidates for sensing, which is a reason for increasing interest in design and investigation of their new representatives. Phosphine derivatives represent perspective type of ligands for Au(I), since phosphine groups provide efficient coordination of the metal ions, while other substituents can be engaged in supramolecular assembly or substrates recognition.

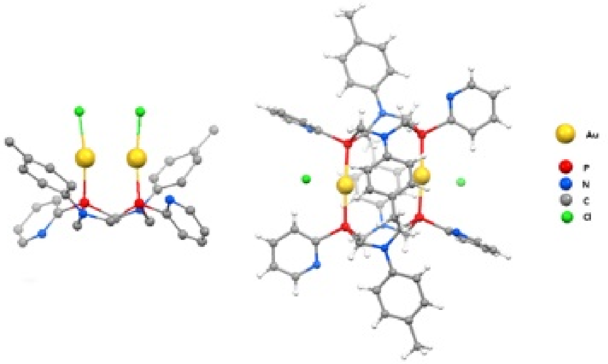

Figure 1. The molecular structures of ($(AuCl)_2L$) (left) and $[Au_2L_2]Cl_2$ (right) complexes

Recently novel luminescent Au(I) complexes ($(AuCl)_2L$) and $[Au_2L_2]Cl_2$ (Fig.1) have been synthesized [1] L=1,5-bis(p-tolyl)-3,7-bis(pyridine-2-yl)-1,5-diaza-3,7-diphosphacyclooctane (L). The ($(AuCl)_2L$) demonstrates emission at 485 – 525 nm in solutions associated with charge transfer from para-tolyl to pyridil moieties (intraligand charge transfer, ^{3}ILCT) with maximum dependent on solvent. It was revealed that ($(AuCl)_2L$) represent an efficient “host” molecule for organic molecules and cations as the “guests”. “Host-guest” binding affects both spatial and electronic structures of ($(AuCl)_2L$), in particular it leads to mutual rearrangement of pyridyl moieties and P-Au bonds of the complex, which results in pronounced effect on the excited state energy of ($(AuCl)_2L$). Thus “host-guest” binding may be used as a tool for tuning ($(AuCl)_2L$) luminescence in solutions. The emission of $[Au_2L_2]Cl_2$ in water solution is manifested by wide band of low intensity with the maximum at ca. 550 nm attributed to metal-to-ligand charge transfer (^{3}MLCT) transitions. This water-soluble complex form ion pairs with hexarhenium cluster complexes ($[\{Re_6S_8\}(OH)_6]^{4-}$ and $[\{Re_6S_8\}(CN)_6]^{4-}$, which are of particular interest due to their prominent luminescent and sensing properties. It has been shown that the ion-pairing is accompanied by significant concentration-dependent sensitizing of the cluster-centered luminescence, due to an energy transfer from $[Au_2L_2]^{2+}$ to hexarhenium clusters.

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METAL-CATALYZED ELECTROCHEMICAL PHOSPHONATION OF HETARYL-AZOLES

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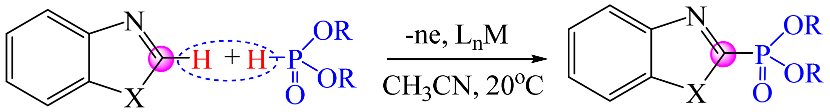
Presently, direct functionalization of C-H bonds, catalyzed by metal complexes, rapidly developing. At present the formation of a bond C-P in catalysis, is a promising methodology to obtain a variety of organophosphorus compounds. In light of the importance arylphosphonate and their derivatives in the field of biochemistry and chemistry of materials, there is a ever-increasing of interest in synthetic methods of designing bonds C-P. Benzo-1,3-azoles and their derivatives possess unique biological properties. They are to be considered as a structural bioisomers natural nucleotides such as adenine and guanine, are widely studied for their anticancer activity. Thus, the introduction of organophosphorus components in a functional framing of aromatic molecules such as benzo-1,3-azoles, is relevant and motivates scientists to create new methods for their synthesis. The development of new efficient chlorine-free technologies is an important trend. Electrochemical methods, characterized by carrying out the process in mild conditions (low temperature, normal pressure) are attractive, and environmental security of production and often a significant economic benefit.

The first Pd-catalyzed direct phosphonation of azoles with dialkylphosphites has been achieved without addition of base or acid. This method involves the oxidative cleavage of C–H and P(O)–H bonds and represents an atom-efficiency alternative to the classical phosphonation of Ar–X [1]. The metal-catalyzed electrochemical oxidative phosphonation of heteroarylazoles (benzoxazoles, benzothiazole and other) with dialkyl-*H*-phosphonate was developed. The joint electrochemical oxidation of a mixture of azoles and dialkyl-*H*-phosphonate in the presence of catalytic quantities of salts of transition metals at room temperature affords the desired ortho C-H substitution product, 2-substituted azoles [2,3].



X = O, S, N

M = Ag, Ni, Co, Pd

Silver salts, nickel, cobalt and palladium complex were tested as catalysts. The experiments were carried out in different conditions to optimize the electrochemical synthesis yields. Electrochemical properties of catalysts and substrates were studied. The mechanism of electrochemical transformations was proposed.

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[2] Y.H. Budnikova, T.V. Gryaznova, V.V. Grinenko, Y.B. Dudkina and M.N. Khrizanforov, *Pure Appl. Chem*. **2017**, *89*, 311–330.
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Cu(I,II), Cu(I), Zn(II) AND Cd(II) COMPLEXES WITH DERIVATIVE OF NATURAL (+)-3-CARENE: SYNTESIS, CRYSTAL STRUCTURE AND PHOTOLUMINECENCE

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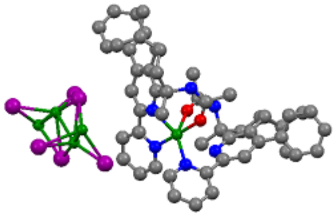
Transition metal complexes, particularly, Cu(I,II), Cu(I), Zn(II) and Cd(II) complexes, with the natural terpene derivatives are of interest as promising chiral fluorescent materials and biologically active compounds.



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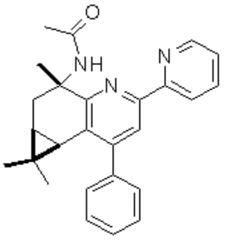

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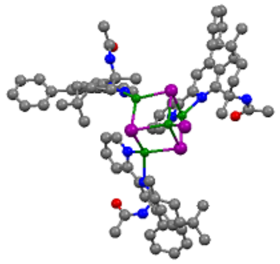

2

The compounds $[CuL_2][Cu_4I_6]\cdot MeCN$ (**1**), $[Cu_4L_3I_4]\cdot 3MeCN$ (**2**), $ZnLCl_2\cdot 2CH_2Cl_2$ (**3**), $CdLCl_2\cdot ½CH_2Cl_2$ (**4**) have been synthesized, where **L** is the chiral ligand, which contains (+)-3-carene fragment. The molecular structure of the green compound **1** consists of complex cations $[Cu^{II}L_2]^{2+}$ (the N_3O_2 polyhedron is a trigonal bipyramid) and tetranuclear complex anions $[Cu^{I}_4I_6]^{2-}$. According to magnetochemical data the compound **1** is the mixed-valence Cu(I,II) complex. The value μ_{eff} is 1.90 μ_B (300 K), which is close to the theoretical value 1.86 μ_B for the Cu^{2+} ion (g factor is 2.15). The values of μ_{eff} are constant in the temperature range 300–20 K, which indicates the absence of significant exchange interactions between the Cu^{2+} ions. The orange compound **2** is tetranuclear Cu(I) complex. Three Cu atoms coordinate two N atoms of **L** and two I atoms. The fourth Cu atom coordinates four I atoms. The coordination polyhedrons are a distorted tetrahedra. The complexes **3** and **4** are probably mononuclear. According to IR data, the N and Cl atoms are coordinated to the Zn and Cd atoms in the complexes **3** and **4**.

Emission properties of the compounds were studied in the solid state at room temperature. The free ligand **L** shows green emission (λ_{max} 500, 540 and 580 nm), whereas the complexes **1** and **2** do not exhibit any luminescence emission. The complexes **3, 4** show bright blue emission (λ_{max} 420 and 460 nm, respectively). The coordination of the ligand **L** with the Zn^{2+} and Cd^{2+} ions leads to a significant blue shift of luminescence bands. The emission intensity of the complexes **3** and **4** is higher as compared to that of the ligand **L,** which indicates the presence of the CHEF effect. The luminescence quantum yields of **L**, **3** and **4** are 6, 23 and 33%, respectively.

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COMPLEXES WITH 4-AMINO-2,1,3-CHALCOGENADIAZOLES AND THEIR PHOTOPHYSICAL PROPERTIES

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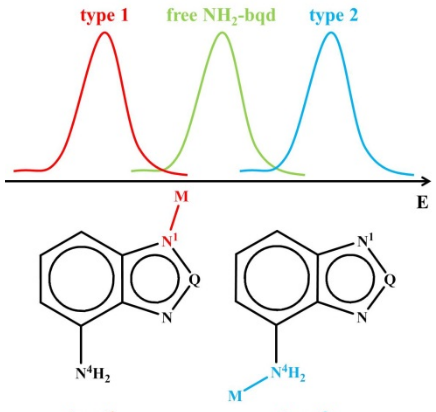
2,1,3-benzothiadiazole (***btd***) derivatives attracted considerable attention over the last decade, mainly due to their electron-withdrawing properties [1] and high luminescence efficiency [2]. Herein we present the synthesis of novel Zn(II), Cd(II) and Ag(I) complexes with 4-amino-2,1,3-benzothia- and selenadiazole (NH_2-*btd* and NH_2-*bsd*), whose photophysical properties were experimentally and computationally investigated.

The reactions of NH_2-*btd* and NH_2-*bsd* with $MHal_2$ (*M* = Zn, Cd; *Hal* = Cl, Br, I) were studied. Depending on reaction conditions, complexes with different *M* : NH_2-*btd* ratios (*viz.*, 1 : 1 and 1 : 2) were prepared. Interaction of $AgNO_3$ and NH_2-*btd* gave three different products with 1 : 1, 1 : 2 and 1 : 3 ratios. The ligands in Cd and Ag complexes are mainly coordinated *via* N^1 atoms (namely, coordination type1, Fig. 1), whereas those in Zn complexes – *via* N^4 atoms (namely, type 2) with some exceptions. According to results from quantum chemical calculations, type 1 molecules are thermodynamically more stable (of *ca.* 10–15 kJ/mol) with respect to type 2 ones. However, intermolecular interactions (π-π stacking, S/Se···N contacts, hydrogen bonds, *etc.*) can significantly influence the coordination type of the ligand in the crystal. These interactions were studied by mean of topological and Reduced Density Gradient analyses.

Photophysical properties of the complexes were also investigated. On the basis of our findings, we conclude that: (1) Replacement of sulphur with selenium in the heterocycle causes bathochromic shift of the S_0–S_1 absorption and emission bands for free ligands as well as the complexes. (2) In case of type 1 complexes, the band is bathochromically shifted with respect to free ligand (even in case of further type 2 ligand coordination). (3) In the case of pure type 2 complexes, the band is hypsochromically shifted with respect to free ligand. These correlations were interpreted using boundary orbitals transitions analysis. (4) Intermolecular and/or *Hal–M* interactions may also affect the position of the band.



Q = S, Se
M = Zn(II), Cd(II), Ag(I)
Figure 1

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THERMODYNAMICS OF IONIC AND MOLECULAR COMPLEX FORMATION REACTIONS OF GLYCYL-GLYCYL-GLYCINE IN MIXED SOLVENTS

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The problems of complex formation reactions in systems containing solvated biomolecules and macrocyclic ligands are of current interest for fundamental studies and their solutions are of considerable importance for applications. Investigations on the complexing properties of crown ethers capable of recognizing other species make it possible to simulate molecular recognitions occurring in biological systems. Equilibria in solutions containing low molecular–weight peptides are actively involved in many life processes. Peptide as a zwitterion in a solution can form "host-guest" molecular complexes with crown-ethers through a hydrogen bonds and electrostatic interactions between positive charged ammonium group of peptide and negative charged cavity of "host" macrocyclic molecules. Moreover, carboxylic group forms complexes with metal ions. Therefore, peptide are ligand in the ionic complexes, and play a role of a complex-former ion at coordination with crown-ethers. Thise features could be useful to design various molecular devices based on crown-ethers, peptides and metal ions with predicted thermodynamic properties in solutions. It is necessary to take into account that the thermodynamic parameters of complex formations depend on solvation states of reagents. This work is an overview of own data on model complex formation reactions between 18-crown-6 (18C6) and glycyl-glycyl-glycine zwitterion (3Gly), as well as between 3Gly, glycyl–glycyl–glycine anion (L^-) and Cu(II) studied in H_2O-EtOH, H_2O-DMSO and H_2O-Me_2CO mixed solvents. The relationships between the thermodynamic parameters of the complex formation reactions and the reactant solvation were analyzed to reveal the key factors that are crucial for the increasing stability of the complexes and the increasing exothermicity of the processes under study at transfer from water to water-organic solvents.

The solvation contributions of the reagents to the Gibbs energy changes ($\Delta_{tr}G_r$) in the formation of the molecular complexes [3Gly18C6] show the same trends in all mixed solvents under study: -replacement of water by non aqueous solvents diminishes the solvation of both 3Gly and 18C6, which is evident from the increasing positive $\Delta_{tr}G$(3Gly) and $\Delta_{tr}G$(18C6) values with an increase of non aqueous component of solvents; -the contributions from $\Delta_{tr}G$(18C6) and $\Delta_{tr}G$([3Gly18C6]) are outweighed by the contribution from the desolvation of 3Gly; -the $\Delta_{tr}G_r$ values correlate with $\Delta_{tr}G$(3Gly) but are opposite in sign, thus suggesting that the diminution of the 3Gly solvation is decisive for the increase in the stability of [3Gly18C6] complexes. A monotonic increase in the exothermisity of $[Cu3Gly]^{2+}$ complexation with additions of EtOH to H_2O was observed. The enthalpy of $[CuL]^+$ complex formation has changed with an exothermic peak at 0.1 ÷ 0.3 mol. fr. of EtOH. A main solvation contributions which control the increasing of exothermicity of $[CuL]^+$ complex formation reaction and the stability of $[Cu3Gly]^{2+}$ in H_2O–EtOH solvent were not established. The resolvation of 3Gly and L^- is the key factors for growth of the stability of $[Cu3Gly]^{2+}$ and $[CuL]^+$ complexes in H_2O–DMSO solvent.

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ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF BORON CHELATE COMPLEXES

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Photophysical properties of boron chelate complexes is constantly drawing interest over last years, because of their high luminescence in the visible spectrum [1], thus, explaining their perspectivity for laser optics. Due to electronic structure of boron difluoride complexes as well as of any chemical compound determines its optical properties, to synthesize new compounds with prescribed properties one needs to establish relations between desired properties of the complexes and their electronic structure. The most complete information about the electronic structure of complexes can be obtained by a combined use of photoelectron spectroscopy and quantum chemistry. Using the absorption and luminescence spectroscopy together with calculated results within the TDDFT approach makes it possible to determine an effect of substituents on the optical properties of complexes. A good correlation of experimental and theoretical energies attests to the reliability of simulation results.

Employees of the Far Eastern Federal University obtained ultraviolet photoelectron spectra (UPS) of vapor from thirty chelate boron chelate complexes and X-ray photoelectron spectra (XPS) of molecular crystals of fourteen boron β-diketonates. The optical spectra of boron β-diketonates in ethanol solution were obtained at the Institute of Chemistry FEB RAS. DFT and TDDFT computations were performed using Firefly 8.1. G quantum chemical software package using TZVP basis set and the hybrid exchange-correlation functional B3LYP.

According to UPS and DFT methods in the series of thirty chelate complexes, the influence of aromatic substituents into α-, β-, and γ-positions of the chelate cycle and the boron atom on the electronic structure has been established. It is shown that in the energy range up to 11 eV the calculated results corrected for the DFA-defect reproduce well the energy ranges between the ionized states of the complexes. Electronic structure and optical properties of fourteen boron β-diketonates have been studied by XPS, absorption and luminescence spectroscopy and quantum chemistry. An increase in the π-system size in a number of the studied compounds leads to a significant bathochromic shift of the maxima of the luminescence spectra and to a growth of the Stokes shift. The relative quantum luminescence yields have been revealed to correlate with charge transfers of HOMO-LUMO transitions, energy barriers of aromatic substituents rotation and the lifetime of excited states in the investigated complexes. XPS spectra structure of O 1s-, C 1s-, F 2s-, O 2s-, C 2s- and F 2p-electrons is in good agreement with Kohn-Sham orbitals therefore justifying modeling results.

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METAL-ORGANIC FRAMEWORKS AS EFFICIENT CATALYTIC SYSTEMS FOR THE CYCLIZATION REACTIONS OF SYNTHESIS OF OXYGEN- AND NITROGEN-CONTAINING HETEROCYCLIC COMPOUNDS

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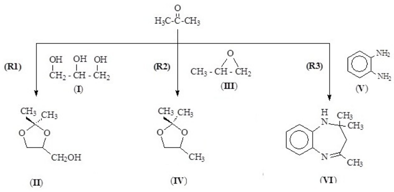
During last few years, metal-organic frameworks have attracted significant interest as catalysts for acid catalysis due to their unique structure, physicochemical properties and ability to adjustment of their acidity by the variation of the nature of the metals and/or organic ligands. The purpose of our investigation was to demonstrate the catalytic potential of the MOFs as heterogeneous catalysts for the cyclization reactions of synthesis of oxygen- and nitrogen-containing heterocyclic compounds, which are widely used in different fields of chemistry and medicine.



We investigated catalytic properties of the isostructural MOFs of the families MIL-100(M) and MIL-53(M) (M = V, Al, Fe and Cr), mixed MIL-53(Al,V) (Al/V – 100/0, 75/25, 50/50, 25/75 and 0/100 atom/atom) and porous aluminium trimesates Al-BTCs (MIL-96(Al), MIL-100(Al) and MIL-110(Al)). A combination of catalytic, theoretical and physicochemical methods was made for reveal the main factors that affect the reaction rate and the isomer selectivity.

It was found that in the R1 and R2 cyclization reactions in the presence of MIL-100(M) the reaction rates and yields of (II) and (IV) decreased in the following MIL-100(M) order: $V^{3+} > Al^{3+} > Fe^{3+} >> Cr^{3+}$. In the presence of MIL-53(Al,V) the reaction rate and yields of (II) and (IV) increased with increasing V^{3+} content. All these trends were related with effects of the type of metal ion, the length of the M-O bond, the rate constant for the exchange of the water molecules from the first coordination sphere of a metal ion and the value of the zero point of the surface charge (pH_{PZC}).

At the same time in the R3 cyclization reaction in the presence of MIL-100(M) the reaction rates and yield of (VI) decreased in the following MIL-100(M) order: $V^{3+} > Fe^{3+} > Cr^{3+} > Al^{3+}$ that was related to the difference in complexing ability of metal ions to NH_2-group of (V). The catalytic performance of the Al-BTCs (MIL-96(Al), MIL-100(Al) and MIL-110(Al)) significantly depended on the structure of the Al-BTCs and the amount of active sites, and decreased as follows: MIL-100(Al) > MIL-110(Al) > MIL-96(Al).

Efficiency of V-containing MOFs were higher in comparison with H_2SO_4, H-ZSM-5 and β-zeolite in all studied reactions. The MIL-100(V) can be used repeatedly without significant loss of catalytic activity during at least four catalytic cycles.

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LANTHANIDE COMPLEXES WITH FULLY FLUORINATED 2-MERCAPTOBENZOTHIAZOLATE LIGANDS: SYNTHESIS, STRUCTURE AND LUMINESCENCE

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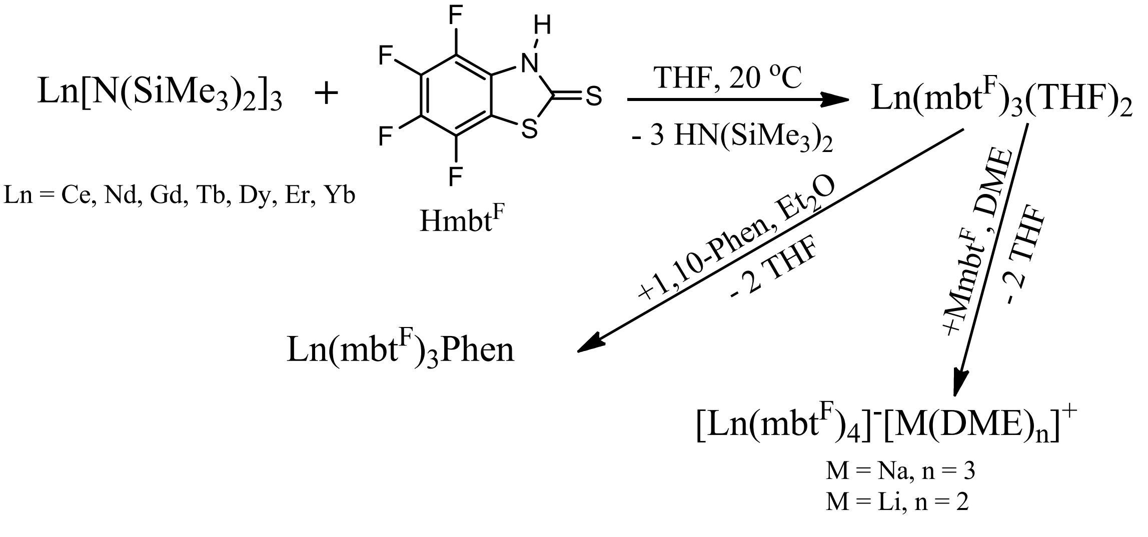
Lanthanide luminescence is in great demand in many modern technologies including bioimaging, light generation, solar energy conversion, lasers, fiber optics etc. Intraconfigurational 4*f*-4*f* transitions of lanthanide ions are parity forbidden which causes the need for sensitization of their luminescence (so called “antenna” effect). Aromatic fully fluorinated organic compounds are especially attractive “antenna” ligands due to lack of C-H, N-H and O-H groups which are well known luminescence quenchers. Use of these ligands leads to an increase in quantum yield and excited state lifetimes of lanthanide ions emitting in near infrared (NIR) range. In search of new perfluorinated ligands to sensitize lanthanide luminescence, the fully fluorinated 2-mercaptobenzothiazolate ligand was used for preparation of a set of lanthanide complexes. Neutral complexes containing ancillary THF or 1,10-phenanthroline ligands have been synthesized as well as ionic ate complexes (scheme 1).



Scheme 1

The structure of some compounds was determined by X-ray analysis. Photoluminescent (PL) properties of obtained complexes have been studied using time-resolved PL spectroscopy. It was found that mbt^F ligand has the triplet energy of 21500 cm^{-1}. This value allows resonant sensitization of metal-centered PL of Tb, Nd and Er ions whereas the excitation of Yb ion proceeds non-resonantly in these complexes. As compare with neutral compounds the ionic ate complexes of NIR emitting lanthanides (Nd, Er, Yb) exhibit enhanced PL intensity and longer excited state lifetimes.

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SOLUTION STUDIES OF THE KEPLERATE-TYPE COMPOUNDS BY VARIOUS PHYSICOCHEMICAL METHODS

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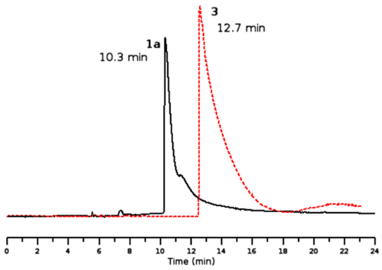
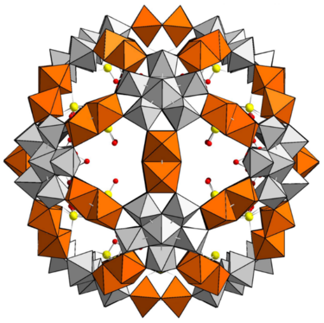
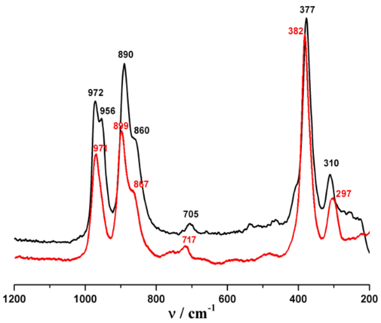
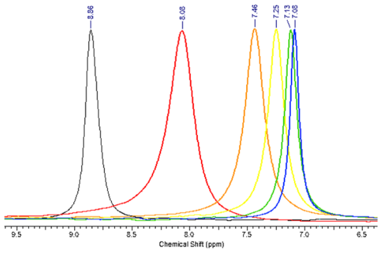
Porous compounds now attract more and more attention of researchers from different countries due to their promising applications. There are numerous examples of porous materials with extended structures [1], but discrete nanoporous compounds are much less studied. Spherical capsules of keplerates provide the ability to study the processes that are associated with the inclusion of specific substrates into the cavity [2,3].

Metallic skeleton of keplerates has 12 pentagonal {Mo(Mo$_5$)} or {W(W$_5$)} units, placed in the corners of an icosahedron, and which are linked by 30 bridging units. In the case of binuclear $\{Mo_2\}^{2+}$ linkers molybdenum atoms are typically coordinate a bidentate ligand in a bridging mode across the Mo–Mo bond, trans to the terminal Mo=O groups. These anionic compounds have high solubility and stability in aqueous media and large diameter of pores that allows to study inclusion processes, behavior and properties of chemical substances inside the cavity.









Herein we report solution studies of such compounds by NMR and Raman spectroscopy and also – by capillary electrophoresis method.

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PALLADIUM(II) COMPLEXES OF CYSTEINE AND HOMOCYSTEINE DERIVATIVES: SYNTHESIS AND BIOLOGICAL ACTIVITY

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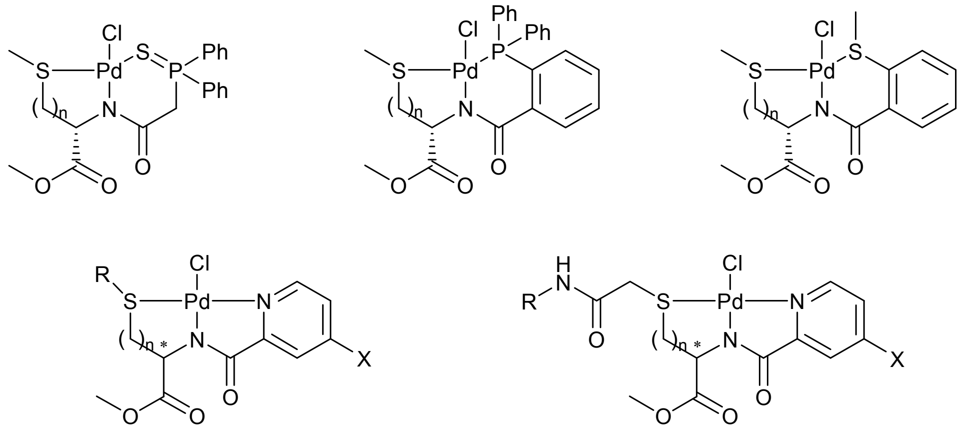
The discovery of anticancer activity of *cis*-$[PtCl_2(NH_3)_2]$ provoked an enormous interest of researchers in development of platinum(II)-based chemotherapeutic agents, and nowadays a range of Pt(II) complexes are successfully used in clinical practice for treatment of various cancers. However, due to the intrinsic and acquired resistance as well as high toxicity of platinum-based drugs, there is a constant need for creation of more effective and selective anticancer agents. Despite the obvious similarities in structure and coordination behavior between Pt(II) and Pd(II) complexes, the latter are often deactivated in biological environment due to high reactivity. However, we anticipated that the application of multidentate ligands, offering ample opportunities for directed structural modifications, can provide the resulting palladium complexes with high thermodynamic and controlled kinetic stability. Taking this into account, several series of Pd(II) complexes based on functionalized carboxamides with pendant amino acid arms have been synthesized and tested for cytotoxic activity (Fig. 1). The ligand backbone was modified by introduction of different substituents both at the N and S atoms of the basic amino acid residues.



R = Me, $PhCH_2$, All, $MeC(O)CH_2$

R = $MeOC(O)CH_2$, $(EtO)_2P(O)CHPh$

X = H, Cl; n =1, 2

Fig. 1. Pd(II) complexes based on multidentate ligands with pendant amino acid arms.

The preliminary investigations on cytotoxic activity against human colon (HCT116), breast (MCF7), and prostate (PC3) cancer cell lines as well as normal human embryonic kidney cells (HEK293) allowed us to follow the effect of ligand structure modification on the properties of the resulting complexes and outline the most promising derivatives.

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HYPERCOORDINATE ORGANIC COMPOUNDS OF 14th GROUP`S ELEMENTS: STRUCTURE, STEREOCHEMICAL NON-RIGIDITY, *IN SILICO* AND BIOLOGICAL STUDIES

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Chelates of hypercoordinate organic compounds of 14th group's elements (silicon, germanium and tin) are well known for their structural diversity, enhanced reactivity, and stereodynamic non-rigidity in solutions [1-3].

The data on structures and stereochemical non-rigidity of novel penta- (TBP) and hexacoordinated (Oh) (C,O)-chelate derivatives of acetamide and lactams with different coordination units (O–M–X, where M = Si, Ge, Sn; X = electron withdrawing functional groups: halogens, triflate, etc.) by X-Ray and special 1D, 2D NMR, CP/MAS, multinuclear (1H, 13C, 17O, 19F, 29Si, 119Sn) and dynamic NMR (DNMR) spectroscopy are discussed.

Dynamic stereochemistry of TBP and Oh complexes were observed: restricted rotation, permutational isomerization, *cis*- / *trans*- isomerization. All activation parameters (change of Gibb's energy, enthalpy and entropy of activation) were determined by DNMR method. The influence of solvent's polarity, nature of the central atom, nucleofugacity of the X substituent in the different coordination sets and the presence of external nucleophiles on the activation parameters of the stereodynamic processes were determined. Possible regular and non-regular mechanisms are discussed on the basis of experimental (multinuclear DNMR) data and quantum-chemical calculations (DFT model).

In silico (PASS Online and GUSAR Online services) and *in vitro* estimation of possible pharmacological effects and acute rat toxicity of these compounds by showed a potential for their further pharmacological studies.

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SOLUTION NMR TECHNIQUES FOR SINGLE MOLECULE MAGNETS

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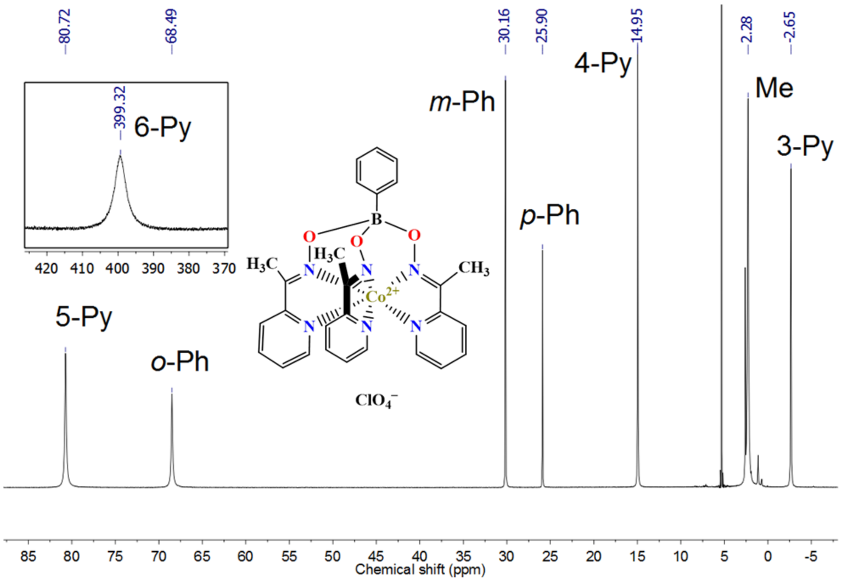
Single molecule magnets (SMMs) are molecules able to retain their magnetization in the absence of an applied magnetic field. This behavior, which may potentially lead to a breakthrough in high-density information storage or quantum computing, is currently observed only at extremely low temperatures. The method of choice for detecting large magnetic anisotropy, which is a necessary condition for a compound to be an SMM, is *ac*-magnetometry. This technique, however, is quite demanding and requires accumulation of large arrays of data at different magnetic fields and at very low temperatures. If the purity of the compound is not ideal, as it is often the case with complexes of metals in unusual oxidation states, the obtained results should be interpreted with extreme care. In many cases, crystal packing effects also can dramatically change the magnetic behavior of an SMM even with a very rigid coordination geometry [1].



Large magnetic anisotropy is not only the key property of SMMs but also a parameter that defines the values of pseudocontact shift in NMR spectra of paramagnetic compounds; their analysis [2,3] provides an access to important magnetic parameters such as zero-field splitting energy and g-tensor anisotropy. To do this, one only needs a high-resolution NMR spectrometer to be available and a reasonable number of ^{1}H NMR spectra to be collected at different temperatures. The presence of impurities is not a problem, as long as they allow detecting the signals of the compound under study. In the talk, we will argue that this concept is also applicable for studying paramagnetic species generated by photo-irradiation or electrolysis *in situ* using simple house-built NMR hybrid cells. Such an NMR-based approach thus paves the way to characterization of magnetic properties of unstable intermediates obtained by electro- and photo-induced switching of the molecular structure of SMMs.

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SPACER-ARMED EFFECTS IN THE COORDINATION CHEMISTRY

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In the last 20 years ‘self-assembly’ has changed from being a process of interest only to biochemists to one of the most exciting areas of modern coordination chemistry. It allows the preparation of elaborate high-nuclear molecules with target properties which can be prepared simply by mixing together some carefully-designed component parts in the correct proportions. This report summarizes our work over the last 10 years in which we have prepared a wide variety of new multinucleating ligands, all of which are based on hydrazone or pyridyltriazole chelating units linked to flexible or rigid spacer groups.

The possibility of obtaining transition metal’s coordination compounds with a given nuclearity on the title ligands basis was studied in detail. It was found that the gradual changing of spacer’s group have a strong impact on structure and physicochemical properties (magnetic, optic etc.) of the corresponding complexes – named “spacer effect”. The most significant results of title effect are the following [1-4]:

Elegant control of nuclearity and topologies of transition metal’s complexes by variation of molar ratio of reactants as well as length of spacer group. This results in cage structures such as M_2L_2, M_2L_3 – helicate, M_4L_4 - square, an M_8L_{12} bicapped trigonal prism (M – Cu(II), Co(II), Ni(II), Fe(II), L - bis[(pyridin-2-yl)-1,2,4-triazol-3-yl]alkanes). The features of the structure and magnetic properties are summarized and analyzed in detail;

Fine-tune control of the energy of spin-spin coupling in Cu(II) and Ln(III) binuclear complexes on bisacylhydrazones basis. Magnetochemistry and EPR technics allowed to establish the limit of delocalization of unpaired electrons through a polymethylene spacer.

Fine-tune control of the intensity of photoluminescent properties of triple helicate binuclear Ln(III) complexes with saturated dicarboxylic acid and 3-methyl-1-phenyl-4-formylpyrazol-5-one hydrazones.

Fine-tune control of SMM properties by changing of rigidity of ligand - increase the rigidity of the ligand yielded a rare example of Single Toroic Magnet for the tetranuclear Dy complex (with $U_{eff} = 42.6$ K) on oxalylamidrazone type ligand.

Optimization of sensibilization Ln(III) emission and thin-film quality in OLED by variation of the length of polymethylene chain in bistriazolylpyridine ligands in molecular heteroleptic complexes of Eu(III). Tb(III), Sm(III), Nd(III), Yb(III) with spacer-armed pyridyltriazoles.

New perspectives of self-assembled high-symmetry copper(II) (trinuclear) and lanthanides (tri and tetranuclear) complexes on hydrazones of 1,3,5-benzene tricarboxylic acid’s basis are firstly described. Specific features of the structure and magnetic properties are discussed in detail.

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THE FIRST ALUMINUM AND GALLIUM HYDRIDES BASED ON ANIONIC DIIMINE LIGANDS

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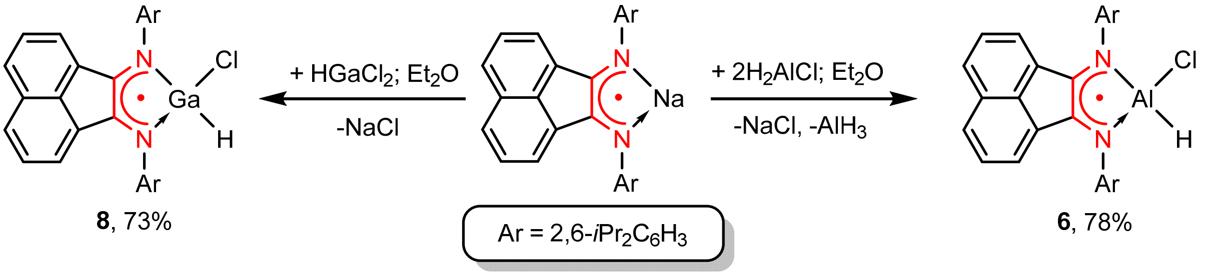
Hydrides of 13 group elements, supporting kinetically stabilizing ligands such as bis(imino)pyridine [1], β-diketiminate and bis(amide) [2], aminotroponiminate [3] are synthetically accessible and are being actively studied last years. Here we report the synthesis, characterization and reactivity of the first aluminium and gallium hydrides based on anionic diimine ligands.

Thus the reduction of dpp-bian (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]-acenaphthene) with lithium aluminum hydride $LiAlH_4$ leads to the mixture of aluminum hydrides $[(\text{dpp-bian})Al(H)_2]Li(thf)_3$ (**1**) and $[(\text{dpp-bian}(H_2))Al(H)_2]Li(thf)_3$ (**2**), containing dianionic diimine ligands. The reaction of compound **1** with 2,6-di-*tert*-butyl-4-methylphenol and benzophenone affords the hydrides $[(\text{dpp-bian})Al(H)O(2,6\text{-}t\text{Bu}_2\text{-4-Me-}C_6H_2)]Li(thf)_4$ (**3**) and $[(\text{dpp-bian})Al(H)OCH(C_6H_5)_2]Li(thf)_2$ (**4**) correspondingly. The compound (dpp-bian)AlH(thf) (**5**) was synthesized by the reaction of dichloroalane $HAlCl_2$ with (dpp-bian)Na_2. The hydrides (dpp-bian)Al(Cl)H (**6**) consisting of radical-anionic dpp-bian have been isolated from the reaction of the (dpp-bian)Na with monochloroalane H_2AlCl (1:2). The reaction of **6** with *tert*-butyllithium leads to the (dpp-bian)Al*t*Bu(Et_2O) (**7**). The gallium hydride (dpp-bian)Ga(Cl)H (**8**) have been prepared by reaction of the dichlorogallane $HGaCl_2$ with (dpp-bian)Na. The compounds **6** and **8** are the first paramagnetic structurally characterized hydrides. Products **1-8** have been characterized by IR, ^1H NMR (**1-5** and **7**) and EPR (**6**, **8**) spectroscopy as well as by the single crystal X-ray analysis.



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ELECTROLUMINESCENCE OF LANTHANIDE AROMATIC CARBOXYLATES

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The triplet excited state involvement in luminescence process makes lanthanide coordination compounds (Ln CCs) promising materials for emission layers in organic light-emitting diodes (OLEDs). They are of particular interest due to such a unique feature as narrow emission bands, resulting in higher color purity. Aromatic carboxylates possess the highest luminescence intensity and stability among Ln CCs, however, these advantages are nullified by their low solubility and extremely low intrinsic charge carrier mobility [1].

To solve this problem we considered two novel approaches [2]. The first one was the introduction of a luminescent material into such a transport material host, which is able to coordinate the lanthanide ion directly and to sensitize its luminescence. The second approach was the increase of the anionic ligand transport properties due to modification of its structure.

To check the prospects of the first approach, materials known for their electron transport have been chosen, among which we selected the derivatives of phosphine oxide and phenanthroline, expecting them to coordinate the lanthanide ion. To select among these materials effective sensitizers, the ternary complexes of the composition $LnCl_3(Host)_n(H_2O)_x$ (Ln = Tb, Eu; n = 1, 2; x = 0-2) were obtained, and their photophysical characteristics, including photoluminescence quantum yields, were measured. Among these materials the effective sensitizers have been selected, where the sensitization efficiency reached 100%.

To implement the second approach, highly conjugated aromatic carboxylate ligands were used, including electron-deficient heteroaromatic carboxylates, due to they were expected to provide electron transport properties (Fig. 2). Quantum yields of new lanthanide complexes with these ligands reached 100% (Ln = Tb), 16% (Ln = Eu) and 2.5% (Ln = Yb); the latter value is the highest for solid state ytterbium complexes and was reached thanks to concentration quenching elimination.

OLED tests revealed the effectiveness of both approaches and allowed obtaining the diodes with pure ionic lanthanide luminescence. OLED brightness in the visible range reached 350 Cd/m^2 and was comparable with the brightness of nowadays OLEDs based on lanthanide complexes of other classes. While in NIR range the EQE=0.2% was obtained, which is the highest-to-date value for >1000 nm emitting OLEDs [3].

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HETEROMETALLIC COMPLEXES BASED ON METHOXY-SUBSTITUTED β -DIKETONATE LIGANDS: ACHIEVMENTS AND PROSPECTS

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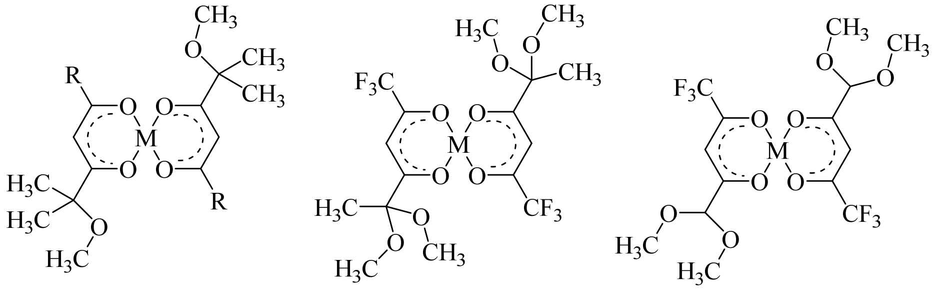
Heterometallic β-diketonates usually consist of monometallic moieties sharing several oxygen atoms between coordination centres. In the majority those bridging oxygen atoms are chelated ones. Their bridging function can be restricted by steric effect of terminal substituents (R', R'') of the β-diketonate ligand R'COCHCOR'' preventing formation of heterometallic product. We proposed to overcome this problem by using ligands with donor groups which are more sterically available being located in terminal substituents. For transition metals a few series of new heterobimetallics was prepared from methoxy-substituted metal β-diketonates (Fig.1). Cocrystallization of monometallic complexes from organic solvents is implemented to prepare heterometallic products.

Volatile Cu/Pd complexes are linear coordination polymers of alternating molecules connected by weak Cu-O contacts by means of methoxy-groups. Volatility and thermal stability of these complexes can be varied by changing the composition of substituents in the ligand. Some of those complexes were demonstrated to be promising precursors for chemical vapour deposition (CVD) of Cu/Pd bimetallic alloys [1-2]. For series of Cu/Pb and Pd/Pb heterometallic complexes the structure, volatility, isomerization and ligand exchange ability were shown to depend upon the composition of initial monometallic complexes [3-4]. The composition and structure of products after cocrystallization of transition metal β-diketonates with lanthanides complexes can be varied depending on the combination of metals and structure of the ligands involved. Cu/Ln complexes demonstrate different magnetic properties depending on the Ln used.



R = CF_3, $C(CH_3)_3$; M = Cu, Pd, Pb, Ni, Co, Zn, Mn

Fig. 1. Monometallic methoxy-substituted β-diketonate precursors for heterometallic complexes

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SONOGASHIRA COUPLINGS OF IRON CYCLOPENTADIENYLDICARBONYLHALIDES WITH ETHYNYLPYRIDINES. THE EXPECTED AND UNEXPECTED REACTION PATHWAYS.

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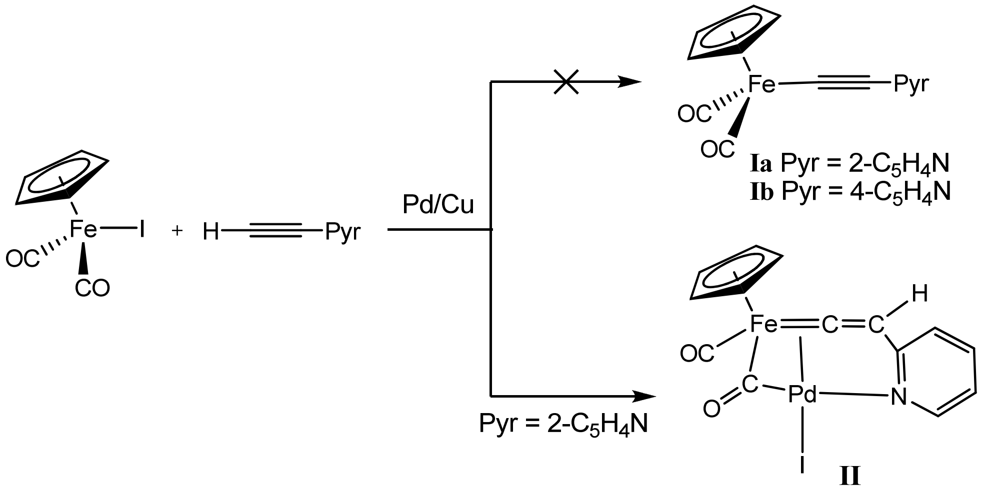
Transition metal σ-ethynylpyridyl complexes attract considerable research interest since they can act as precursors for pyridylvinylidene complexes and as buildings blocks for supramolecular assemblies in molecular electronics, as well as materials for nonlinear optics. With the aim of developing a convenient route to the iron σ-pyridylethynyl complex $Cp(CO)_2Fe\text{-}C{\equiv}C\text{-}(2\text{-}C_5H_4N)$ (**Ia**), we studied the Pd/Cu-catalyzed reaction of $Cp(CO)_2FeI$ with 2-ethynylpyridine. The reaction was found to afford a binuclear FePd μ-pyridylvinylidene complex $[Cp(CO)Fe\{\mu_2\text{-}\eta^1(C_\alpha){:}\eta^1(C_\alpha)\text{-}\kappa^1(N)\text{-}C_\alpha{=}C_\beta(H)(2\text{-}C_5H_4N)\}(\mu\text{-}CO)PdI]$ (**II**) in a low yield (2%), rather than the expected Sonogashira product **Ia**. The molecular structure of complex **II** was determined by X-ray diffraction [1].



In the course of optimizing the synthesis of the FePd complex, the conditions for high-yield isolation of **II** were found, and the factors resulting in the “abnormal” reaction pathway were revealed. An alternative synthetic approach to the σ-pyridylethynyl complex **Ia** and its analogue **Ib** was developed. Possible reasons for the coupling reaction to proceed along the “abnormal” and “expected” pathways are proposed.

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ELECTRONIC STRUCTURE OF EU(III) TRIS-Β-DIKETONATES ADDUCTS: PHOTOELECTRONIC AND THEORETICAL STUDIES

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To the number of chemical compounds of rare earth elements of interest for the development of light-transforming materials applies a wide class of adducts *tris*-β-diketonates with general formula $Ln(OC_\beta(R_1)C_\gamma HC_\beta(R_2)O)_3\cdot L$ [1].

The development of modern computing technology and methods of quantum chemistry makes available theoretical studies of adducts of β-diketonate complexes of lanthanides. As a result, it became possible to interpret photoelectron spectra using theoretical calculations.

In this work we investigate the electronic structure of the adducts $Eu(OC_\beta(R^1)C_\gamma HC_\beta(R^2)O)_3\cdot L$, where $R^1 = R^2 = CH_3$, CF_3; L = Phen (1,10-phenantroline, $C_{12}H_8N_2$), TPPO (triphenylphosphine oxide, $OPC_{18}H_{15}$), HMPA (hexamethylphosphoramide, $OPC_6H_{18}N_3$) by using methods: 1) ultraviolet (hν = 21.2 eV) photoelectron spectroscopy of vapors; 2) X-ray photoelectron spectra of the valence region and core levels in the condensed phase with a source of radiation MgKα; 3) DFT, TDDFT.

As a result, defined geometric structure of the compounds, which agrees with the X-ray diffraction data. The electronic structure, features and nature of chemical bonds are analyzed in detail. The assignment of bands to computed Kohn–Sham orbitals was obtained for the UV (gaseous phase) and X-ray (condensed state) photoelectron spectra. Quantum-chemical calculations (DFT) made it possible to determine patterns of changes in the electronic structure of chelate complexes depending on the fluorination of the ligand (substitution in the ligands of methyl groups for trifluoromethyl), to study the electronic effects of adduct formation. The ion-dipole interaction of neutral ligands with a metal is shown for adducts.

The absorption mechanism with further luminescence and the effect of adduct formation on optical properties are analyzed in detail using theoretical (TDDFT) and experimental (absorption, excitation and luminescence spectroscopy) methods.

This work was supported by the Ministry of Education and Science of the Russian Federation within Government Assignment no. 3.2168.2017/4.6 Far Eastern Federal University.

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STEREOSELECTIVE EFFECTS IN STRUCTURE, FORMATION THERMODYNAMICS, AND LIGAND SUBSTITUTION REACTIONS KINETICS OF 3d-METAL COMPLEXES WITH AMINO ACIDS AND OLIGOPEPTIDES

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Deep understanding the causes of specificity and selectivity of processes in living nature is one of the biggest problems of modern natural science. To solve this problem, it is necessary to discover and explain the regularities and mechanisms of the metal-ligand interactions, the mutual influence of ligands, and the outer-sphere and solvation interactions in the complex formation and ligand substitution processes that are common in biological systems. For this purpose in the present work the structure, formation thermodynamics, and dynamic behavior of homo- and heteroligand complexes in aqueous solutions of nickel(II), copper(II), and zinc(II) with enantiomerically homogeneous and racemic forms of the amino acids (glycine, alanine, valine, tryptophan, serine, threonine, proline, hydroxyproline, sarcosine, asparagine, glutamine, aspartic acid, glutamic acid, lysine, arginine, methionine, cysteine, and histidine) and natural di- and tripeptides (glycylglycine, glycyl-L-histidine, glycyl-L-tyrosine, glycyl-L-glutamic acid, glycylglycylglycine, glycylglycyl-L-histidine, glycylglycyl-L-tyrosine, and glycylglycyl-L-glutamic acid) on the different salt backgrounds were investigated in detail. Using thermodynamic and structural data derived, kinetics and mechanisms of the substitution reactions of the di- or tripeptides for histidine in the copper(II) – oligopeptide (glycylglycine, glycyl-L-tyrosine, glycylglycylglycine, glycylglycyl-L-tyrosine) – L/D-histidine systems on the 1.0 M KNO_3 background have been studied.

Reliable results were obtained by using complex of complementary techniques, including pH-metry, SF-metry, EPR, multi-frequency NMR relaxation, and stopped-flow method combined with mathematical modeling by the multipurpose author's program STALABS [1] and quantum-chemical computations in the GAMESS program at the CAM-B3LYP/TZVP and other levels with accounting solvent effects in discrete models and polarizable continuum model (C-PCM).

For the enantiomeric ligands the statistically significant stereoselective effects in geometric parameters, formation constants of complexes, and rate constants of the ligand substitution reactions were discovered in many investigated systems. Comparative analysis of the obtained data made it possible to identify the main factors that determine the stereoselectivity of complex formation and ligand substitution reactions, including *trans* influence, the inter-ligand electrostatic or steric repulsion, formation of intra-complex hydrogen bonds, the metal-ligand *d*-π-interaction, the "softness" of the ligand and central ion, pentacoordination environment of copper(II) in solutions, solvation interactions, and the outer-sphere association with components of the background electrolyte.

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MULTIFUNCTIONAL METAL-ORGANIC FRAMEWORKS BASED ON $[Re_6Se_8(CN)]^{4-}$ CLUSTER ANIONS AND Gd^{3+} DICARBOXYLATES

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Synthesis and investigation of coordination polymers and metal-organic frameworks for those porous ones has become one of the most attractive research fields during the past two decades lying on the crossing of fundamental inorganic chemistry and materials chemistry [1, 2]. In order to find new promising classes of multifunctional materials, we explore formation of coordination polymers and MOFs based on octahedral chalcocyanide rhenium clusters of $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se, Te) type. The interesting properties of $\{Re_6Q_8\}$-type clusters such as intensive red luminescence and reversible redox transformations make them interesting as a building block for synthesis of functional coordination polymers [3]. A number of coordination polymers based on $[Re_6Q_8(CN)_6]^{4-}$ cluster anions and transition metal cations were synthesized in recent years, and their structures were studied in details. However, the challenge to utilize the useful properties of cluster complexes through the creation of multifunctional coordination polymers has not been solved to date.

In that work we present a synthesis and properties of new MOFs based on octahedral rhenium clusters. Self-assembly reaction of $[Re_6Se_8(CN)_6]^{4-}$ cluster anions, Gd^{3+} cations and furan-2,5-dicarboxylate (fdc) or thiophene-2,5-dicarboxylate (tdc) in aqueous solution led to formation of new metal-organic frameworks with a composition $[\{Gd(H_2O)_3\}_2LRe_6Se_8(CN)_6]\cdot nH_2O$ (L = fdc or tdc). Compounds crystallize as orange hexagonal-shaped rods in trigonal crystal system, $R\bar{3}c$ space group, and display permanently porous non-charged frameworks. The combination of redox-active cluster building unit and paramagnetic Gd^{3+} cation determine a set of useful properties of new compounds. Among the latter are highly selective gas sorption, red luminescence and sensitivity to oxidizing agents e.g. Br_2 and O_2.

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BORON DIPYRRIN BASED COMPLEXES IN SOLVENTS, POLYMERIC MATRICES AND THIN FILMS AS MULTIFUNCTIONAL FLUORESCENT SENSORS AND MARKERS

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Considerable research interest to organic luminophores is caused by wide possibilities of their practical use in molecular sensorics and as components for the optically active devices. Boron dipyrrins (BODIPY) complexes are under scrutiny due to they combine the necessary set of spectral and photophysical characteristics for use as a fluorescent sensors and the components of optical converters, namely, the narrow absorbance and emission peaks, high photo- and chemical stability, ease of complexes chemical modification for the fine tuning of spectral characteristics. In this regard we conduct comprehensive studies on the synthesis, immobilization in matrices or thin films, investigation of photophysical characteristics and the ways for practical evaluation of the BODIPY complexes. The report discusses the issues of obtaining new structures containing one or more BODIPY domains, the spectral and photophysical characteristics of the compounds obtained in solutions and polymer matrices, as well as the practical applications of the compounds as components of photo-converting devices and fluorescent sensors for different molecules and solvent parameters.

Synthetical approaches for obtaining of BODIPY complexes with substituents variation would be discussed. Although, general synthetic way for BODIPY obtainment is well known, the variation of pyrrole precursors and substituent groups nature cause necessity for the procedures modification for increasing the yields of target products. We focused on the variation of *meso*-position substituent due to its flexibility in practical ways. Thus incorporation of bulky aromatic moiety allowed to obtain complexes with fluorescent molecular rotor properties; using alkyl chains of different length we obtained amphiphilic complexes for further thin films fabrication using Langmuir-Shaffer approach; and the substituent with Nitrogen and Oxygen heteroatoms allowed to impart the sensoric activity for media polarity and acidity/basicity. The next stage of the work was to obtain BODIPY complexes with several dipyrrin ligands in one molecule for further increasing of sensoric activity. Along with the investigation of the complexes in solutions, the hybrid materials based on organic polymeric or inorganic silica matrixes were fabricated. Spectral characteristics of obtained complexes were investigated in solvents of different nature, thin films and polymeric matrices The nature of *meso*-substituent (aromatic moiety or aliphatic chain) allowed to confer the compounds the properties of fluorescent sensors. Thus, for BODIPY with bulky substituents at the 8-position, the properties of fluorescent molecular rotors, i.e. the dependence of the fluorescence intensity on the dynamic viscosity of the solvent, are revealed. This spectral behaviour allowed to measure dynamic viscosity of solvents, biofluids and polymers during the polymerization. Introduction as a substituent grouping containing donor atoms, causes sensory activity in relation to cations and anions. So BODIPY, containing donor atoms of nitrogen and oxygen can be used as pH indicators. Due to the possibility of specific interaction with biological molecules, the compounds under consideration can be used for fluorescent control of protein content in biological samples.

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EXPERIMENTAL ELECTRON DENSITY STUDIES OF INTERMOLECULAR INTERACTIONS – INSIGHT INTO "STRUCTURE-PROPERTY" RELATIONS

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Over the years, experimental studies of electron density distribution in molecular crystals proved to be very helpful in addressing many important chemical problems in modern material and bio-sciences [1]. By using high-resolution X-ray diffraction from high-quality single crystals (although techniques exist that allow overcoming these limitations), it provides insight into fine details of chemical bonding; those include qualitative and even quantitative information on intermolecular interactions, from well-accepted H-bonds to extremely weak Van-der-Waals contacts, that affect all properties of molecular crystalline materials and ensure their mere existence.

This can be achieved by analysing the topology of an experimental electron density within the R.Bader's quantum theory of "Atoms in Molecules" [2], a convenient tool for finding all the bonding interactions by means of bond critical points or *bcps* (which are a necessary and a sufficient condition for a chemical bond to occur) and estimating their energy (based on a simple relation to the values of an electron density-derived function in these *bcps* [3]). By partitioning the 3D electron density distribution into non-overlapping atomic domains, it also allows speaking about chemical bonding in terms of charge, volume and even energy of individual atoms or molecular fragments in a crystal, thereby assessing the effect that intermolecular interactions have on the molecules, the 'building blocks' of molecular materials.

In the talk, I will focus on the selected successful applications of this approach for explaining some properties of crystalline materials, from simple density to optical and magnetic phenomena, and their implications for material science. Assisted by quantum chemical calculations, the experimental electron density studies were shown to help identifying those interactions that are responsible for an observed property, such as mediating superexchange pathways and tuning magnetic behaviors. That said, even the weakest and sometimes the weirdest (those that go against 'chemical intuition') interactions should be kept in mind while designing new molecular materials.

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SPATIAL HYDROGEN-BOND NEIWORK IN AQUEOUS ETHYLENEDIAMINE SOLUTIONS

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Binary ethylenediamine—water system is interesting particularly due to its unique physical and physicochemical properties that nonmonotonically change with the change in the relative content of components and reach extreme values at certain compositions, the values dramatically differing from those typical of individual substances. To clarify the structural and energetic features of the ethylenediamine—water system, nonempirical analysis of model $(NH_2CH_2CH_2NH_2)_m(H_2O)_n$ clusters with m=1—4 and n=2—18, including those with n=2m, was undertaken. Quantum chemical calculations were carried out at two levels, namely the second order of the Moeller—Plesset perturbation theory (MP2) and density functional approximation with B3LYP hybrid exchange—correlation functional (DFT-B3LYP), with a sufficiently flexible split valence Gaussian basis set augmented with diffuse and polarization functions (6-31++G(d,p)), which are known to provide reliable description of hydrogen-bonded systems.

Analysis of the results obtained enabled us to identify the predominant local structure motive that originates upon the solvation of ethylenediamine amino groups with water molecules and is typical of individual amino groups in binary systems with a relatively low ethylenediamine content (10 mol %), as well as of «compact hydration bridges», which bind amino groups of the molecules in the systems with a high ethylenediamine content (about 30 mol %). In the systems of the latter kind, structural building blocks of $(NH_2CH_2CH_2NH_2)_2(H_2O)_4$ composition were identified and shown to provide the possibility of constructing a continuous network of the corresponding supramolecular structure stabilized by the maximum possible number of hydrogen bonds. Hydrogen bonds in the suprastructure form predominantly square-rhombic rings with alternating covalent and hydrogen bonds in NH OH NH OH sequences, the neighboring rings being either coplanar or nearly orthogonal to each other. This kind of the mutual arrangement of molecules predetermines not only the highest stabilization of each structure unit, but also the possibility of extending any preformed structure by adding subsequent similar units.

The discovered character of the spatial hydrogen-bond network in mixed ethylenediamine—water systems of diverse compositions can explain the nature of many peculiar physicochemical properties of the solutions and the processes that take place in them.

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COMPARISON OF REGULARITIES OF THERMOLYSIS FOR THE Fe(II), Co(II), Ni(II), Cu(II), AND Zn(II) SALTS OF CARBOXYLIC ACIDS WITH THE FORMATION OF METAL NANOPARTICLES

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Production of metal nano-sizes particles (NSPs) with a diameter smaller than 10 nm and a narrow size distribution, stabilized by a polymer matrix by the thermolysis of Fe(II), Co(II), Ni(II), Cu(II), Zn(II) salts of unsaturated (maleic) and aromatic (ortho-phthalic) acids is a self-regulated process enabling concurrent formation of NSPs and polymer matrix [1-3]. Decomposition of Co/Zn solid solution of maleates is the method of the growth of the “brushes” of carbon nanotubes at lower temperature also.

Thermal decomposition of both maleates and phthalates in the series from Fe(II) to Ni(II) and Cu(II) phthalates proceeds in three stages. At the additional stage of process of destruction of Cu(II) and Zn(II) maleates, the maleate ion isomerizes to the trans-form with simultaneous reduction of Cu(II) to Cu(I) and copper (I) or zinc (II) fumarate formation, respectively.

The results demonstrate correlation between structural and thermoanalytical characteristics in the series of transition metals maleates and phthalates. The onset dehydration temperatures of the coordination water increases in the series of both maleates and phthalates, the onset decarboxylation temperatures decreases in these series. The onset decomposition temperature of the maleates is insignificantly higher than that of the phthalates for the salts of similar metals.

The thermolysis of the Fe(II), Co(II), and Ni(II) salts of maleic acid affords the spherical iron particles to 150 nm in size, the diameter of the cobalt particles is 3-4 nm, and nickel particles is 4-5 nm. The spherical conglomerates embedded in the carbon-polymer matrix of the composites derived by decomposition of Cu(II) maleates and phthalates contain numerous spherical metal particles with a diameter of 5-10 nm.

The decomposition of solid solutions in the system 10 % Co(II) acid maleate – 90% Zn(II) acid maleate resulted in the isolation of metal cobalt NSPs embedded in ZnO matrix as catalysts of self-arbitrary growth of “nanobrushes” of carbon tubes at the surface of composite. The process is concluded by the temperature at 350°C lower that at the CVD-method by the use of cobalt acid maleate as precursor of the CN_x–nanotubes growth catalyst.

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4th Conference-School for Young Researchers “Physicochemical Methods in Coordination Chemistry”

LANTHANIDE AROMATIC CARBOXYLATES AS EMITTERS FOR OLEDS: NEW APPROACH FOR HOST SELECTION

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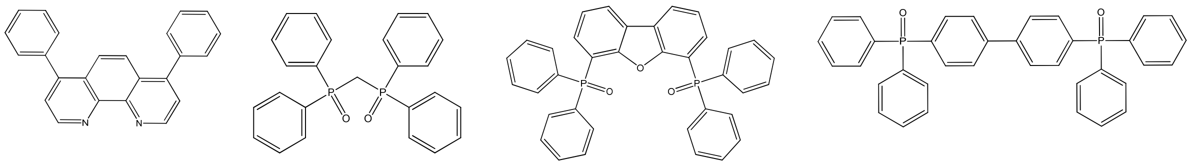
Over the past few decades lanthanide coordination compounds (Ln CCs) have found their applications in many areas of research, one of which is the fabrication of emission layers in organic light-emitting diodes (OLED). Among other classes of Ln CCs, aromatic carboxylates are interesting as luminescent materials due to the effective luminescence, as well as high thermal and UV stability. However, their broad implementation as emission layers is difficult, since they do not possess the intrinsic charge carrier mobility.

In order to improve the transport properties of the Ln-based emission layers, we proposed the new approach: the use of a transport host material for luminescent Ln CC, which is able to coordinate the lanthanide ion directly and to sensitize its luminescence [1].

In order to implement this approach, the derivatives of phenanthroline (**Bphen**) and triphenylphosphine oxide (**PO1-PO3**) have been chosen as host materials (Fig. 1) due to their electron transport properties and ability to coordinate the lanthanide ion. The europium 2,3,5,6-tetrafluorobenzoate Eu(**tfb**)$_3$(H$_2$O)$_2$ and terbium o-phenoxybenzoate Tb(**pobz**)$_3$(H$_2$O)$_2$ with quantum yield up to 100% [2] were chosen as emitters.



Bphen **PO1** **PO2** **PO3**

Fig. 1 Host materials

The ternary complexes of the composition LnL$_3$(Host)$_n$ (Ln = Tb, Eu; L = **tfb**$^-$, **pobz**$^-$; n = 1, 2) were obtained, and their photophysical characteristics, including photoluminescence quantum yields, were measured, which allowed selecting among these materials the effective sensitizers of lanthanide ions, which sensitization efficiency Host→Ln reached 100%.

Composite films (Ln CC):nHost were tested in OLEDs, and it was shown that the use of this approach resulted in the obtaining of diodes with pure ionic terbium or europium electroluminescence. The luminance reached 25 Cd/m^2 for OLED with a heterostructure ITO/PEDOT:PSS/PVK/Tb(**pobz**)$_3$:**PO3**/TAZ/Al, which is a record value for lanthanide aromatic carboxylate electroluminescence.

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SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF METAL-ORGANIC FRAMEWORKS BASED ON PERFLUORINATED 4,4’-BIPHENYLDICARBOXYLATE

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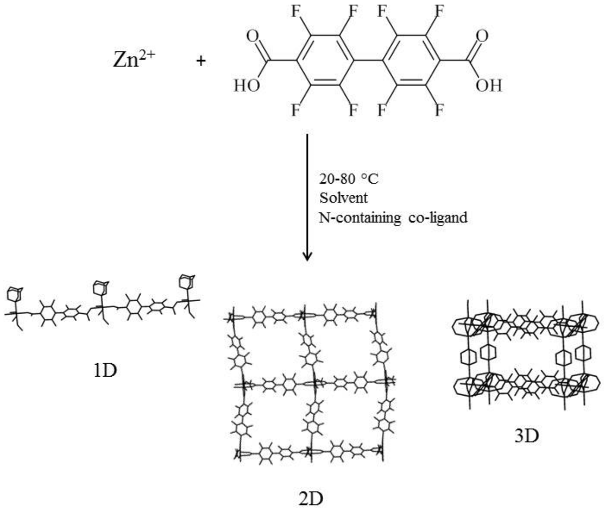
Metal-organic frameworks (MOFs) are of paramount interest due to unique sorption and separation properties, catalytic behavior and luminescence which allow one to design sensors. The substitution of aromatic carboxylate acting as an organic linker within the MOF structure by its perfluorinated derivative must lead to a material with enhanced luminescent properties and different surface characteristics.

This work aims at the synthesis of Zn coordination polymers based on perfluorinated 4,4’-biphenyldicarboxylate. Zinc is non-toxic metal which compounds are interesting in terms of their luminescent properties. In addition, it easily forms carboxylate complexes with a huge variety of secondary building units.

The conditions for the synthesis of fluorinated MOFs are absolutely different from those for non-fluorinated material. Using nitriles, alcohols, water, THF instead of amides as a solvent together with the decrease of the temperature down to a room temperature appeared to be very productive. This approach allows 1D, 2D and 3D coordination polymers to be obtained.



All the compounds were further investigated in terms of their luminescent properties. Sorption characteristics were measured for potentially porous materials.

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REVERSIBLE WATER-INDUCED PHYSICAL PROPERTIES OF 2D COORDINATION POLYMERS BASED ON 1,1'-FERROCENDIYL-BIS(H-PHOSPHINIC ACIDS)

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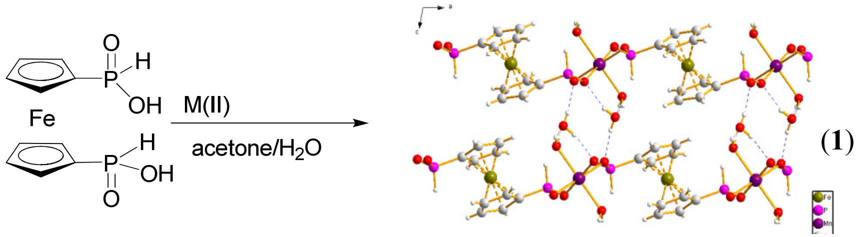
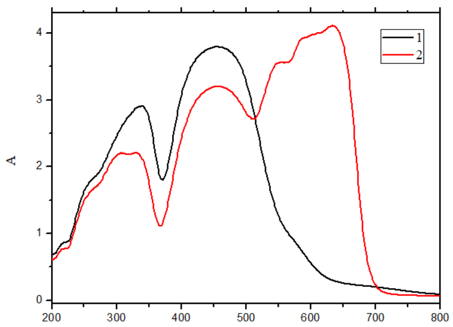
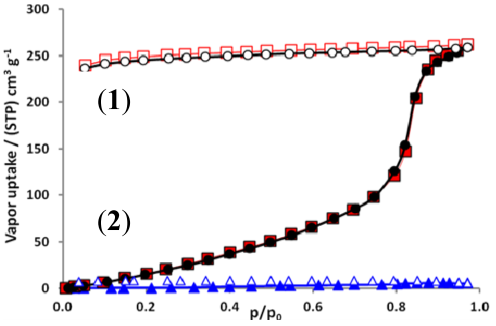
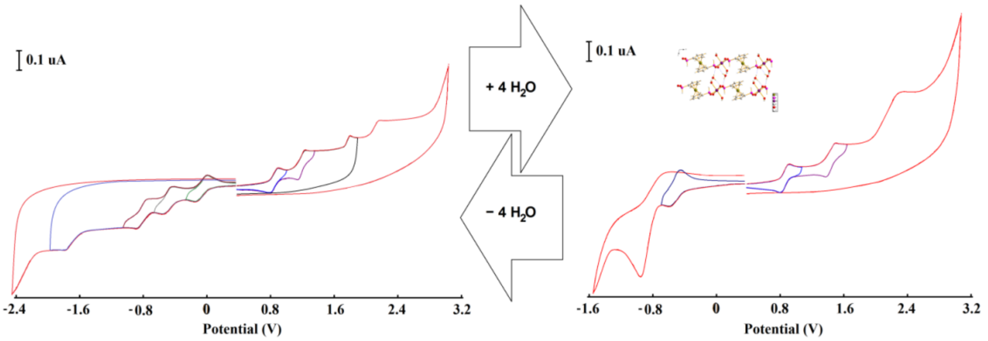
We have synthesized series of porous coordination polymers $[M(H_2O)_2(Fc(PHOO)_2)\cdot 2H_2O]n$ (1) with M(II) = Mn(a), Co(b), Cu(c) based on phosphinic acid, which demonstrates reversible crystal-to-crystal transformation and is able to form two different stable forms controlled by specific guest. The dehydrated compound $[M(Fc(PHOO)_2)]$ (2) can selectively adsorb H_2O molecules (17% on weight) over other adsorbtives such as methanol, ethanol, acetone, and tetrahydrofuran at 298K. The network is also not accessible for nitrogen and hydrogen at 77K. The structural transformations is also reflected in magnetic, UV, electrochemical properties of the coordination polymer.









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MIXED LIGAND COMPLEXES OF RARE EARTH TRIFLUOROACETATES AND PIVALATES WITH DIETHYLENETRIAMINE AS PRECURSORS FOR MOCSD

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At present many functional materials are produced from metal-organic precursors. Rare earth carboxylates are widely used for synthesis of rare earth oxide and fluoride functional materials by means of Metal Organic Chemical Solution Deposition (MOCSD) in form of films and nanoparticles. These materials find applications in electronics, optics, nanotechnology, etc. Thus, it is crucial to develop the new metal-organic precursors and to study the processes of mixed ligand complexes formation in precursor solutions. Mixed ligand complexes of rare earth trufluoroacetates and pivalates (Htfa—trifluoroacetic acid, Hpiv—pivalic acid) with diethylenetriamine (deta) were subjects of the present research.

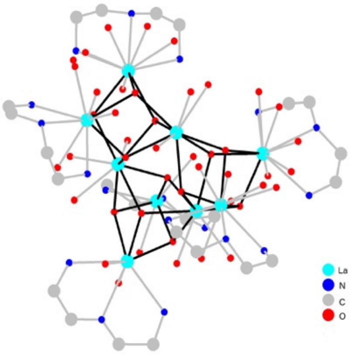

Fig. 1.
$La_9(tfa)_{15}(deta)_6(OH)_{12}\cdot H_2O$

All syntheses of mixed ligand complexes were performed in air or under dry argon atmosphere. For the light rare earth trifluoroacetates we obtained either gels which could be used as rare earth fluoride precursors or hydroxo-compounds among which we succeeded to obtain single crystals with peculiar cluster crystal structure (Fig. 1). For the heavy rare earths (Y, Dy—Lu) the family of mononuclear $[Ln(tfa)_2(deta)_2](tfa)$ complexes were reproducibly isolated and characterised by powder and single crystal X-ray diffraction, IR and NMR spectroscopy, TGA, conventional elemental analysis [1]. The stability of the complexes for the heavy rare earths were examined by DFT calculations (B3LYP/TZVP) and proven to be dependent on the central ion radius. Solution of $[Y(tfa)_2(deta)_2](tfa)$ has been found to be suitable precursor for $NaYF_4$ thin film deposition.

Syntheses of pivalate rare earth complexes led to isolation of $La(piv)_3(deta)_2$ molecular mixed ligand complex which was characterized by powder and single crystal X-ray diffraction, IR and NMR spectroscopy, TGA, conventional elemental analysis. For the rare earths from Pr to Er mainly amorphous products of hydrolysis were formed.

However, it worth noting that in the same conditions octahedral clusters $Ce_6O_8(piv)_8(deta)_4$, $Pr_6(OH)_8(piv)_{10}(deta)_4\cdot C_6H_6$ and $Gd_6(OH)_8O(piv)_{10}(deta)_4\cdot 2CH_3CN$, predicted by DFT calculations and containing stable fluorite-like fragment Ln_6O_8 ,could be isolated.

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ZINC(II) BROMIDE COMPLEX WITH CAFFEINE: SYNTHESIS, PROPERTIES AND CYTOTOXICITY STUDIES

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It is known that zinc(II) mixed-ligand complexes may be considered as promising alternatives to platinum(II) complexes in the molecular design of new antitumor drugs [1, 2]. Caffeine (1,3,7-trimethylpurine-2,6-dione, $C_8H_{10}N_4O_2$ - caf) and its derivatives are perspective source for receiving therapeutic agents to be used in a combined therapy for brain tumors due to their possibility to penetrate through the Blood-Brain-Barrier (BBB) [3].

The aim of the present work consists in the synthesis and studies (IR-spectroscopy, powder XRD, DTA/TA/MS), MTT assay (the mice fibroblasts NCTC clone L929 cells, the human lung cancer cell line A549, prostate cancer cell line PC-3, colon cancer cell line HCT-116, breast cancer cell line MCF-7, leukemia cancer cell line Jurcat) on $[Zn(caf)(H_2O)Br_2]$ complex compound. The complex has been synthesized in aqueous medium from $[Zn(H_2O)_6][Zn_2Br_6]$ and a ligand taken in the molar ratio Zn:caf = (1-3):1. The compound composition has been confirmed by elemental analysis (CHN, Zn), the caffeine content being determined as well by the modified gravimetric analysis with the application of extraction with organic solvents. The compound is melted at 205-210° C with simultaneous (ca. 3.61 wt. %) water removing with subsequent ligand decomposition and sublimation. It was demonstrated that cytotoxicity of the studied compound is the dose-dependent one with respect to L929 cells and the compound inhibits the growth of a number of cancer cells particularly the Jurcat leukemia ones. It has been concluded that the studied complex compound is the promising one for further investigations both *in vitro* and *in vivo*.

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Acknowledgements

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NEW DOUBLE COMPLEX SALTS CONTAINING Rh AND Pd – PRECURSORS FOR PREPARATION OF THREE-WAY CATALYSTS (TWC)

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Modern three-way catalysts (TWC) are employed for neutralization of harmful components of exhaust gases of gasoline-powered engines (CO, NO_x and HC). Three-way catalysts contain as active components nanoparticles of Pd and Rh [1].

Incipient wetness impregnation of the support with aqueous solutions of precursors is used to prepare Pd-Rh catalysts. Then they are heated in different temperature conditions. As the precursors, most often used are $H_2[PdCl_4]$, $H_3[RhCl_6]$, $PdCl_2{\cdot}nH_2O$, $RhCl_3{\cdot}nH_2O$, $Pd(CH_3COO)_2$, $Rh(CH_3COO)_3$, $[Pd(H_2O)_2(NO_3)_2]$, $[Rh(H_2O)_x(NO_3)_{6-x}]$, etc. But the use of this approach doesn't guarantee stability of nanoparticles on the surface of support. Increase of the activity and thermal stability of catalysts can be achieved by the distribution of Pd and Rh on the surface of support in the form of alloyed nanoparticles. The decrease of particle size will increase the catalytic activity, and the formation of a solid solution reduces the probability of sintering of Pd particles and the diffusion of Rh^{3+} ions into the support bulk.

Prospective precursors for the preparation of nanoscale alloys for the preparation of catalysts are double complex salts containing in their composition simultaneously the atoms of Pd and Rh. It was shown earlier that the thermal decomposition of double complex salts makes it possible to obtain these metals in the state of an alloy (solid solution), which increase their catalytic activity and stability [2].

The report presents the synthesis and properties of double complex compounds with nitrogen-containing ligands NH_3, En, NO_2 and different ratio of metals. The objects of investigation are new double complex salts: $[Rh(NH_3)_5Cl][Pd(NO_2)_4]$, $[PdEn_2]_3[Rh(NO_2)_6]_2{\cdot}nH_2O$, $[RhEn_3]_2[Pd(NO_2)_4]_3{\cdot}nH_2O$. There were found crystalline structures for each of double complex salts. All of them were studied by a complex of physicochemical methods. The possibility of obtaining nanoparticles of solid solutions in a Pd-Rh system with a different component ratio is shown.

The most promising compounds were used for the synthesis of bimetallic particles on the surface of oxide support. It was also established that in the process of thermal decomposition it is possible to obtain alloyed bimetallic nanoparticles Pd-Rh fixed on the surface of the oxide support. The activity and stability of the resulting catalyst compositions were confirmed in model reactions of CO oxidation and hydrogenolysis of the C-C bond.

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SYNTHESIS AND LUMINESCENT PROPERTIES OF LANTHANIDE COMPLEXES WITH SUBSTITUTED 2-TOSYLAMINOBENZOYLHYDRAZONES

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Luminescent lanthanide coordination compounds (LCCs) are excellent candidates as emitters for bioanalyses and bioimaging due to their unique optical properties. Near infrared (NIR) emitting LCCs attract the most of attention because NIR range has a little interference with biomaterials so that photons can penetrate deeply into biological samples, cells and tissues. Nevertheless, the quantum yields (QYs) of NIR luminescent LCCs is still very low because of the low efficiency of lanthanide ion sensitization and high NIR luminescence quenching on O-H vibration, and the typical values of QYs do not exceed the fractions of percent. Another important demand for bioimaging materials is high stability against dissociation, and LCCs with polydentate Schiff bases seem promising candidates. Beside substituent variation may result in low lying triplet state and high absorption which is also important for bioimaging. Thus, we presented the syntheses of lanthanide complexes with the series of substiteted 2-tosylaminobenzoylhydrazones that, from one hand, resulted in the effective NIR emitting materials and, from the other hand, allowed to understand the influence of substituents on the luminescence properties of the complexes.

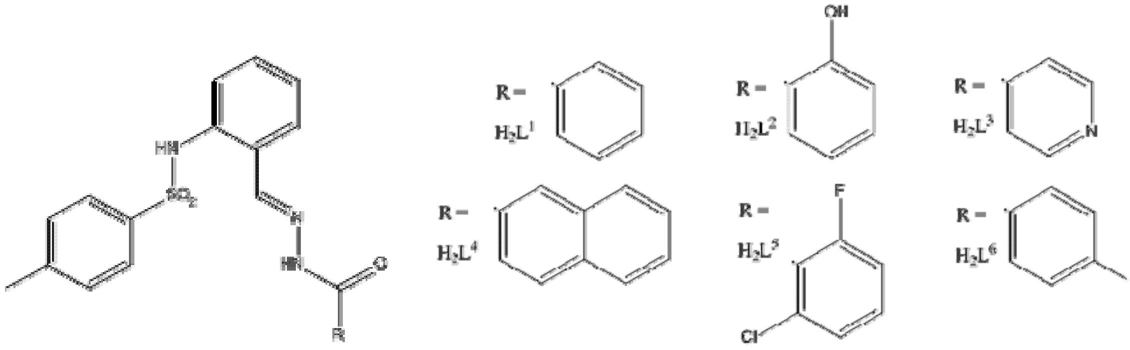

Figure 1. The structure of the ligands

It was shown that LCCs with the selected ligands were only formed if R contained up to one *ortho*-substituent. Despite the different composition the obtained complexes $Ln(L^n)(HL^n)$ (n = 1 – 4) and $Ln(HL^1)_2X$ (X = Cl, NO_3) have very similar structure, consisted of monomeric species $[Ln(H_kL)(HL)]^{k+}$ (k = 0,1), and demonstrate very high stability even in DMSO solutions. Ytterbium complexes possesses high value of QY up to 1,5% owing to the absence of vibrational quenching and effective energy transfer to ytterbium ions from the ligand-to-metal charge transfer (LMCT) state. The presence of LMCT state was confirmed by the investigation of DR spectra of complexes and temperature dependence of europium complex luminescence.

Thus, ytterbium complexes with high values of NIR QY and high stability in DMSO solution were synthesized, which could be recommended for bioimaging applications.

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COORDINATION COMPOUNDS OF BORON (III) AND ZINC (II) WITH DIPYRROMETHENES AND AZA–DIPYRROMETHENES: SPECTRAL-LUMINESCENT, GENERATION AND PHOTOCHEMICAL CHARACTERISTICS IN SOLUTIONS

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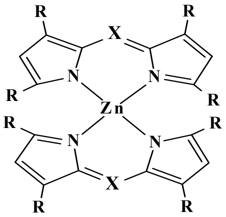
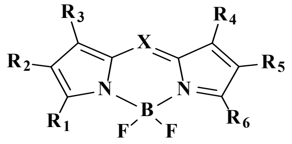
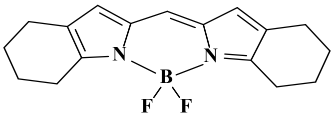
Dyes and luminophores based on B (III) and Zn (II) coordination compounds with dipyrromethenes have intense absorption and fluorescence, along with photo- and thermostability. Actual modern problems are the search for ways to influence and adjust the spectral-luminescence, generation and photochemical properties of this class dyes for specific practical and theoretical problems of sensorics, biochemistry, and other fields. Analysis of modification various types of the dipyrromethenates molecular structure on the characteristics of electronic absorption spectra, fluorescence, and long-lived radiation of complexes was carried out using eleven Zn (II) and B (III) complexes with alkyl-, halogen, phenyldipyrromethenes and their *meso*-aza analogues in organic solvents of different polarity, electron and proton-donor capacity.



1: R: CH_3; X: CH
2: R: Ph; X: CH
3: R: Ph; X: N



4–6 Fig. 1



7

4: R_1=R_3=R_4=R_6=CH_3; X=CH
5: R_1=R_3=R_4=R_6=CH_3; R_2=R_5= C_7H_{15}; X=CH
6: R_1=R_3=R_4=R_6=CH_3; R_2=R_5=CH_2Ph; X=CH
8: R_1=R_3=R_4=R_6=Ph; R_2=R_5=H; X= CH
9: R_1=R_3=R_4=R_6=Ph; R_2=R_5=H; X= N
10: R_1=R_3=R_4=R_6=Ph; R_2=R_5=Cl; X=N
11: R_1=R_3=R_4=R_6=Ph; R_2=R_5=Br; X=N

We carried out for the first time a complex study of the spectral-luminescence properties, photo- and thermostability of Zn (II) and B (III) complexes with alkyl-, halogen-, phenyldipyrrometenes and their meso-azanalogues in proton and electron-donor organic solvents ($C_6H_{14,}$ C_6H_{12}, $C_6H_{6,}$ C_6H_5-CH_3, $CHCl_3$, PrOH-1, EtOH, ДМФА). Complexes **1–11** are intense dyes with lgε = 4.80-5.10 and fluorophores (with the exception of meso-aza-dipyrromethenate **3**) with quantum yields (φ) of 0.1-30% (**1** and **2**), 30-100% (**4-7**) And 1-20% (**9–11**). Phenyl and *meso*-aza-substitution make it possible to shift the electronic absorption spectra and the fluorenescence of the complexes to the red region by ~ 70-150 nm. Spectral-luminescence, generation and photochemical characteristics of the alkyl-, benzyl-, bis-cyclohexyl-substituted BODIPY series of were obtained. Forced radiation generates BODIPY **4–7**, the maximum value of the generation efficiency yields complex **6**. Among BODIPY **4–7** and **10**, BODIPY **10** demonstrates the greatest photostability.

Chemosensory properties of 3,3 ', 5,5'-tetraphenyl-substituted dipyrromethene were studied for the first time. It was found that 3,3 ', 5,5'-tetraphenyldipirromethene is a highly sensitive and selective sensor of Zn^{2+} cations with the detection limit under the studied environmental conditions up to 10^{-7} mol / l. The possibilities of zinc (II) dipyrromomethate **2** practical application as a medium polarity sensor, BODIPY **4–7**, **10** as components of laser active media, as well as tetraphenyldipyrromethane ligand as a fluorescent sensor of Zn^{2+} ions, are substantiated.

The study was carried out with the financial support of the Russian Foundation for Basic Research in the framework of the scientific project № 16-33-00611 mol_a.

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EFFECT OF WEAK INTERACTIONS ON STRUCTURE AND REACTIVITY OF PALLADIUM(II) DIAMINOCARBENE COMPLEXES

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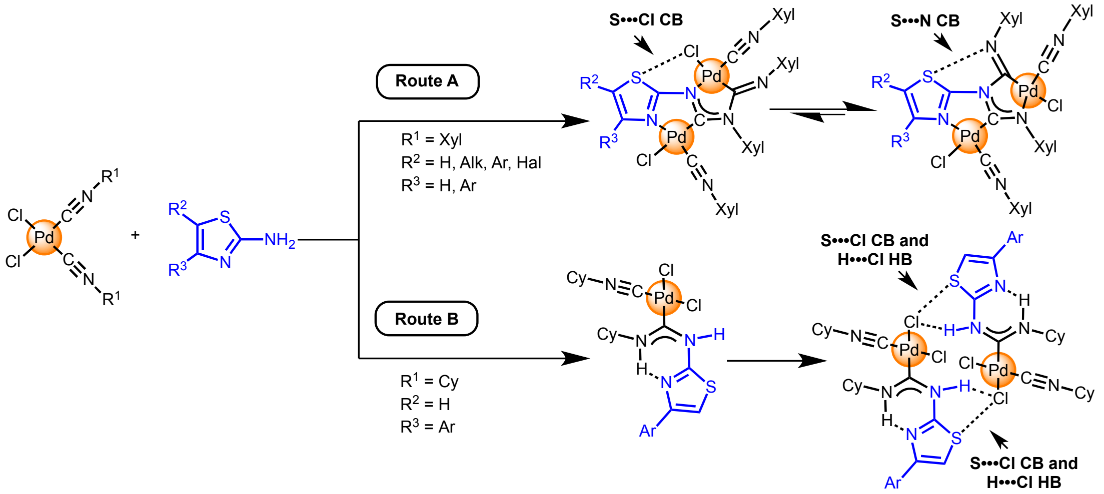
An area of non-covalent interactions currently attracts great attention due to their application in biochemistry, drug design, polymer science, crystal engineering, and supramolecular chemistry. One of the less studied type of such interactions is chalcogen bonding (CB). The phenomenon of CB is based on interaction between a localized positive region, the so-called σ-hole, on a chalcogen atom and electron donor species serving as CB acceptors. The ability of CB to control the structures of coordination compounds was repeatedly reported, whereas the effect of CB on reactivity was exceptionally rarely verified.



Scheme 1. Reaction of *cis*-[$PdCl_2(CNR)_2$] with various thiazol-2-amines.

In this work we studied the reaction of palladium(II) isocyanide complexes with various thiazol-2-amines possessing sulfur-center as CB donor. Depending on substituent in the isocyanide ligand the reaction gives different types of products displaying different types of non-covalent interactions. The reaction of isocyanide complex with aryl substituents gives a mixture of two regioisomeric binuclear diaminocarbene complexes which are subject to reversible isomerization in to each other (Route A) [1]. The difference in energy between two types of intramolecular CBs drives regioisomerization and determines the relative stability of these complexes. In the same time, the reaction of isocyanide complex with alkyl substituents leads to mononuclear diaminocarbene complexes (Route B). The presence of cooperative CB and hydrogen bonding (HB) provides the dimerization in the solid-state and in solution.

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COORDINATION OF ISONITRIL AND POLYFLUORO-SUBSTITUTED THIOLATE LIGANDS TO OCTAHEDRAL CLUSTERS OF MOLYBDENUM, TUNGSTEN AND RHENIUM

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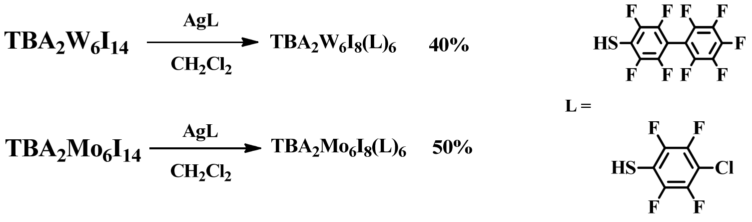
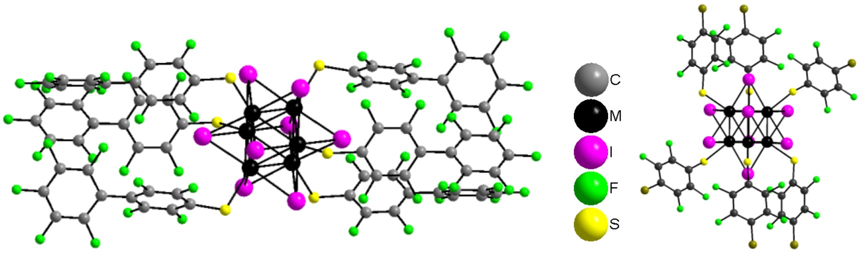
New approaches to the syntheses, the study of the properties and structures of cluster compounds of transition metals are one of the most important trends in modern chemical researches. Six-core iodide clusters of molybdenum and tungsten and rhenium chalcogenide cluster complexes exhibit remarkable luminescent properties and can be used in many practical applications (in catalysis, as new luminescent materials). Clusters with extended ligands can serve as structural blocks in liquid crystals.

The redox and luminescent properties of iodide $[\{M_6I_8\}L_6]^{2-}$ (M = Mo, W) and chalcogenide $[\{Re_6Q_8\}L_6]$ (Q = S, Se, Te) species can be used for development of functional materials and sensors. We have synthesized hexa-substituted complexes of molybdenum and tungsten clusters which contain coordinated polyfluoro-substituted thiolate aromatic ligands.

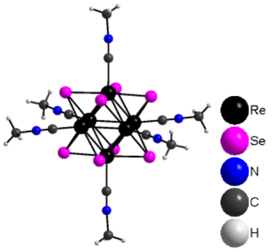

$TBA_2W_6I_{14} \xrightarrow[CH_2Cl_2]{AgL} TBA_2W_6I_8(L)_6$ 40%

$TBA_2Mo_6I_{14} \xrightarrow[CH_2Cl_2]{AgL} TBA_2Mo_6I_8(L)_6$ 50%



The new octahedral cluster complexes $[\{M_6I_8\}L_6]^{2-}$ (M = Mo, W) exhibit intense and long-lived emission in the red and near-IR diapasons under UV irradiation and contain extended ligands. The treatment of rhenium cyanide cluster with trimethylooxonium tetrafluoroborate leads to the new cationic rhenium luminescent cluster complex.

$$(Ph_4P)_4[Re_6Se_8(CN)_6] \xrightarrow[CH_2Cl_2]{(CH_3)_3OBF_4} [Re_6Se_8(CN\text{-}CH_3)_6](BF_4)_2$$



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NEW WAYS TO THE SYNTHESIS OF RHENIUM CLUSTER COMPLEXES

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Cluster compounds of transition metals are the ones of the fastest growing area of the modern chemistry and chemistry of material science. Interest in the study of these compounds is due to the obtaining of the fundamental data on the structure and reactivity, as well as the set of manifested physicochemical properties, including those of applied importance. For example, rhenium cluster complexes are very interesting for the procedure named photodynamic therapy, and also can be promising candidates as a radiopaque media.

This work was carried out in the field of synthetic and structural chemistry and aimed at searching the high-performance approaches to the synthesis of new rhenium cluster complexes and studying their structure and properties.

In this research, interactions in the systems ReO_2-X-KCN, ReI_3-X-KCN и ReI_3-KCN, where X = P, As, S, Se, Te were studied. All samples obtained were characterized by X-ray diffraction on single crystals and powders, elemental analysis, IR spectroscopy and cyclic voltammetry.

Proceeding from rhenium iodide, new pnictogen cluster rhenium complexes were obtained. Besides, by the reaction of ReI_3 with KCN tetrahedral complex with μ_3-bridged CCN^{3-} ligands was synthesized. The unusual ligand CCN^{3-}, formed during the reaction, can be considered as a deprotonated acetonitrile.

Using X-ray photoelectron spectroscopy, it was shown that the pnictogen complexes obtained in this work are the first examples of tetrahedral rhenium cluster complexes with a formal charge of the metal atom +3.

Obtained as a result of work fundamental knowledge are of interest for cluster chemistry as a whole and can be used to further investigation of the possibility of the use of metal oxides and halides applied to other metals forming clusters.

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NOVEL COBALT AND MANGANESE COMPLEXES BASED ON O-SEMIQUINONATO AND IMINOPYRIDINE LIGANDS

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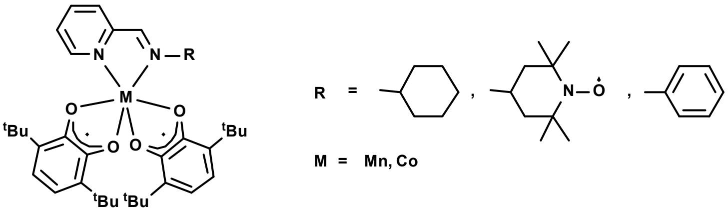
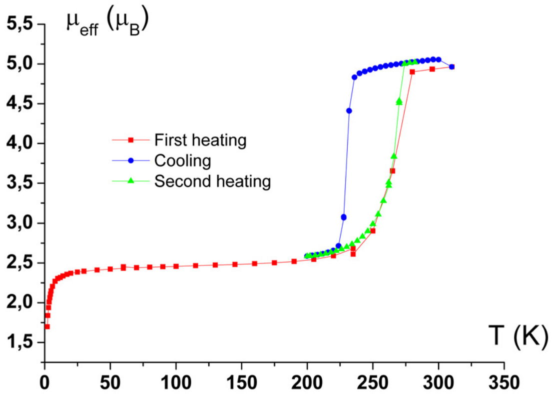
Six-coordinated bis-*o*-semiquinonato transition metal derivatives attract the great interest which is caused by two fundamental scientific aspects. At first, investigation of magnetic properties of these compounds allows to understand the regularities of intramolecular magnetic interactions in paramagnetic molecules and to obtain the new magnetic materials in perspective. On the other hand, for the members of the aforementioned type of metal complexes the redox-isomerism phenomenon is observed [1].

The series of cobalt and manganese complexes containing redox-active 3,6-di-tert-butyl-*o*-quinone and various iminopyridine ancillary ligands was synthesized.



The obtained complexes were characterized by IR-spectroscopy and variable temperature magnetic susceptibility measurements. Molecular structure of complex containing free-radical 2,2,6,6-tetramethylpiperidine-1-oxyl substituent in the N-donor ligand was established by X-Ray analysis. This compound in the solid state undergoes temperature-induced redox-isomeric transition in the temperature range 200-275 K. It should be noted that the hysteresis loop on the curve of the effective magnetic moment temperature dependence is observed.



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SYNTHESIS AND PHYSICO-CHEMICAL PROPERTIES OF COMPLEXES OF DABCO HEXADECYL DERIVATIVE WITH COBALT(II) AND NICKEL(II) NITRATES

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The incorporation of metal fragments into amphiphilic compounds impacts new physicochemical properties to the surfactant molecules and it extends the possibility of their practical application. Synthesis of complexes of 1-hexadecyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide (**D-16**) with cobalt(II) and nickel(II) nitrates was carried out in methanol at room temperature. The metal complexes have been characterized by IR, ^{1}H NMR spectroscopy and elemental analysis.

The stoichiometry and stability constant of complexes formed in acetone are determined by Ostromyslenskii – Job and molar ratio methods. D-16 with cobalt(II) and nickel(II) nitrates forms two complex compositions of stoichiometry 1:3 and 1:1. The micelle-forming properties of complexes in an aqueous medium are investigated by fluorimetry, dynamic light scattering and conductometry. Their critical micelle concentration, aggregation numbers, size of aggregates, Kraft temperature are determined. The Kraft temperature of nitrate complexes is within the range of 10.6 - 12.2 °C, that is 12-14 °C lower than that of CTAB and 3-5 °C lower than that of D-16. Fluorimetric study of complex solutions with a hydrophobic probe pyrene was carried out. The CMC value of complexes of cobalt(II) and nickel(II) equal to 0.65 and 0.59 mM respectively. For the D-16 the CMC value equals 0.99 mM. In the concentration range from 2 to 8 mM, aggregation numbers of D-16 vary from 20 to 55, and for complexes of cobalt(II) and nickel(II) with concentrations from 1 to 8 mM in the range 22-44 and 21-64 respectively. Hydrodynamic diameter of complexes supramolecular assemblies is determined by dynamic light scattering. Three types of particles in aqueous solutions of complexes of D-16 with transition metals are formed. In the CMC region, aggregates are formed with a hydrodynamic diameter 40-150 nm and 250-550 nm. After the CMC, there is a reorganization of systems with a tendency to preferred formation of micellar aggregates of small size - about 6-8 nm.

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INTERACTIONS OF PLATINUM(II) WITH SOME POLYFUNCTIONAL ORGANIC DISULFIDES IN HYDROCHLORIC AQUEOUS SOLUTIONS

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Organic disulfides are vital participants and products of biochemical processes occurring in living systems. Interactions of platinum metals' complexes with sulfur-containing molecules play an important role in the metabolism of anticancer drugs, materials science, hydrometallurgy, analytical chemistry and refining.

Based on the quantum-chemical thermodynamic calculations of interactions of $[PtCl_4]^{2-}$ with polyfunctional organic disulfides (L-cystine, cystamine, DL-homocysteine, and 3,3'-dithiodipropionic acid) on the assumptions of stepwise complexation, disproportionation and oxidative addition have shown, that the most favorable are the reactions of oxidative addition.

The best matching of the spectrophotometric titration data is achieved under the assumption of the formation of a highly stable binuclear complex and a product of the oxidative addition reaction. The kinetic studies of reactions have been studied under the pseudo-first order conditions in $[PtCl_4]^{2-}$*. Sigmoidal kinetic curves are described by the stepwise addition of two* $[PtCl_4]^{2-}$ *ions via a disulfide group (R-S-S-R) by the associative mechanism. The resulting binuclear complex quickly becomes a product of an oxidative addition* $[PtCl_4(S\text{-}R)_2]$*. It has been found, that the kinetics are not affected by C(HCl) and C(ethanol), but by the ionic strength of a solution.*

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SELECTIVE DISTRIBUTION OF LN(III) IONS INTO CATIONIC AND ANIONIC POCKETS OF HETEROMETALLIC COMPLEXES $[LN\{NI(ALA)_2\}_6]^{3+}[LN'(NO_3)_3(OH)_3(H_2O)]^{3-}$

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Nowadays, special attention is being paid to polynuclear 3*d*-4*f* complexes, self-organizing from simple "building blocks": lanthanide (III) ions and amino acid salts of *d*-metals.

According to the results of the electron absorption spectroscopy, it was found that the complex cation $[Ln\{Ni(ala)_2\}_6]^{3+}$ is formed only for Ln = La(III), Ce(III), Pr(III) and Nd(III). These complex cations could be isolated into the solid phase in the form of cation-anionic compounds with counter-ions $[La(NO_3)_6]^{3-}$ or $[Ln'(NO_3)_3(OH)_3(H_2O)]^{3-}$ (Ln' = Ce, Pr, Nd). Based on the results of the study, a hypothesis about the different stability of complex cations as a function of the central REE ion was proposed. So, the purpose of this work was (a) to study the structural features of these cation-anionic compounds to identify factors that affect the stability of the complex cation, and (b) to develop an approach to the directed synthesis of compounds with a selective distribution of Ln^{3+} ions over the cationic and anionic positions.

It was shown that the concentrations of "free" La^{3+}, Ce^{3+}, and Pr^{3+}, which are not encapsulated into the complex cation, were below the detection limit of the method (**ICP MS**). For Nd^{3+}, the degree of binding to the $[Ln\{Ni(ala)_2\}_6]^{3+}$ complex was 90%, which indicates a lower stability of this complex cation compared to the analogous La^{3+}, Ce^{3+} and Pr^{3+} complexes. A study of the crystal structure of the compounds showed that the Ln^{3+} ion in the complex cation is located inside the icosahedral cavity formed by the oxygen atoms of the $\{Ni(ala)_2\}_6$ fragment. The supramolecular unit $\{Ni(ala)_2\}_6$ has a rather rigid structure, as a result, the diameter of this cavity does not change as the ionic radius of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+} decreases. In the anion $[La(NO_3)_6]^{3-}$, the center ion is surrounded by six bidentate nitrate ions, whereas other lanthanides form partially hydrolyzed anions $[Ln(NO_3)_3(OH)_3(H_2O)]^{3-}$. It is proved that in the complex anion the REE ion is in a more flexible environment. In crystals, complex cations and anions assembled by hydrogen N–H···O and O–H···O bonds, forming a close packing. The established facts made it possible to obtain for the first time in solid form compounds with various REE in different crystallographic positions.

The cation-anion compounds $[Ln\{Ni(ala)_2\}_6]^{3+}[Gd(NO_3)_3(OH)_3(H_2O)]^{3-}$ (Ln = La, Ce, Pr, Nd) were characterized by the methods of X-ray diffraction, EDX and ICP MS. The molar ratios of REE in the complexes showed that La^{3+} and Ce^{3+} are located exclusively in the cation, and Pr^{3+} and Nd^{3+} are present not only in the cation, but also in the anion. Thus, the first example of compounds with a selective distribution of lanthanide ions between cationic and anionic positions in polynuclear complexes with amino acids is the complex $[La\{Ni(ala)_2\}_6]^{3+}[Gd(NO_3)_3(OH)_3(H_2O)]^{3-}$.

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"FACE TO TAIL" INTERACTION OF MONOPHOSPHORYLATED PILLARARENE WITH ALIPHATIC AMINES

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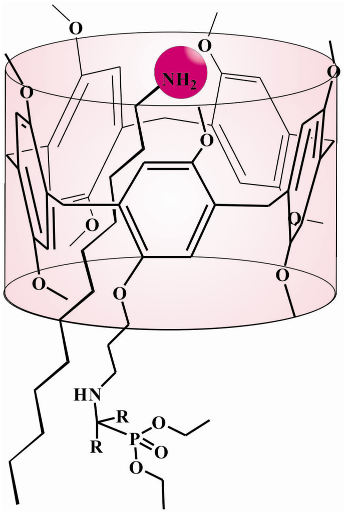
Investigation of pseudorotaxane structures are attracted attention of researchers over all the world due to their similarity with rotaxanes. Pseudorotaxane can used as simple molecular machines, as well as they could be used in the modification of physical and chemical properties of guest molecules, and protection of substrates from chemical attack and aggregation. Strong interest to this supramolecular architectures leads to continuous research of new macrocyclic host-molecules and linear guest-molecules, which can form pseudorotaxane structures. In the last few years the study of supramolecular polymers based on macrocyclic compounds became widespread in chemistry. Very convenient precursor to prepare the host-compounds above is new class of paracyclophanes, namely pillar[n]arenes. In case of pillararenes the host-guest interaction is the driving force for forming pseudorotaxanes. These macrocyclic hosts with the rigid framework can be easily functionalized per hydroxyl groups, and this possibility allows changing their specific binding abilities to various guests.



For the first time, monosubstituted derivatives based on pillar[5]arene containing 1-aminophosphonate fragment were obtained by the Kabachnik-Fields reaction. In this work it was shown the efficiency and selectivity of binding ability of synthesized host-molecules with a number of aliphatic amines (i-propylamine, benzylamine, octylamine, dodecylamine, octadecylamine) by DLS, UV-, one- and two-dimensional NMR spectroscopy (NOESY, DOSY).

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SPECTRA AND SYMMETRY ASSIGNMENT FOR EUROPIUM STARK COMPONENTS IN COMPLEXES BASED ON 2,2'-BIPYRIDILDICARBOXYLIC AMIDE

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Complexes of rare earth elements with organic ligands are widely used in optoelectronics to create organic light emitting devices, in biomedical research and pharmacology for biovisualization purposes. Such complexes are able to emit narrow lines in the red and near infrared spectral range depending on the type of the lanthanide ion [1]. Luminescence of complexes with rare earth elements results from light absorption in the UV region by the ligand and further energy transfer to the resonance energy level of the lanthanide. Luminescence of Eu^{3+} ion can provide spectroscopic information regarding the local site symmetry and environment within the host.

In this work we studied photophysical properties of europium complexes with ligands based on 2,2'-bipyridildicarboxylic amide. Luminescence spectra of powders were registered using luminescence spectrometer Hitachi F-7000 at 77 and 300 K (excitation wavelength 320 nm, emission wavelength interval 0.2 nm, spectral slit widths 5 and 1 nm for excitation and emission).

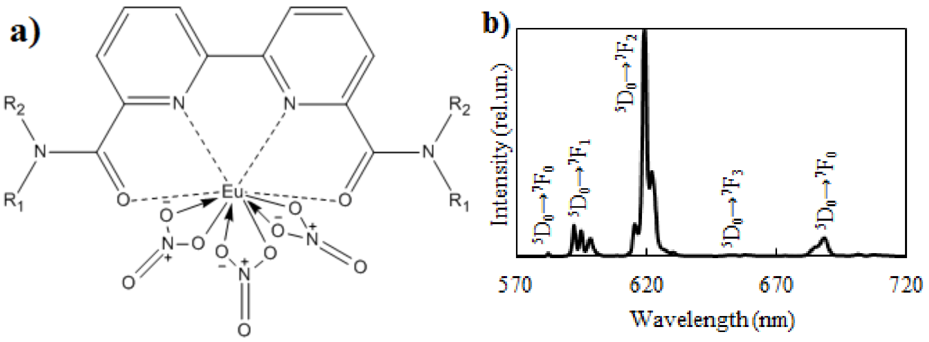

Figure 1. Structure of europium complexes: R_1=Ph, 4-EtPh, 4-iPrPh, 4-HexPh, 4-tBuPh, 4-cycloHexPh, 2-F-Ph, 3-F-Ph, 4-F-Ph, 2,4-diMePh, 3,4-diMePh, 2,5-diMePh, 2,4,5-triMePh, R_2=Et (a) and typical luminescence spectra of europium complex (b).

A typical europium emission spectrum shows intense luminescence signals and includes several lines in the red region corresponding to transitions $^5D_0\to{}^7F_J$ (J = 0–6). In this study we observed only the first five maxima. Most intense luminescent maximum corresponds to transition $^5D_0\to{}^7F_2$ (610-630 nm). Analysis of fine structure of narrow emission lines at 77K allowed to determine the number of Stark components for Eu^{3+} crystal-field splitting and the type of the syngony. The following photophysical parameters were calculated using luminescence spectra: the ratio I_{618}/I_{592} showing deviation from an inversion center in complexes, radiation and observed lifetimes τ_{rad}, τ_{obs}, internal quantum yield Q_{Eu}.

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TRANSITION METAL COMPLEXES OF P,N-CONTAINING CYCLOPHANES.

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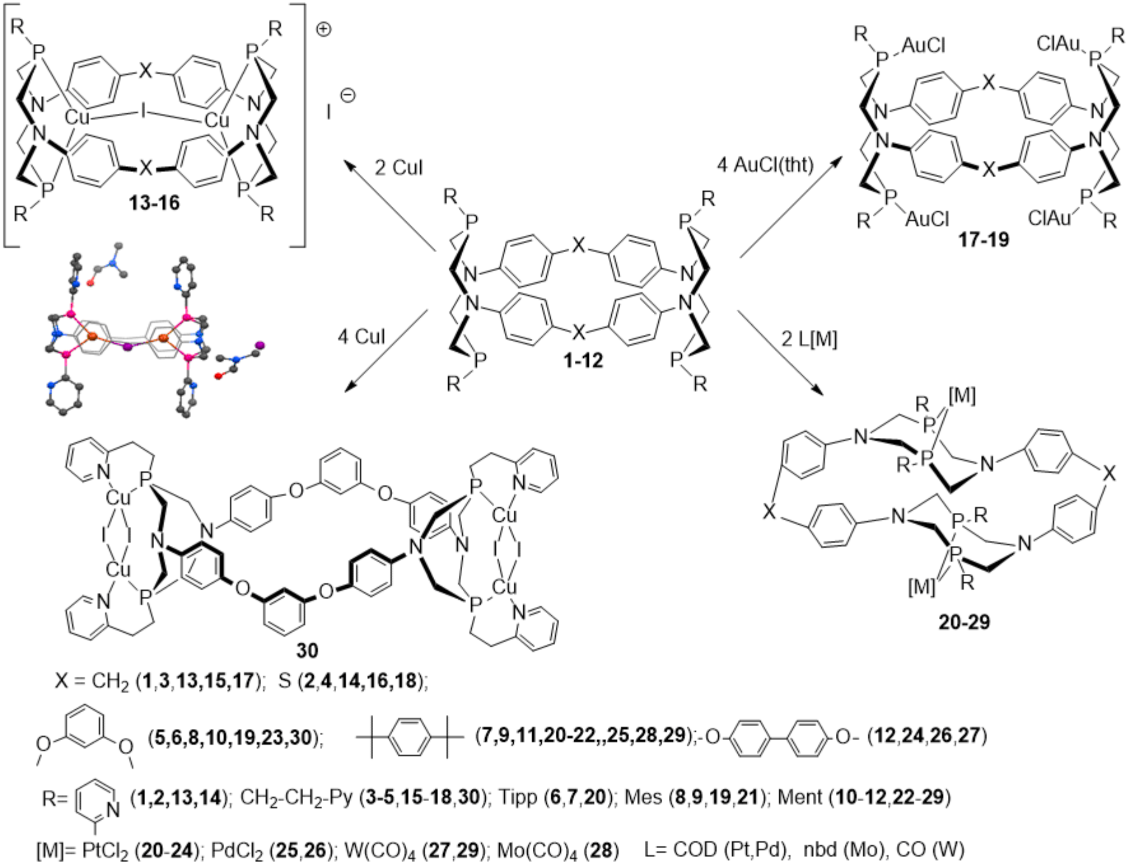
P,N-containing cyclophanes with two 1,5-diaza-3,7-diphosphacyclooctane fragments [1-3] are capable to form transition metal complexes of various structures. 28-Membered macrocycles **1-4** acted as P-ligands to give charged binuclear complexes where two copper atoms located inside the cavity are connected by an iodine bridge; 28-membered **3**, **4** and 36-membered **8** macrocycles formed tetranuclear complexes **17-19** with gold (I) chloride. 36-membered ligand **5** formed tetranuclear copper (I) complex **20** with P,N-chelate coordination of copper ions (scheme 1).



Scheme 1

P,N-containing cyclophanes **6-12** reacted with VIII and VI group metals derivatives to give binuclear bis-P,P-chelate complexes **21-30**. Metal-containing unities of these complexes are located outside the macrocyclic cavities but in close proximity to them, so these complexes are of interest as the potential basis of new catalytic and molecular recognition systems.

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INVESTIGATION OF PROSPECTIVE COMPLEXES OF F-ELEMENTS WITH ANILIDES FOR SEPARATION OF RARE-EARTH ELEMENTS

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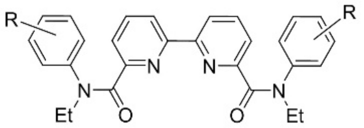
Lanthanides are widely used as pigments, catalysts, magnets and phosphors, so lanthanides possess high photophysical and luminescent characteristics, for this reason they are difficult to replace with cheaper elements. One way to reuse lanthanides from radioactive waste is selective extraction. In order to increase the selectivity, it is necessary to choose the correct complexing agent having significant differences in the stability constants with different f-elements. We propose to use prospective 2,2'-bipyridyl-6,6'-dicarboxamides as complexing agent to study of the stability of their complexes with trivalent lanthanides to explain the effect of reagent structure on its complexing efficiency. The aim of our work is to determine influence of substituents in the amidic moiety of diamides (1-4) on the stability constants of their complexes as well as changes in the stability in the lanthanides series.



R = *o,p*-diMe (**1**) *o,m*-diMe (**2**); *o,m,m*-triMe (**3**); *p*-tret-Bu (**4**); *o*-F (**5**); *m*-F (**6**); *p*-F (**7**); *o*-Br (**8**); H (**9**[1])

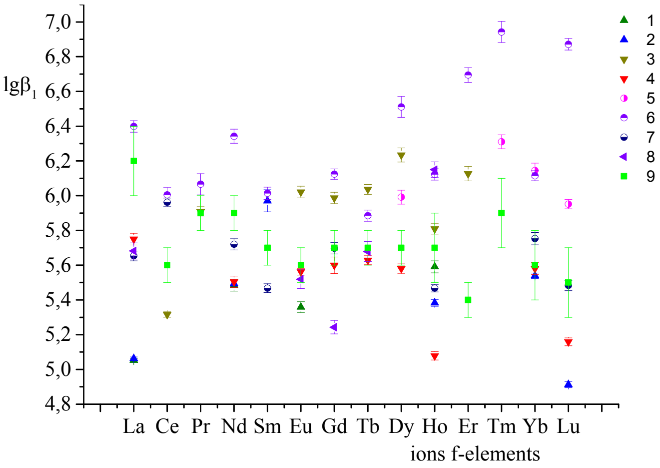


Figure 1. The lanthanide ion dependence of the stability for anilides

We investigated two groups of ligands: containing electron-rich substituted methylated ligands **1-4** and electron-withdrawing substituted halogenated diamides **5-8**. An unsubstituted amide (**9**) was used as a reference. The stability constants of series of lanthanide ions complexes with ligands **1-8** (*Figure 1*) were determined in dry acetonitrile by UV/VIS titration. All diamides form one complex with 1:1 metal-to-ligand stochiometry. The lgβ$_1$ complexes of investigated anilides with lanthanide ions fall into 5,5-6,2 region. According to the electronic properties of the substituents, ligands demonstrate different behavior. The electron properties of substituents placed in aromatic part of amidic moiety of ligands influenced strongly on stability of complexes (*Figure 1*). We observed that o-fluiorine-substituted anilide stabilizes the complex due to conjugation of halogen long pairs with the aromatic ring, which does not occur in the case of the m-isomer. The electron-rich substituents have effect on the stability of complexes with introduction of meta-substituted diamides. Examination of only o-substituted diamides, may cause a decrease in the stability of complexes due to steric effects.

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NEW STRATEGY TO ENHANCE CO_2 UPTAKE IN THIOPHENE BASED MOFs

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Carbon dioxide (CO_2) release poses one of the biggest anthropogenic impacts to the environment. CO_2 sequestration through selective adsorption is viewed as one of the most promising approaches due to its simple implementation, the absence of hazardous materials, tunable selectivity and low energy costs. Thus, porous materials, such as metal-organic frameworks (MOFs), with the highest CO_2 adsorption capacity at relatively low partial pressures (< 5 bar) are valuable targets for such applications. High adsorption selectivity and high uptake under ambient conditions may be enhanced in porous materials by the incorporation of specific binding sites at the pore surface. We demonstrate herein that the incorporation of thiophene moieties with polarizable sulfur heteroatoms, capable of induced dipole-dipole interactions, results in a remarkable increase of the CO_2 binding affinity of the microporous metal-organic framework. This increases both the storage capacity and selectivity of the framework at ambient conditions by as much as 50%, comparing thiophene with phenyl functionalisation, and also maintains the heat of adsorption at a low level to minimize penalty costs for regeneration.

The complex $[Zn_2(tdc)_2(dabco)]$ (H_2tdc = thiophene-2,5-dicarboxylic acid; dabco = 1,4-diazabicyclooctane) shows a remarkable increase in CO_2 uptake and CO_2/N_2 selectivity compared to the non-thiophene analogue $[Zn_2(bdc)_2(dabco)]$ (H_2bdc = benzene-1,4-dicarboxylic acid; terephthalic acid). CO_2 adsorption at 1 bar for $[Zn_2(tdc)_2dabco]$ is 67.4 $cm^3 \cdot g^{-1}$ (13.2 wt.%) at 298 K and 153 $cm^3 \cdot g^{-1}$ (30.0 wt.%) at 273 K. For $[Zn_2(bdc)_2(dabco)]$ the equivalent values are 46 $cm^3 \cdot g^{-1}$ (9.0 wt.%) and 122 $cm^3 \cdot g^{-1}$ (23.9 wt.%), respectively. These adsorption data for $[Zn_2(tdc)_2dabco]$ are among the highest values reported so far under these conditions, exceeding many MOFs with open metal sites. Furthermore, X-ray diffraction data for CO_2@$[Zn_2(tdc)_2(dabco)]$ indicate a decisive contribution of thiophene cycles in the capture of carbon dioxide molecules. The experimental data and the theoretical insights suggest a viable strategy for the design of new promising compounds as well as improvement of adsorption properties of already known materials through an incorporation of S-based heterocycles within porous structures.

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NEW LUMINESCENT AL_2O_3 MONOLITHIC AEROGELS MODIFIED WITH TRIS(8-HYDROXYQUINOLINATO)ALUMINIUM

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Aerogels are highly porous solid materials with extremely low densities, high open porosity and specific surface areas. Aerogels combining these features with visible luminescence are of special interest as they could be used as lasers, chemical sensors and Cherenkov detectors for high-energy physics. Such materials could be obtained by modification of oxide aerogels with luminescent molecules or metal complexes [1].

In this work, we report on the first synthesis of luminescent Al_2O_3 aerogel monoliths modified by tris(8-hydroxyquinolinato)aluminium. The method used allows synthesizing monolithic luminescent alumina aerogels through one-pot approach, which could be used for the synthesis of a new family of aerogel materials.

The synthesis of the modified alumina aerogel involved three major steps: (1) the sol–gel preparation of the alcogel by mixing 8-hydroxyquinoline with the sol formed by adding propylene oxide to $Al(NO_3)_3$ solution; (2) solvent exchange by washing with *i*–PrOH; and (3) supercritical drying of the wet gels in CO_2 to remove the trapped solvent from the pores of the gels.

It was shown that the adding of the 8-hydroxyquinoline to the aluminium-containing sol lead to a significant increase in gelation time, which in turn affects the microstructure of the obtained materials. The fabricated aerogel monoliths possessed high surface areas of 500–600 m^2/g and highly porous three-dimensional network containing 5–20 nm mesopores. The composition of the materials was confirmed by means of IR-spectroscopy and combined thermal analysis/mass spectroscopy of gases evolved. The aerogels demonstrated intense photoluminescence under 345 nm illumination.

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COORDINATION PEROCOMPLEX OF GERMANIUM FOR GEO$_2$ THIN FILM DEPOSITION ON GRAPHENE OXIDE

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Peroxocomplexes of germanium were isolated from aqueous hydrogen peroxide solutions and characterized by single crystal and powder X-ray diffraction studies, FTIR, Raman spectroscopy and thermal analysis. The crystal structure of peroxogermanates consists of centrosymmetric hexanuclear peroxogermanate $[Ge_6(\mu\text{-}OO)_6(\mu\text{-}O)_6(OH)_6]^{6-}$ anions [1]. Peroxogermanate sol was used for a peroxogermanate thin film deposition in high yield at room temperature on graphene oxide (GO). The deposition of the peroxo-precursor onto graphene oxide and the transformations to amorphous GeO_2, crystalline tetragonal GeO_2 and then to cubic elemental germanium were followed by electron microscopy, XRD and XPS [2]. All of these transformations are influenced by the graphene oxide support. The initial deposition is explained in view of the sol composition and the presence of graphene oxide, and the different thermal transformations are explained by reactions with the graphene support acting as a reducing agent. As a test case, the evaluation of the different materials as lithium ion battery anodes was carried out revealing that the best performance is obtained by amorphous germanium oxide@GO with > 1000 mAh g-1 at 250 mA g-1 (between 0-2.5 V vs. Li/Li^+ cathode), despite the fact that the material contained only 51% wt germanium. This is the first demonstration of the peroxide route to produce peroxogermanate thin films and thereby supported germanium and germanium oxide coatings [2].

The advantages of the coated particulates via peroxide route [3-7] are demonstrated for LIB anodes, which show high specific charging capacity (based on the expensive germanium ingredient) that can be obtained at lower costs compared to all previously reported germanium oxide LIB anodes.

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MULTIPHOTONIC EMISSION IN THE COMPLEXES OF LANTHANIDS

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Lanthanide coordination compounds (Ln CCs) attract much attention due to their luminescent properties. The use of an auxiliary ion that partially replaces the luminescent ion in its crystallographic positions allows one to further influence the luminescent properties. In the present work to study the influence of the auxiliary ion we selected bimetallic lanthanide terephthalates $(Ln_xM_{1-x})_2(tph)_3(H_2O)_4$ and dehydrated $(Ln_xM_{1-x})_2(tph)_3$ (Ln = Tb, Eu; M = Y, Gd) since monometallic $Ln_2(tph)_3(H_2O)_4$ are isostructural in the whole row, and complexes of Ln = Tb or Eu possess high quantum yields.

Starting the investigation on $(Eu_xY_{1-x})_2(tph)_3(H_2O)_4$ luminescence we found that when luminescent Ln = Eu was substituted with non-luminescent Ln = Y, an amazing feature called multiphotonic emission was discovered: the quantum yield of luminescence remained unchanged over a wide range of luminescent ion concentrations of $0.005<x<1$. This effect consists in multiple photon emission by a single Eu ion after a single excitation, and is witnessed by biexponential character of luminescence decay curve [1]. We suggested that multiphotonic emission can be caused by (1) a large ratio of the observed lifetimes of the ligand and lanthanide ($\tau_{obs}(L)/\tau_{obs}(Ln)$) or (2) high efficiency energy transfer across the crystal, which is characterized by a large exciton free path length. We increased the ratio $\tau_{obs}(L)/\tau_{obs}(Ln)$ by replacing Eu with Tb, known for a longer lifetime, or by dehydrating the compounds. It turned out that for $(Tb_xY_{1-x})_2(tph)_3(H_2O)_4$ the range of constant quantum yield and lifetime decreased down to $0.1<x<1$ due to smaller $\tau_{obs}(L)/\tau_{obs}(Ln)$ ratio, and the character of luminescence decay became monoexponential, witnessing no multiphotonic emission.

Dehydration did not lead to a change in the range of effect manifestation, but allowed to detect the luminescence concentration quenching, which was expressed in a decrease in the observed lifetime with an increase in the fraction of the luminescent ion. The analysis of these data allowed determining the criteria of concentration quenching in the Ln CC, which are associated with the values of the lifetimes and volume concentrations of the luminescent ion. The use of paramagnetic M = Gd instead of diamagnetic M = Y did not lead to a change in the range of manifestation of the multiphotonic emission, however, the intensity of ligand luminescence decreases due to the increase in the efficiency of intersystem crossing (ISC).

To study the influence of the free path length of an exciton, which for $(Eu_xY_{1-x})_2(tph)_3(H_2O)_4$ was estimated as λ=40 Å, bimetallic $Eu_xY_{1-x}(dbm)_3(Phen)$ (λ= 250 Å) were chosen. It turned out that the multiphotonic emission is actually observed in $(Eu_xGd_{1-x})(dbm)_3(Phen)$ in the range of $0.1<x<1$, which confirms the role of the exciton free path length as one of the reasons for the appearance of the effect. In addition, the use of paramagnetic gadolinium in place of diamagnetic yttrium in $(Eu_xM_{1-x})(dbm)_3(Phen)$ leads to an increase in the quantum yield due to the increase in the efficiency of ISC [2].

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KETOIMINE DERIVATIVES OF BENZOTHIADIAZOLE AND THEIR COMPLEXES WITH D- AND F- ELEMENTS: SYNTHESIS, STRUCTURE AND PROPERTIES

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The benzothiadiazole (btd) derivatives are particularly interesting as structural blocks of organic light-emitting diodes and low band gap polymers for photovoltaic applications [1]. Besides, they can be used as precursors of stable radical anions due to their positive electron affinity [2]. Herein we report about synthesis and properties of ketoimine derivatives of btd and their complexes with some *d*- and *f*- elements.

H^{R}acnacbtd ($R = CF_3$, Me, Ph) were obtained by condensation reaction of 4-NH_2-btd with corresponding acetylacetones (Fig. 1). Complexes $[M(^{R}acnacbtd)_2]$ (M = Zn, Co, Ni, Pd) and $[Ln(^{R}acnacbtd)_3]$ (Ln = Sm, Eu, Er, Gd, Dy, Nd) were synthesized and characterized by X-Ray analysis. It was found that $(^{Me}acnacbtd)^{-}$ can serve as bidentate or tridentate ligand, whereas $(^{Ph}acnacbtd)^{-}$ only as tridentate one.

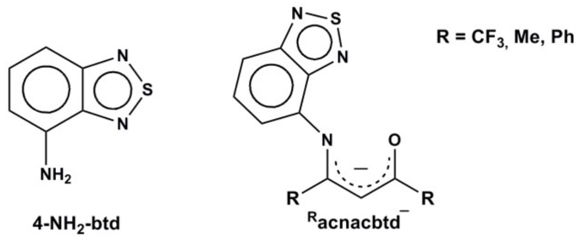

Fig. 1. Organic ligands

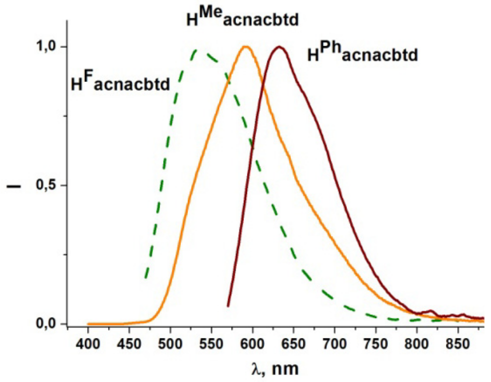

Fig. 2. FL spectra of H^{R}acnacbtd ($R = CF_3$, Me, Ph)

Photophysical properties of the organic compounds and complexes were studied. The steady state FL spectrum of solid H^{R}acnacbtd represents a broad band with maximum of emission at 550 nm. Replacement of the methyl groups with CF_3 results in blue shift of the maximum, replacement with phenyl groups in red one (Fig. 2).

The electrochemical properties of H^{R}acnacbtd (R = Me, Ph) and their complexes were studied by cyclic voltammetry. It was shown that compounds are reduced reversibly. $E_{1/2}$ depends on the substituent in the β-ketoimines and the nature of the central atom.

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OCTAHEDRAL TUNGSTEN CLUSTER COMPLEXES: SYNTHESIS, INVESTIGATION OF OPTICAL PROPERTIES AND X-RAY INDUCED LUMINESCENCE

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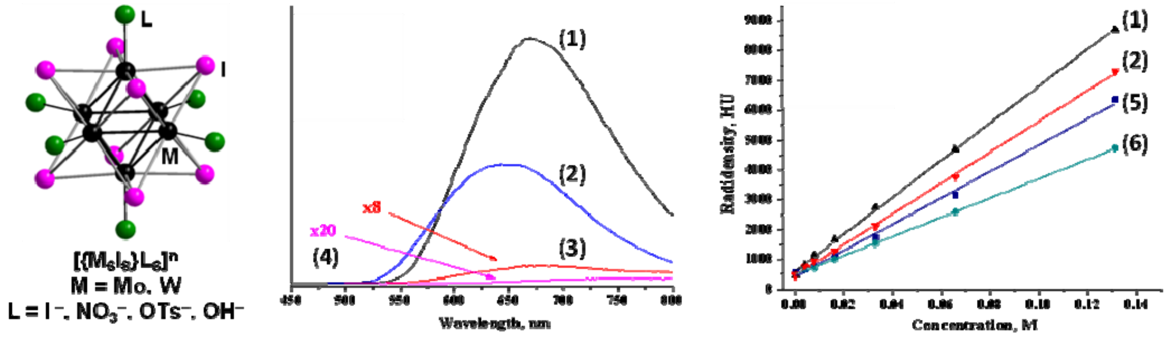
The octahedral iodide cluster complexes with formula $[\{M_6I_8\}L_6]^{2-}$ (M = Mo, W; L = organic or inorganic ligands) have a high potential for biomedical applications, due to they possess high quantum yields, high efficiency in generating of singlet oxygen [1]. The potential of octahedral molybdenum cluster complex $(Bu_4N)_2[\{Mo_6I_8\}(OOC\text{-}1\text{-}adamantane)_6]$ for X-ray excited optical luminescence and X-ray induced photodynamic therapy (PDT) was recently revealed [2]. But $\{W_6I_8\}^{2+}$ cluster complexes are generally far less studied, despite the recent data that suggests these complexes can also be highly luminescent. In addition, the octahedral clusters based on heavier metals should have a significant advantage of increased photoelectric absorption and scatter for X-ray excitation. Therefore we have obtained the octahedral tungsten complexes: $(Bu_4N)_2[\{W_6I_8\}I_6]$ (**1**) and new complexes $(Bu_4N)_2[\{W_6I_8\}(NO_3)_6]$ (**2**), $(Bu_4N)_2[\{W_6I_8\}(OTs)_6]$ (**3**) (OTs– is p-toluenesulfonate), $[\{W_6I_8\}(OH)_4(H_2O)_2]\cdot 6H_2O$ (**4**) and compared their optical and X-ray excited optical luminescence properties with those of the corresponding molybdenum analogues: $(Bu_4N)_2[\{Mo_6I_8\}I_6]$ (**5**), $(Bu_4N)_2[\{Mo_6I_8\}(NO_3)_6]$ (**6**), $(Bu_4N)_2[\{Mo_6I_8\}(OTs)_6]$ (**7**) and $[\{Mo_6I_8\}(OH)_4(H_2O)_2]\cdot 2H_2O$ (**8**). The detected photodegradation for the compound (**2**) is discussed.



(a) (b) (c)

The general structure of cluster anions in compounds **1**–**8** (a); corrected and normalized X-ray induced luminescence spectra for tungsten complexes (b); the dependence of radiodensity of **1**, **2**, **5** and **6** in DMSO solution in Hounsfield unit scale *vs.* concentration (c).

[1] A. Solovieva, Y. Vorotnikov, K.Trifonova, *J. Mater. Chem. B* **2016,** *4*, 4839-4846.
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This work was supported by the Russian Science Foundation [grant number 16-34-00542]

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COORDINATION POLYMERS BASED ON BITOPIC 1,3-BIS(1,2,4-TRIAZOL-1-YL)ALKANES AND TEREPHTHALATE ANIONS

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Coordination compounds of transition metals containing flexible azole-based bitopic ligands are intensively studied. These compounds can find many applications in different areas such as gas separation, sensitive materials, emitting devices etc.

In the present work, zinc and cadmium coordination polymers based on 1,3-bis(1,2,4-triazol-1-yl)alkanes (L) (methane-btrm, propane-btrp, hexane-btrh) and terephthalate anions (bdc^{2-}) were synthesized. Syntheses were carried out in solvothe1rmal conditions at temperatures of 90-110 °C in dimethylformamide (DMF). A series of new metal organic frameworks were obtained and their crystal structures were revealed by the X-ray diffraction method. The structural features of synthesized coordination polymers were discussed. The experiments showed that varying the experiment conditions we can obtain 3D polymers of two different compositions [Zn(bdc)(L)]·nDMF and $[Zn_3(bdc)_3(L)]$·nDMF. Polymers of the first type form interpenetrated net, while second type polymers do not form – mainly because of bulk rigid $\{Zn_3(bdc)_3\}$ units formation. The coordination compounds [Zn(btrm)(bdc)]·nDMF and [Zn(btrp)(bdc)]·nDMF form the 3D framework, while [Zn(btrh)(bdc)]·nDMF containing longer ligand forms only layered polymer. The terephtalate anions coordinated to the zinc atoms form zigzag chains similar to those in [Zn(btrp)(bdc)]·nDMF, but btrh ligands bind Zn^{2+} cations not in a chain, but in pairs, that prevents the formation of a three-dimensional structure. Comparing the synthesized cadmium complexes with btrp to the zinc analogues we were also able to obtain only 2D polymer [Cd(bdc)(btrp)]·nDMF. Due to short Cd-Cd distance between chains the conformation of btrp ligand is significantly distorted.

Synthesized compounds were studied by thermal analysis methods in inert and oxidizing atmospheres. The luminescent properties of coordination polymer [Zn(btrp)(bdc)]·1.5DMF were studied and the quantum yields were evaluated. Further we performed activation of synthesized 3D polymer by removing guest molecules. Activation was achieved by the exchange of DMF molecules for easily removable CH_2Cl_2 and drying under vacuum. A series of guest-impregnated coordination polymers were prepared by treatment of activated compounds with a number of organic solvents (o-xylene, p-xylene, benzene, aniline, toluene, nitrobenzene) and their luminescent properties were investigated.

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DEVELOPMENT OF SYNTHETIC METHOD FOR PREPARATION OF HETEROCYCLE-BASED BIS (PHOSPHINE OXIDES)

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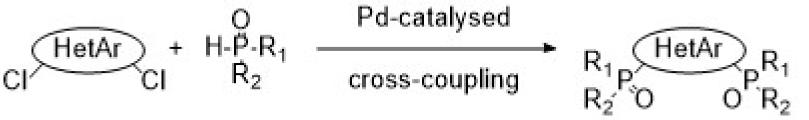
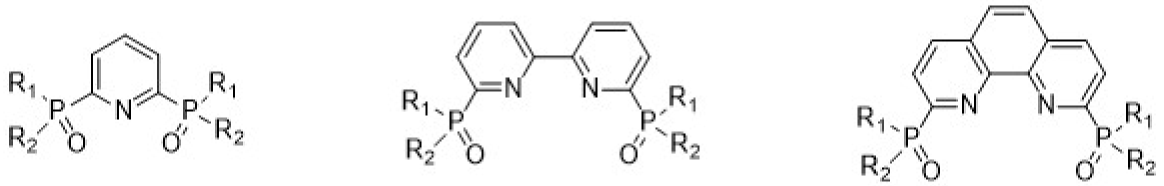
Bis (phosphine oxide)-based chelating ligands attract attention from the point of view their hydrolytic, thermal and oxidative stability. N,O-polydentate hard-and-soft heterocyclic compounds can play the role of extractants by binding of f-block elements ions. These chelating agents also have interesting photophysical and magnetic properties.

We report a method for the preparation of tetradentate chelating ligands by one-step Pd-catalysed cross-coupling between heteroaryl chlorides and secondary phosphine oxides.

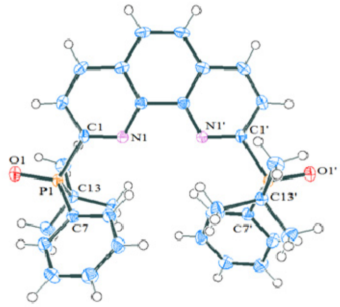


1,10-phenanthroline, 2,2'-bipyridine and pyridine were used as heterocyclic frameworks. Their chloro-substituted derivatives were prepared according to known procedures or supplied by commercial sources. Bis (phosphine oxide)-based ligands were obtained in gram-scale with high yield. All products were determined by NMR, IR and HRMS.



R_1=R_2=Ph; R_1=Ph, R_2=t-Bu; R_1=R_2=Cy

Tert-butyl(phenyl)phosphine oxides were obtained as mixtures of diastereomers (ca. 1:1) for all three heterocycles. Properties of 2,2'-bipyridine and pyridine derivatives are very similar and their separation in pure form is difficult and was not carried out. In contrast, one diastereomer obtained from 2,9-dichloro-1,10-phenanthroline was isolated. The X-ray analysis revealed that this diastereomer has *trans*-configuration. The phosphorous atoms are near tetrahedral, both P=O groups occupies anti-conformation relative to the heterocycle ring. The P-O bond length is 1.485(1) Å – the typical distance for aromatic phosphine oxide compounds. The P1-C7 bond length are 1.808(2) Å while corresponding value for P1-C13 are much longer 1.835(2) Å. The significant elongation of the P-C bond length observed for bulky substituted phosphine oxides.



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MECHANISMS OF CARBON-CARBON TRIPLE BOND ACTIVATION BY NEW GERMYLENES BEARING N_2BGe RINGS

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Studies of germylenes have formed an attractive and quickly developing area of coordination chemistry. The stabilization of Ge(II) metal centres within more or less strained four-membered rings has been well-documented in numerous researches. In contrast to amidinates and guanidinates which have been extensively studied, the investigations of germylenes incorporated into the N_2BGe rings are significantly less developed. Recently new digermylene (**1**, Fig.1) has been successfully synthesized [1]. In the present work **1** has been found to react with various alkynes with a facile formation of substituted 1,2-digermacyclobut-3-enes (**4**). To provide insights into the plausible reaction mechanism DFT modeling at the M062X/DGDZVP level has been undertaken within the framework of PCM (C_6H_6 solvent). According to NMR studies there is an equilibrium between dimeric and monomeric forms of the **1** germylene in solution. Therefore, several pathways of dimethylacetylene addition have been analysed. Corresponding elementary reactions have been characterized by changes of thermodynamic functions and activation energies. To search transition states the QST3 method has been applied. Our calculations predict the addition via monogermylenes **2** to be the preferable pathway both thermodynamically and kinetically (E_a = 15.7 kcal/mol). At the same time, the formation of the expected three-membered germirene ring appears to be unfavourable (E_a = 24.7 kcal/mol). Changes in the nature of the Ge-Ge interactions in key intermediates have been analysed using natural bond orbitals (NBO), bonding critical point properties (QTAIM computations) and the electron localization function (ELF) topology.

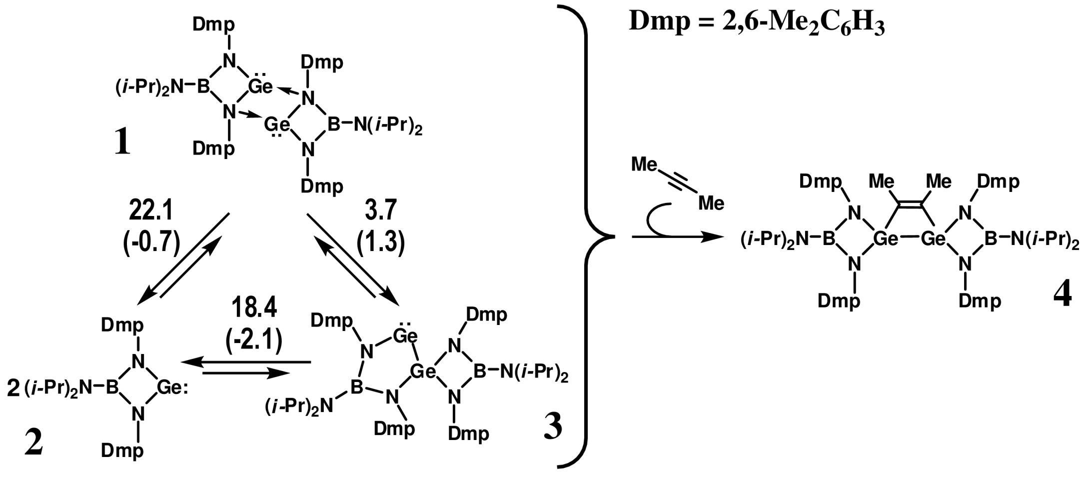

Fig.1. Equilibriums between germylenes in solution and formation of **4** by alkyne addition. The calculated changes of the electronic and free Gibbs (in parentheses) energies are given in kcal/mol.

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Acknowledgements. This work was supported by the Russian Science Foundation (Project No. 17-73-20298).

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POLYBROMIDE AND MIXED-POLYHALIDE COMPLEXES OF BISMUTH(III): NEW FAMILY IN THE COORDINATION CHEMISTRY OF BISMUTH

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Coordination compounds with polyhalide ligands attract much interest in the last years. However, whereas there is a great diversity of compounds containing polyiodide moieties, the number of corresponding polybromide complexes is extremely limited. Only few examples of polybromide complexes of Cu, Au, Pt, Sb and W are known to date. In this contribution, we present our recent advances in the chemistry of Bi(III) polybromides and so-called mixed-polyhalides bismuth-containing complexes in particular.

Reactions of $[BiBr_6]^{3-}$ and different organic nitrogen-containing cations, conducted in water-HBr solutions in presence of Br_2, generally result in the formation of polybromide structures, because the "inclusion" of Br_2 molecules into the structure takes place [1]. In our work, we discovered six structural types of polybromides (which were characterized by XRD and other methods). They differ from each other by the structure of bismuth-bromide fragments (Fig. 1), their nuclearity (from discrete units to polymer chains) and the $\{Br_2\}$/Bi ratio that was found to be from 0.5 to 3 [1],[2]. All these complexes show high thermal stability: release of Br_2 occurs only above 150°C. In the case of type **1** the reactivity as a relatively selective bromination agent towards different substituted alkenes was investigated [3].
Experiments similar to the described above, but conducted in HBr-I_2-water or HCl-Br_2-water solutions, result in new mixed halide compounds whose structures are similar to the but contain different metal-coordinating and bridging halogens, Br/I_2 and Cl/Br_2, respectively.

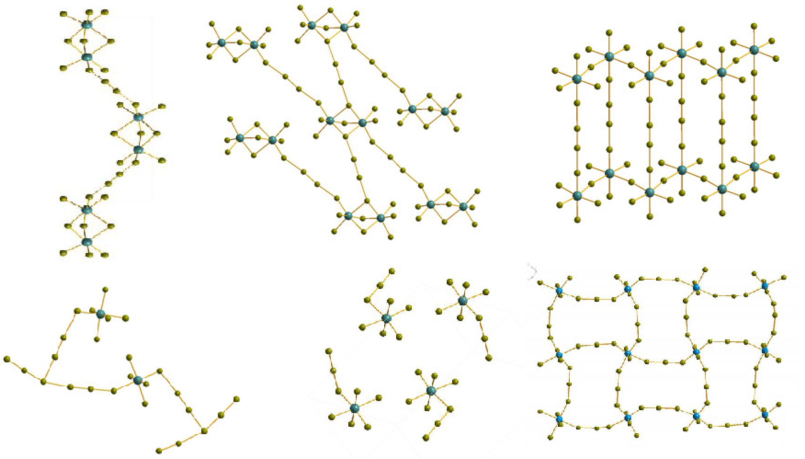

Figure 1. Types of Bi(III) polybromides: type 1 (top left), type 2 (top middle), type 3 (top right), type 4 (bottom left), type 5 (bottom middle), type 6 (bottom right)

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[2] S. A. Adonin, I. D. Gorokh, D. G. Samsonenko, et al, *Chem. Comm.*, **2016**, 52, 5061-5063
[3] S. A. Adonin, D. S. Perekalin, I. D. Gorokh, et al, *RSC Adv.*, **2016**, 6, 62011-62013

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COORDINATION COMPOUNDS OF CHLORIDES AND BROMIDES OF RARE EARTH ELEMENTS WITH DIAMINOTETRAPHOSPHONIC ACIDS

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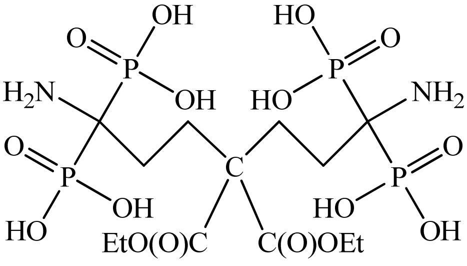
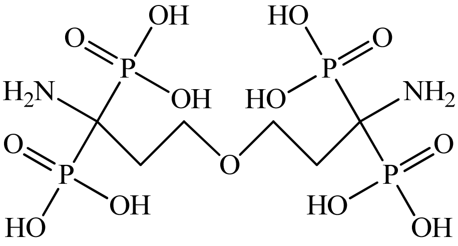
Modern osteotropic radiopharmaceuticals are on a large scale water-soluble coordination compounds of radiometals cations with organic ligands. The latter should ensure fast and efficient radionuclide binding and its selective accumulation in bone tissues. Promising ligands for diagnostic and therapeutic osteotropic radiopharmaceuticals are phosphonic, aminophosphonic, oxydiphosphonic, and aminodiphosphonic acids [1, 2].

In the present work for the first time synthesized and investigated coordination compounds of chlorides and bromides of rare earth elements ($La^{3+,}$ Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Yb^{3+}, Gd^{3+}, Er^{3+}) with diaminotetraphosphonic acids (L^1и L^2).



L^1



L^2

Synthesis of coordination compounds was carried out by mixing aqueous solutions of chlorides and bromides of rare earth elements with these ligands in a molar ratio of 1:1. In the course of the reaction of complexation was observed by the formation of a gel-like mass over time, turning into precipitation, painted in the color of rare-earth ion. The composition of obtained compounds were determined on the basis of elemental analysis, IR spectroscopy, thermal analysis (thermogravimetric analysis and differential scanning calorimetry). As a result of performed investigations it was found that the formed complexes are of composition 1:1. It is proved that the coordination of the lanthanide ion through the oxygen atoms of phosphonic residues. For the first time obtained a complete picture of the thermal decomposition of these compounds.

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COMPLEXES OF Cu(II) WITH TETRAZOLE AND TRIAZINE DERIVATIVES: SYNTHESIS, CHARACTERIZATION AND CYTOTOXICITY STUDIES

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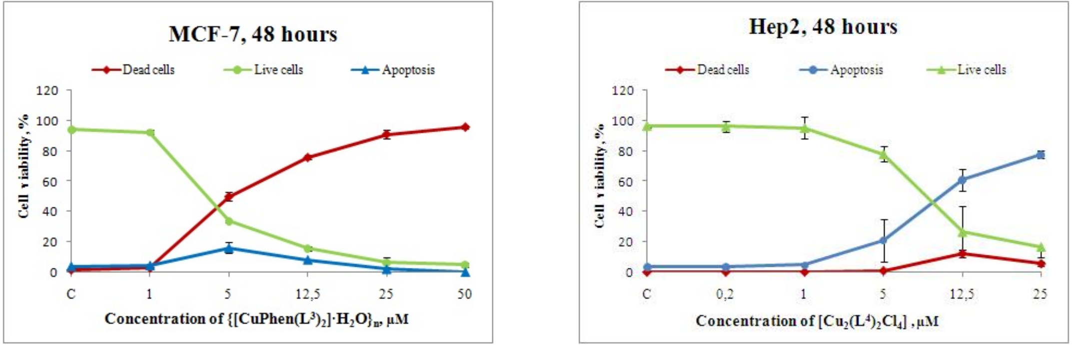
Nowadays physiologically active substances based on inorganic, organometallic and coordination compounds are widely used in medicine as drugs. Because of the increasing incidence of cancer, search for new anticancer drugs and study of their toxicity against different tumour cultures is an important aim. Moreover, coordination compounds usually show higher antitumor activity than initial organic ligands. Cisplatin is regarded as one of the most effective anticancer drugs, but severe toxicities and drug resistance phenomena limit its clinical use. Among non-Pt compounds, copper complexes are potentially attractive as anticancer agents, because complexes of endogenous metals may be less toxic than Pt compounds.

At the present work the biologically active ligands such as 5-phenyl-1H-tetrazole (HL^1), 1,3,3,5-tetrakis(tetrazole-5-yl)pentane (H_4L^2), 5-methyl-1H-tetrazole (HL^3), 2,2′-bipyridine (bipy), 1,10-phenantroline (Phen), and 6-phenyl-3-(pyridine-2-yl)-1,2,4-triazine (L^4) have been used for the synthesis of copper(II) complexes. All of the complexes were characterized by various spectral and physical methods: elemental analysis, powder diffraction and IR-spectroscopy. The molecular and crystal structures some of the complexes have been obtained using single-crystal X-ray diffraction analysis.

The cytotoxic activity of copper(II) complexes have been investigated on Hep2 (laryngeal cancer) and MCF-7 (human breast adenocarcinoma) cancer cells. Cytotoxicity has also been investigated for the initial ligands and metal salts, which did not show cell death in different tumor cultures. Cell viability has been evaluated by means of IN Cell Analyzer 2200 by Hoechst/PI staining. The 48-h incubation of MCF-7 cells with $\{[CuPhen(L^3)_2]\cdot H_2O\}_n$ (5 μM) was the most efficient and initiated cell death at a level 50 % (Fig.a). Exposure of Hep2 cells to the 12,5 μM concentration of $[Cu_2(L^4)_2Cl_4]$ for 48 h resulted in a cytotoxic effect inducing death of 12 % cells and apoptosis of 61% of cells (Fig. b).



a b

The cytotoxic activity of $\{[CuPhen(L^3)_2]\cdot H_2O\}_n$ (a) and $[Cu_2(L^4)_2Cl_4]$ (b)

Acknowledgements: The reported study was funded by RFBR (projects Nos. 16-33-00929, 16-53-00047).

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SOD-LIKE ACTIVITY OF CYCLOAMINOMETHYL DERIVATIVES OF DIHYDROXYBENZENES AND THEIR ZINC(II) COMPLEXES

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It is known that active oxygen forms (superoxide, hydrogen peroxide, singlet oxygen and hydroxyl radical) which are generated in phagolisosome and are involved in bactericide mechanisms can produce an antimicrobial effect. But some microorganisms, being active producers of extracellular superoxide themselves, are able to prevent their action [1]. Superoxide dismutases (SOD) are oxidoreductases catalyzing transformation of superoxide into hydrogen peroxide and oxygen. SOD are demanded as pharmaceuticals, but the use of native SOD in medicine is limited by their thermolability, low ability to penetrate cells and others [2]. Many of the limiting factors could be overcome by developing synthetic, low-molecular-weight mimics of the SOD enzyme and by using a direct method to measure the SOD-like activity of these complexes. Besides, it was found that Zn(II)-containing low-molecular analogues of Cu,Zn-SOD can interfere in the mechanism of inactivation of active oxygen forms of fungi and some bacteria and exhibit antimicrobial activity through competition with the native SOD [3]. Thus there are facts suggesting that redox-active metal complexes with antioxidants as ligands possess antimicrobial activity together with the SOD-like one.

Redox-active cycloaminomethyl derivatives of 1,2-dihydroxybenzene and 1,3-dihydroxybenzene as well as their Zn(II) complexes have been synthesized. It was found potentiometrically that complexes with the ratio M:L = 1:2 were formed in solution, their overall stability constants were equal to $4.0 \cdot 10^{14}$–$1.0 \cdot 10^{17}$. The Zn(II) complexes were shown to be amorphous, neutral, and stable up to 120 °C. Their coordination core is a tetrahedral chromophore $[ZnO_2N_2]$, the phenolic ligands being coordinated in monoanionic form (phenolate).

Using non-enzymatic method of superoxide generation employing alkaline DMSO assay [4], the SOD-like activity (IC_{50}) of the ligands and their complexes was determined. The derivatives of 1,2-dihydroxybenzene (IC_{50}=1.1–15.6 $\mu mol \cdot l^{-1}$) and 1,3-dihydroxybenzene (IC_{50}>100 $\mu mol \cdot l^{-1}$) were found to be substantially different in their inhibiting action. Complexation of the compounds with Zn(II) ions has generally no noticeable influence on their ability to neutralize superoxide, which suggests the ligand-centered redox interaction of Zn(II) complexes with the latter. Thus, the high SOD-like activity of the derivatives of 1,2-dihydroxybenzene and their Zn(II) complexes allows one to consider them as the most promising hit-compounds to produce new effective antioxidants – traps for superoxide.

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27th International Chugaev Conference on Coordination Chemistry
4th Conference-School for Young Researchers “Physicochemical Methods in Coordination Chemistry”
October 2-6, 2017, N. Novgorod, Russia

THE INFLUENCE OF STRUCTURAL MODIFICATIONS IN BIS-*O*-IMINOSEMIQUINONATO TRANSITION METAL (Cu, Ni, Co, Fe, Mn) COMPLEXES ON SPECTRAL PECULIARITIES AND MAGNETISM

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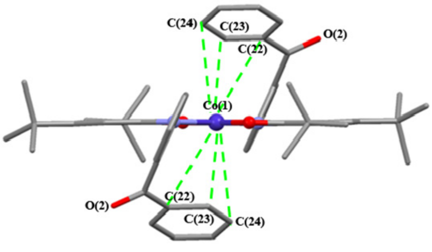
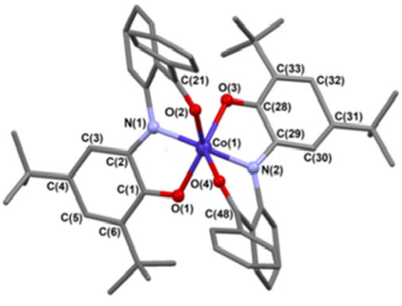
The wide range of sterically hindered *o*-aminophenols featuring the potentially coordinating groups (-C(O)OMe, -C(O)Ph, -OMe, , -C(O)OH, etc.) in the N-aryl fragment was synthesized. The reaction between the foregoing ligands and transition metals halides/acetylacetonates (ratio 2:1) in the course of the two-step synthesis produces the tetracoordinated bis-*o*-iminosemiquinonato derivatives as well as pentacoordinated species augmented by a chlorine substituent. All compounds were isolated in the individual state and characterized by X-ray analysis, EI-MS, IR, EPR, UV-Vis/NIR and Mössbauer spectroscopy. The variable-temperature magnetic susceptibility measurements were carried out in the range 2-300K. The electrochemical behaviour was investigated by cyclic voltammetry. TD-DFT calculations are also performed.



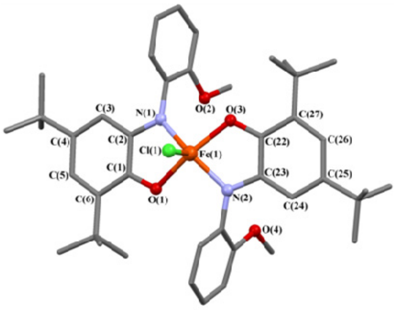
Molecular structure of complex (1)

The complexes on the base of *o*-aminophenol with benzoyl functions possess a square-planar geometry and the supplementary non-bonded interactions between the phenyl rings of -C(O)Ph groups and low spin metal ions: Co(**1**), Cu, Ni. The high residual paramagnetism was detected for Ni(II) derivative. The Cu(II) and Co(II) compounds exhibit an S = 1/2 ground state due to a strong antiferromagnetic coupling “ligand-ligand”.



Molecular structure of complex (2)

It was shown that the ability of an incorporated functional groups to be coordinated on the metal center depends on the charge of entire compound: additional positive charge promotes the bonding interaction (*complex 2*), but the reduction decreases the ligand denticity. Such structural modifications produced the turn from low to high spin state for Ni(II) compound. Notably the phenomenon of temperature dependent spin crossover (S = 3/2 → S = 5/2) is established for Fe(III) complex (**3**) which based on *o*-aminophenol with –OMe groups, however the such behaviour for Mn(III) analogue is impossible. Aminophenol with -C(O)OH functions demonstrates the tridentate character in hexacoordinated Fe(III) compound. Structural, spectro-and electrochemical features and magnetism of aforesaid and other metal complexes will be comprehensively discussed in the report.



Molecular structure of complex (3)

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SYNTHESIS, STRUCTURE AND PROPERTIES OF COMPLEXES BASED ON THE TRIS(2-HYDROXYETHYL)AMINE, BIOGENIC METALS AND CARBOXYLIC ACIDS

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Chelate compounds of tris(2-hydroxyethyl)amine (TEA) are widely known as atranes and are characterized by a unique tricyclic structure and biological activity of broad spectrum. Atranes are metalatranes (silatranes, germatranes,etc.), protatranes (tris(2-hudroxyethyl)ammonium salts of protic acids) and complexes of TEA with metal salts.

With the purpose of obtaining new biologically active compounds with atrane structure, coordination compounds of TEA, biogenic metals (Cu(II), Zn(II), Co(II)) and biologically active carboxylic acids (benzoic, salicylic, cinnamic and succinic) were synthesized. Binuclear, mixed-ligand complex $[Zn(TEA)(C_6H_5COO)_3]$ was obtained by the interaction of TEA with zinc benzoate in methanol [1]. In the complex, one zinc atom is six-coordinated by nitrogen and three oxygen atoms of tetradentate triethanolamine (TEA) and two oxygen atoms of two different benzoate ligands, forming the distorted octahedron of the $ZnNO_5$ type. The second zinc atom is five-coordinated, forming the distorted trigonal bipyramid. Two zinc atoms are bridged by two carboxylate groups of two benzoate ligands and one oxygen atom of the deprotonated hydroxyethyl group of TEA.

Cationic complexes of Co(II), Cu(II), TEA and succinic (Suc), cinnamic (Cin), salicylic (Sal) acids were synthesized and characterized. The central metal atom is coordinated by nitrogen and two oxygen atoms of each TEA molecule, thus forming the MN_2O_4 octahedron. The equilibrium geometry of the $[M(TEA)_2]^{2+}$ cations have been optimized at the B3LYP/cc-pVDZ level. Complex $[Co_2(N(CH_2CH_2OH)_3)_2(NO_3)_2(Suc)]$ was prepared by the interaction of two cationic Co (II) complexes of TEA.

Two binuclear Cu(II) complexes – $[Cu_2(TEA)_2(Sal)_2](H_2O)$ and $[Cu_2(TEA)_2(Cin)_2](H_2O)$ were obtained by the interaction of TEA with Cu (II) salicylate or cinnamate in the water. The crystal structure of complexes consists of the dimeric binuclear complex and one water molecule. Each copper atom is coordinated by nitrogen atom and three oxygen atoms of TEA as well as by one oxygen atom of salicylate (cinnamate) ligand.
All obtained coordination compounds of TEA have been characterized by single-crystal X-ray diffraction, IR spectroscopy, quantum-chemical methods, elemental analysis, and complex thermal analysis.

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Acknowledgements Scientific researchers were performed at the "Centre for Optical and Laser Materials Research", "Chemical Analysis and Materials Research Centre", "Centre for X-ray Diffraction Studies" of Research park of St. Petersburg State University. The work was supported by the Grant of FASIE (No 10280GU (16.06.2016).

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LUMINESCENCE OF ARYLPYRAZOLECARBOXYLATES OF LANTHANIDES

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Lanthanide aromatic carboxylates (LCCs) satisfy most of the requirements for modern luminescent materials, but their practical application is hampered by low solubility. In addition, for the use as emission layers of organic light-emitting diodes (OLED) transport of charge carriers is required, which LCCs usually do not possess.

Donor nitrogen heteroatom in α-position to the COO^-–group can saturate lanthanide coordination sphere, preventing the formation of coordination polymers, which are the main cause of low solubility. Nitrogen heteroatom in aromatic ring can also improve LCC electron mobility. At the same time, luminescent bioimaging requires high absorption that can be increased using aromatic substituent.

Thus, we selected lanthanide complexes with the anions of substituted pyrazolecarboxylic acids (Figure 1) as objects of investigation, and the goal of this work is the synthesis of lanthanide pyrazolecarboxylates and the study of the influence of substituent and methyl group position isomerism on their luminescent properties.

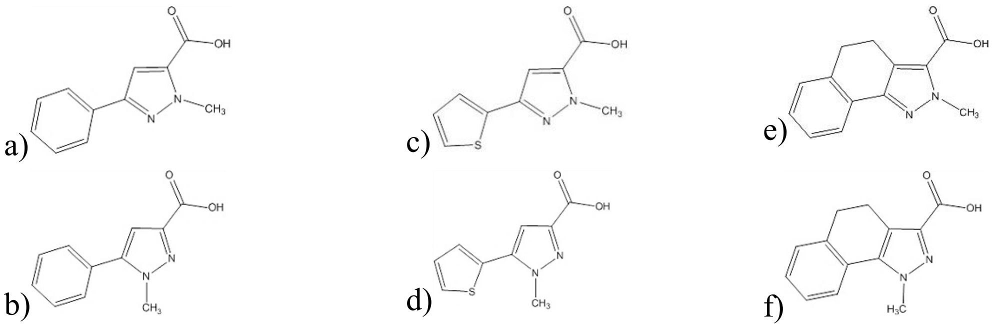

Figure 1 Pyrazolecarboxylic acids a) H(α-PhPA), b) H(β-PhPA) c) H(α-TPA), d) H(β-TPA), e) H(α-BIA), f) H(β-BIA)

All the complexes indeed possessed high solubility in organic solvents. The study of their luminescent properties revealed that $Tb(L)_3(H_2O)_x$ quantum yields (QY) strongly depended on the substituent, and complexes with α- and β-TPA demonstrated no luminescence, while other Tb CCs possessed QY up to 100%. On the contrary, Eu CC luminescence depended on the position of methyl group, and complexes with α-isomers had QY~0% due to the presence of the quenching ligand-to-metal charge transfer state. Complexes with β-isomers possessed high QY and low toxicity that allowed their successful use as biomarkers.

Bright emitting $Tb(L)_3(H_2O)_x$ were tested as OLED emission layers in the structure ITO/PEDOT:PSS/PVK/**EML**/TAZ/Al, where **EML** - emission layer. It was shown that CCs possessed high electron mobility, which in combination with high QY resulted in effective electroluminescence of diodes.

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SOME BARBITURATE COMPLEXES OF METALS: SYNTHESIS, STRUCTURE AND THERMAL PROPERTIES

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Synthesis of metal-organic complexes with polyfunctional ligands is one of the priority directions of modern chemistry [1]. Such ligands include barbituric (H_2ba), 1,3-diethyl-2-thiobarbituric (HDetba) acids and other H_2ba derivatives widely used in medicine [2]. We obtained, structurally characterized, studied the thermal and spectroscopic properties of 11 new metal complexes with H_2ba and HDetba: $[Co(H_2O)_4(Hba{-}O)_2]$ (**1**), $[Co(H_2O)_2(\mu_2\text{-}Hba\text{-}O,O)_2]_n$ (**2**), $[Co(\mu_3\text{-}Hba)_2\text{-}O,O',O'']_n$ (**3**), $[Mn(H_2O)_4(Detba\text{-}O)_2]\cdot H_2O$ (**4**), $Mn_3(H_2O)_{10}(\mu_2\text{-}Detba{-}O,O')_2(Detba{-}O)_4$ (**5**), $[Mn(H_2O)_2(\mu_2\text{-}Detba\text{-}O,O')_2]_n$ (**6**), $[Li(H_2O)_2(\mu_2\text{-}Hba\text{-}O,O')]_n$ (**7**), $[Ba(H_2O)_2(\mu_3\text{-}Hba{-}O,O,O')_2]_n$ (**8**), $[Co(H_2O)_6](Detba)_2\cdot 2H_2O$ (**9**), $[Ni(H_2O)_6](Detba)_2\cdot 2H_2O$ (**10**), $[Co_2(BuOH)_4(\mu_2\text{-}Detba\text{-}O,O')_2(\mu_2\text{-}Detba)_2\text{-}O]$ (**11**), BuOH – n-Butanol.

In **1**-**6**, barbiturate and 1,3-diethyl-2-thiobarbiturate ions are coordinated to the metal ion only through the O atoms, and the ions M^{2+} (где M=Co, Mn) have an octahedral environment. The structure of the synthesized complexes is compared with the literature data for other metal ions and related ligands. Depending on the synthesis conditions **1**-**6**, various hydrates are crystallized. The influence of a number of factors on the composition of crystalline hydrates is analyzed. In complex **7**, each ion Li^+ bound with two ions $\mu_2\text{-}Hba^-$ and two terminal water molecules forming tetrahedron. In **8** two ligands $\mu_3\text{-}Hba{-}O,O,O'$ and two water molecules are coordinated to Ba^{2+} forming tree-caped trigonal prism. Compounds **9** and **10** have a discrete structure, where each M^{2+} (M=Co, Ni) is bound to six water molecules forming octahedron, and the $Detba^-$ ions in the outer sphere connected to $M(H_2O)_6{}^{2+}$ via hydrogen bonds. The Co^{2+} ions in the dimer complex **11** are combined in pairs by the bridging ligands $\mu_2\text{-}Detba{-}O,O'$ and, in addition, each of them is connected with one terminal ion $Detba^-$ and two BuOH molecules to form a polyhedron in form of trigonal bipyramid. Structures are stabilized by intermolecular hydrogen bonds and $\pi{-}\pi$ interactions. IR spectra and thermal decomposition of compounds have been studied, which includes the steps of dehydration and oxidation of the organic ligand.

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ASYMMETRIC OXIDATIVE COUPLING OF *β*-NAPHTHOLS IN THE PRESENCE OF CHIRAL AMINOPYRIDINE IRON COMPLEXES

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Optically pure 1,1'-bi-2-naphthols (BINOLs) have been widely used as chiral auxiliaries and ligands for asymmetric transformations. These compounds have also been used for preparation of organic materials such as organic light-emitting devices and chiral sensors [1]. The most attractive strategy for the synthesis of optically pure BINOLs is direct oxidative coupling of *β*-naphthols in the presence of chiral catalysts [2].

In this work, a series of chiral iron(III) aminopyridine complexes have been prepared and tested in the aerobic oxidative coupling of substituted *β*-naphthols. Upon 1 mol. % catalyst loadings, these complexes ensure moderate to good yield of the corresponding BINOLs (up to 94 % within 24 h), having up to 55 % optical purity. The effect of ligand substitutents, counteranion, solvent, *β*-naphthol structure, and oxygen pressure on the catalytic performance has been systematically examined. Novel dinuclear antiferromagnetically coupled Fe^{II}/Fe^{III} complex (Figure 1) demonstrates the same performance as its mononuclear iron(II) counterpart. Plausible reaction mechanism is discussed.

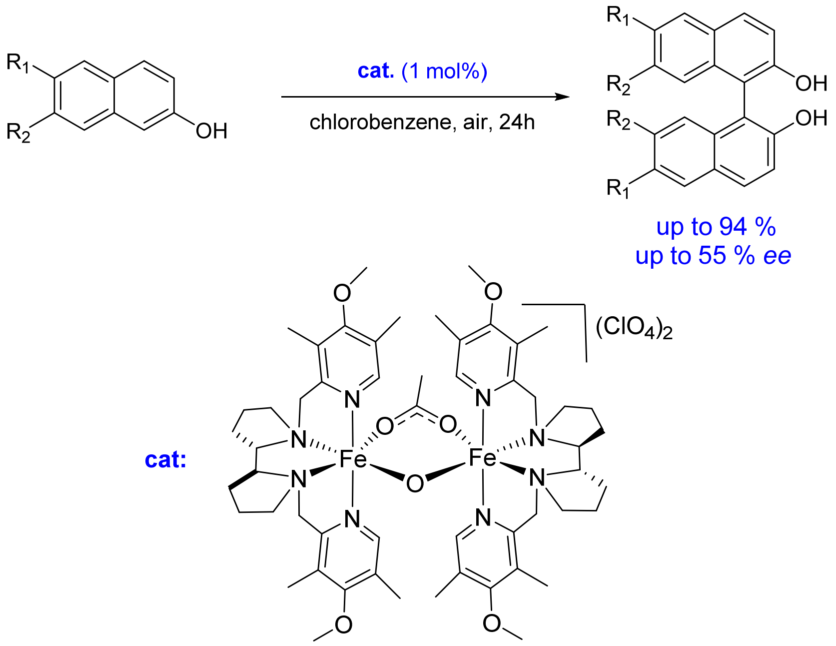

Figure 1. Asymmetric oxidative coupling of substituted 2-naphthols

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COMPLEX FORMATION THERMODYNAMICS, SUBSTITUTION REACTIONS KINETICS AND STEREOSELECTIVE EFFECTS IN THE COPPER(II) – OLIGOPEPTIDE – *L/D/DL*-HISTIDINE SYSTEMS

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Understanding the causes of the specificity and selectivity of processes in nature is one of the most important problems in modern science. This problem has direct relation to coordination chemistry, because many essential ferments contain metal ions. The investigations of homo- and heteroligand complex formation between biometals and bioligands are also important for the understanding of metal transport in living organisms.

In the present work the thermodynamics of complex formation, kinetics and mechanisms of ligand substitution reactions in the copper(II) – oligopeptide (glycylglycine, glycyl-*L*-tirosine, diglycylglycine, glycylglycyl-*L*-tirosine) – *L/D/DL*-histidine systems at 25 °C with the 1.0 M KNO_3 background have been investigated by pH-potentiometry, spectrophotometry, and stopped-flow methods with the usage of quantum chemistry and mathematical modelling.

Compositions, formation constants and individual absorption spectra of complex forms have been established by the processing of pH-potentiometric and spectrophotometric titrations results with STALABS computer program [1]. The data of complex formation in the copper(II) – *L/DL*-histidine systems were taken from the work [2]. Significant stereoselective effects have been detected for some heteroligand complexes with tyrosine-containing peptides and histidine.

Kinetics investigations of histidine substitution for oligopeptide ligands by stopped-flow method shown that in the pseudo-first order conditions kinetic dependences are exponential for the systems with glycylglycine, glycyl-*L*-tirosine, diglycylglycine, but in the case of glycylglycyl-*L*-tirosine substitution kinetic dependences are bi-exponential. Reactions rates increase with pH-value increasing. Significant stereoselective effects have been detected for the oligopeptides substitution by the anionic form of histidine.

The structures of some complex forms were optimized in the GAMESS program [3] using the DFT method at the CAM-B3LYP/TZVP level. Polarizable continuum model (C-PCM) was used to account for solvent effects. On the basis of experimental data and quantum-chemical calculations results stereoselective effects in the complex formation and ligand substitution have been interpreted.

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INVESTIGATING OF COORDINATION POLYHEDRONS DISTORTION OF SB(V) AND BI(V) IN ORGANOMETALLIC COMPOUNDS

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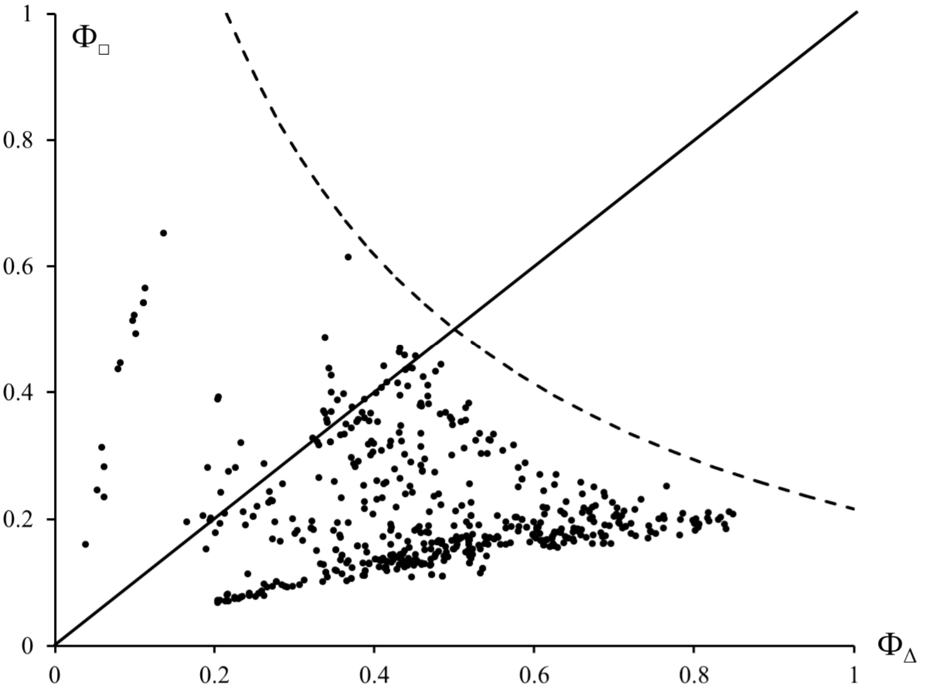
The degree of similarity Φ of two polyhedrons is introduced. Coordination polyhedrons were considered as sets of vectors. Every vector connects the centre of the coordination polyhedron and its vertex. The value Φ could be calculated as a function of vectors sets T and S for distorted ("real") and standard coordination polyhedrons, correspondingly. For equal polyhedrons $\Phi = 1$ and for not equal polyhedrons$0 \leq \Phi < 1$.

The experimental data comprising more than 500 polyhedrons of Sb(V) and Bi(V) for 428 crystal structures from CCDC [1] was considered. For every coordination polyhedron there were calculated two values of the degree of similarity for two standard polyhedrons: trigonal bipyramid and tetragonal pyramid (semioctahedron). There is $\Phi_\square$–Φ_Δ diagram presented on Fig. Dashed curve on Figure corresponds to Berry pseudorotation [2].



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PALLADIUM (II) COMPLEXES WITH TETRADENTATE SCHIFF BASES AND BIMETALLIC MOCVD PRECURSORS OBTAINED FROM THEM

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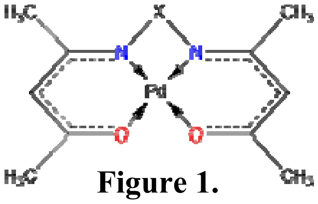

Figure 1.

Pd-Cu coatings are used primarily in hydrogen purification systems [1] and for catalysis of a number of chemical reactions [2]. The method of chemical vapor deposition using volatile complexes with organic ligands (MOCVD) is an effective one for obtaining such structures. It could be realized from two different precursors by co-deposition or from one individual bimetallic complex. Palladium (II) complexes with tetradentate Schiff bases (Fig. 1) is the new class of MOCVD precursors, which allows to expand the number of thermochemically characterized palladium (II) compounds to simplify the selection of effective precursor combinations in MOCVD processes. Also these chelates can be used for the synthesis of bimetallic complexes with copper (II) β-diketonates because of the presence of two free coordination positions of Cu atom. $Cu(hfac)_2$ (copper (II) 1,1,1,5,5,5-hexaflouroacetylacetonate) and $Cu(ptac)_2$ (copper (II) 1,1,1-triflouro-6,6-dimethyl-2,4-hexanedione) was used for obtaining of bimetallic Pd-Cu and model Cu-Cu binuclear complexes because of acceptor properties of CF_3 groups.

Thus, the aim of this work is investigation of dependence of thermal properties on the structure of the ligand of monometallic Pd(II) complexes, as well as to show the possibility of the formation of Pd-Cu bimetallic precursors. All the compounds were obtained for the first time with the exception of Pd(acacen) (acacen^{2-}– N,N'-(ethylene)-bis(acetylacetoniminato)). The monometallic chelates were characterized by elemental analysis, NMR and IR-spectroscopy. The structures of all the obtained monometallic complexes were investigated by single crystal X-ray diffraction. The influence of the ligand structure on compounds thermal properties (volatility and stability) was studied using thermogravimetric analysis and tensiometry (flow method). It was shown that the replacement of ethylene diimine bridge with propylene in Schiff base (letter "X" on Fig. 1) causes an increase in volatility of the complexes obtained. The temperature dependences of saturated vapour pressure were measured and the thermodynamic parameters of sublimation processes were calculated for all the monometallic palladium (II) chelates.

Pd-Cu bimetallic and model Cu-Cu binuclear complexes were characterized by elemental analysis and single crystal X-ray diffraction, thermal properties of $[Pd(acacen)Cu(hfac)_2]$, $[Cu(acacen)Cu(hfac)_2]$ in condensed phase were studied by thermogravimetry. Quantum-chemical calculation of geometric structure, formation energy, decomposition temperature and vibrational spectra of bimetallic complexes is performed.

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POLYNUCLEAR ZINC-LANTHANIDE COMPLEXES WITH ANIONS OF MONOCARBOXYLIC ACIDS AND N-DONOR HETEROCYCLIC LIGANDS: SYNTHESIS, STRUCTURE AND LUMINESCENCE PROPERTIES

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[b]*A.N. Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia*
[c]*P.N. Lebedev Physical Institute RAS, Moscow, Russia*
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Heterometallic lanthanide complexes with diamagnetic metal ions, such as Cu^{I}, Zn^{II}, Cd^{II} and others attract the attention of researchers, since the combination of the lanthanide ion and the fragment containing aromatic ligand and d-metal ion can enhance the photoluminescence of the 4*f*-ion due to large number of reasons. Thus, the aim of our investigation is the search of new photoactive heterometallic 3*d*-4*f* carboxylate compounds, the determination of spatial and electronic structures, towards to the enhancing of the luminescence activity and finding the "structure-property" correlation for the coordination compounds.

The trinuclear complex $[Zn_2Eu(NO_3)(Piv)_6(MeCN)_2]$ (Piv = $^{-}O_2CCMe_3$) (**1**) was obtained earlier in our laboratory. The terminal molecules of MeCN in this compound can be replaced by either mono- or bidentate chelating ligands [1]. To study the influence of the bulky substituent on the structural characteristics of such compounds and on their photophysical properties we used 2-phenylpyridine (2-PhPy) as a terminal ligand and synthesized the series of complexes $[Zn_2Ln(NO_3)(Piv)_6(2\text{-}PhPy)_2]$ (Ln = Y, La–Nd, Sm–Lu). The systematic series of molecular coordination compounds allowed us to implement the detailed X-ray diffraction research of the influence of the lanthanide ion radius on the structural features and packing of complexes.

The interaction of the 1-naphthylacetic acid (1-naphacH) and N-donor heterocyclic ligands on the compound **1** leads to reorganization of the metal core from trinuclear $\{Zn_2Ln\}$ of the original complex to tetranuclear $\{Zn_2Ln_2\}$. In this manner we obtained tetranuclear coordination compounds $[Zn_2Ln_2(NO_3)_2(1\text{-}naphac)_8(L)_2]$ (Ln = Eu, Tb; L = 4,4'-di-*tert*-butil-2,2'-bipyridyl). Using the excess of the pyridine (Py) in the similar reaction is leading to the formation of the complexes $[Zn_2Ln_2(1\text{-}naphac)_{10}(Py)_2]$ (Ln = Eu, Tb, Gd, Nd, Dy). This result is important, because we have shown recently that the presence of the nitrate anion in the coordination sphere of the heterometallic compounds causes a noticeable decrease in the quantum yield of photoluminescence [2]. The use of pyridine both as organic base and as N-donor ligand allows avoiding incorporation of nitrate anion in molecules of heterometallic complexes in spite of applying zinc and rare-earth elements nitrates as initial reagents.

The major attention in the presentation will be devoted to the synthetic methods, results of the X-ray diffraction analysis as well as photoluminescence properties of the obtained complexes.

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TWO-ELECTRON AND LIGAND-COOPERATED ADDITION REACTIONS ON GALLIUM DIIMINE COMPLEX

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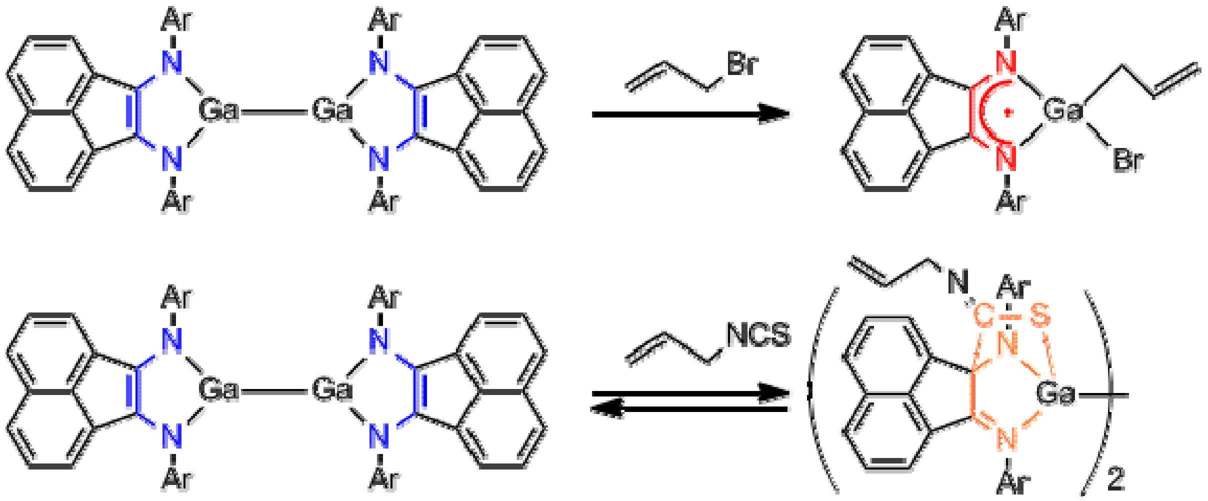
Oxidative addition in conjunction with its reverse reaction, reductive elimination, are important classes of reactions in organometallic chemistry. They are often steps of catalytic cycles. Complexes of transition metal undergo these transformations and have a widespread application as homogeneous catalysts. It would be environmentally-friendly and economically-beneficial to involve main group metals complexes into catalysis. We suggest the solution of the problem by complexation of main group metals with redox-active diimine 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian). Within the last decade this idea has been extensively elaborated [1]. In this work we report a series of reactions of digallane, (dpp-bian)Ga–Ga(dpp-bian), which give rise to two-electron addition products and ligand-cooperated addition products.



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ADDUCTS OF CARBENES WITH 3A,6A-DIAZA-1,4-DIPHOSPHAPENTALENE

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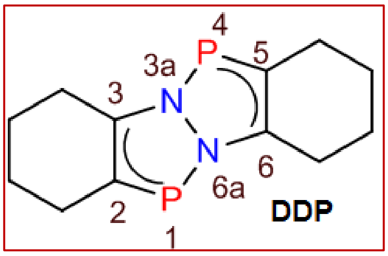
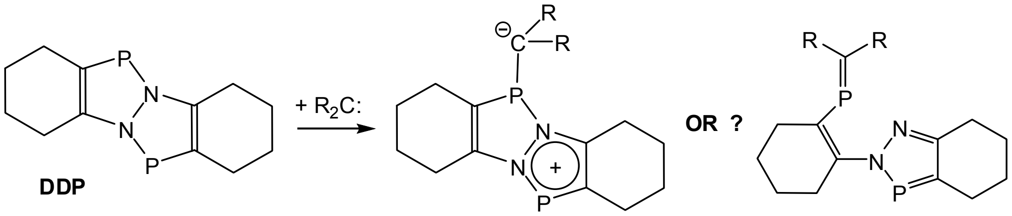
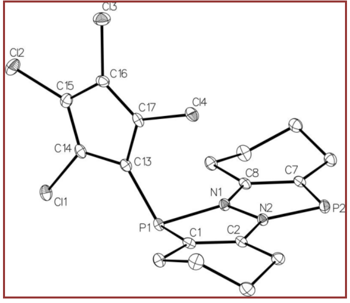


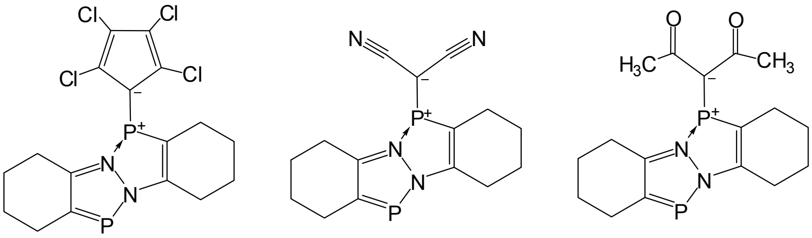
3a,6a-Diaza-1,4-diphosphapentalene (**DDP**) represents a novel type of heterophospholes, based on a planar hydrazine block containing two-coordinate and formally divalent phosphorus atom [1]. This compound is related to azaphospholes, but displays quite untypical chemical properties. It is known that azaphospholes do not interact with halocarbons, while tertiary phosphines give quaternary phosphonium salts. DDP reacts with halocarbons providing 1,1- or 1,4-addition products [2,3]. **P_1** atom in 1,1-adducts becomes hypervalent (trivalent, four-coordinate) with N¨P non-valent interaction. In this interactions DDP using its labile 10-π electron aromatic system, while lone pair at the phosphorus atom does not take part in reaction.

It’s well known, that phosphonium ylides, $R_3P{=}CR_2$, may be considered as a products of carbene addition to a tertiary phosphines. The phosphorus atom in this case becomes four coordinate pentavalent. However, complexation of carbenes with **DDP** is intriguing since that phosphorus atom must remains trivalent.



We have found 3a,6a-diaza-1,4-diphosphapentalene forms complexes with carbenoid particles (R_2C**:**) with different structure and type of bonding. Consideration the geometric and electronic structure of stable adducts allows to classify these compounds as a new class of organophosphorus compounds – phosphenium ylides or ylides of trivalent tri-coordinated phosphorus. The chemical behavior of these compounds is determined by the "superposition" or mixture of the properties of phosphonium ylides, phosphaalkenes and phosphenium ions.





Phosphenium ylides (ylides of trivalent phosphorus)

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TERBIUM-EUROPIUM BIMETALLIC COMPOUNDS AS THE BASE OF A LUMINESCENT THERMOMETER IN PHYSIOLOGICAL RANGE

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The creation of materials for luminescent bioimaging is an important problem, since this diagnostic method possesses high sensitivity and resolution. Moreover, as a development of this method, it is also possible to carry out non-contact temperature measurement in living tissues using "luminescent nanothermometers". To obtain such thermometers, various classes of materials (organic, inorganic or hybrid) are already used, where luminescence intensity or the excited state lifetime variation is used to measure temperature.

However, the materials available to date do not accurately measure the temperature in the physiological range (35-45 °C) due to insufficient sensitivity or low resolution of the detected bands. Terbium-europium bimetallic compounds may be meant to be an alternative to such materials since temperature is determined not by the value of the absolute signal intensity, but by the intensity ratio of the various bands. Therefore, the use of such compounds does not require special calibration due to "internal standard" effect. Furthermore, lanthanide compounds have long lifetimes of excited states and narrow emission bands that additionally simplifies the biomarker signal detection in the presence of autofluorescence.

To obtain materials with a high temperature sensitivity of luminescence thermometer in the temperature range from 35 to 45 °C two classes of materials were chosen: i) bimetallic fluoride nanoparticles $L@Tb_xEu_{1-x}F_3$, surface-modified with an organic ligand, which have already proved to be effective non-toxic biomarkers [1], and ii) bimetallic europium-terbium coordination compounds ($Tb_xEu_{1-x}L_3(H_2O)_2$). As ligands L, benzoate- (bz^-), o-phenoxybenzoate ($pobz^-$) and terephthalate anions (½tph^{2-}) were chosen.

Depending on the chosen ligand and the metals ratio, well-resolved terbium and europium luminescence bands of different ratio was observed in the luminescence spectra. The presence of various energy transfer processes (L→Tb, L→Eu, Tb→Eu) resulted in a temperature dependence of the intensity ratio of the luminescence bands of terbium and europium ions.

It was shown that for $L@Tb_xEu_{1-x}F_3$, the temperature dependence is determined by the Tb→Eu energy transfer efficiency of in the particle volume, and the ligand triplet state did not participate in temperature-dependent luminescence processes. At the same time, the inclusion of the triplet state in temperature-dependent energy transfer processes, for example, in case of $Tb_xEu_{1-x}(bz)_3(H_2O)_2$, allowed achieving a temperature sensitivity up to 50% $^oC^{-1}$, which is much higher than the maximum sensitivity value for bimetallic compounds of 16% $^oC^{-1}$ achieved to date.

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Acknowledgements This work was supported by RFBR (16-29-10755, 16-53-76018 and 17-32-80050) and President's grant MK-2810.2017.3.

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SYNTHESIS, CHARACTERISATION AND BIOLOGICAL ACTIVITY OF ZINC(II) CHLORIDE COMPLEX WITH CAFFEINE

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It has been found [1, 2] that zinc(II) mixed-ligand complexes may be considered as promising alternatives to platinum(II) complexes in order to overcome their toxicity. Bioactivity of zinc-containing compounds and caffeine (1,3,7-trimethylpurine-2,6-dione, $C_8H_{10}N_4O_2$ - caf) is discussed in [3, 4]. Description of synthesis and structure for $[Zn(H_2O)_6][Zn(C_8H_{10}N_4O_2)Cl_3]_2\cdot 2H_2O$ (**1**) is given in [5] but its bioactivity was unknown. That is why the aim of the present work consists in the synthesis and cytotoxicity studies for (**1**).

The complex has been prepared in aqueous solution by a reaction of zinc(II) chloride dihydrate with caffeine taken in the molar ratio $ZnCl_2$:caf = (1-3):1. The complex obtained: $[Zn(caf)(H_2O)Cl_2]$ (**2**) – has been identified and studied by a number of methods (chemical analysis, powder and single crystal X-ray diffraction, IR-spectroscopy and thermal analysis).

Compound (**2**) is a molecular complex with inner coordination sphere consisting of zinc(II) cation, water molecule, two chloride ions and caffeine molecule. Tetrahedral particles are connected by intermolecular H-bonds involving coordinated water molecules and oxygen atoms of caffeine molecules from the inner coordination sphere of the neighboring species.

The results of cytotoxicity studies using the DPSC (postnatal dental pulp stem cells) and breast cancer MCF-7 cells demonstrate the dose-dependent effect, the cytotoxicity of (**2**) being higher with respect to cancer cells in comparison with the normal ones (the minimal survivability is around 20% at the concentration of $1\cdot10^{-4}$ mol/L).

Possible equilibria between (**1**) and (**2**) are considered and discussed.

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SYNTHETIC CAPABILITIES OF CATALYSTS BASED ON NICKEL COMPLEXES WITH DIAZABUTADIENE LIGANDS

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Nowadays nickel compounds are of particular interest because they can be used as more practical analogues of expensive platinum and palladium catalysts. It should be noted that for the nickel catalytic chemistry a successful choice of the ligand plays a crucial role, and this field of homogeneous catalysis expanded significantly due to investigations in this important direction. Lately, N-containing ligands attract considerable attention because they are nontoxic, highly available and can be easily separated from the reaction products in contrast to the traditionally used phospine ligands.

Among various N-containing ligands the substituted diazabutadienes can be considered as the most promising ones. First, they are very convenient for investigation focused on influence of the sterical factors of the ligands on activity of the respective nickel complexes due to easy synthesis of the ligands from inexpensive starting materials. Secondly, the nickel complexes based on such ligands showed high activity towards reactions with aryl halides. Earlier, we have shown that the nickel compounds bearing diazabutadiene ligands can be used for synthesis of biaryls via homocoupling of aryl halides [1] as well as benzophenones or benzhydroles via reaction of aryl halides with aromatic aldehydes [2].

In this work, we investigated in detail reactions between aryl halides and different organic substrates, such as RCN, ArOR, AlkX, where X – halogen etc., catalyzed by the above-mentioned nickel complexes. Thus, influence of such factors as solvent nature, reaction temperature, nickel source, loading and nature of the reducing agent on the product yield was studied in detail, and also some insight into the reaction mechanism was achieved.

As a result it has been demonstrated that the use of the catalytic systems under consideration allowed to obtain successfully many important organic products of different structures, such as imines, ketones, amines etc.

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KINETIC INVESTIGATION OF THE REACTION OF ARYL HALIDES WITH ORGANIC NITRILES CATALYZED BY NICKEL COMPLEXES

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Due to some features of nickel, catalysts including this metal can be used in the reactions that are challenge for palladium compounds. In particular, it was established [1] that nickel catalysts bearing phosphine ligands are highly active in reaction of organic nitriles with aryl iodides. Also, it was shown [2] that more available and less expensive aryl bromides and chlorides can be used in this reaction, if the nickel compounds bearing N-containing ligands are taken as catalysts.

The primary product of such catalytic reaction between suitable organic nitrile and aryl halide is the respective imine which can be further converted into the corresponding ketone or amine depending on post-treatment protocol and reagent used. Thus, the reaction under discussion can be considered as convenient and practical method for synthesis of various biologically active compounds with ketone and amine functions. Kinetic study of this catalytic reaction can give valuable information about its mechanism and, therefore, predict its possible scope and limitations.

In this work, kinetics of the nickel-catalyzed reaction between organic nitriles and aryl halides at different temperatures was studied in detail. Additionally, possible side reactions, such as dehalogenation and homocoupling of aryl halide as well as side condensation of the substrates, were considered. Finally, we studied influence of solvent and the reducing agent as well as different additives on performance of the catalytic reaction.

Given the obtained results several important conclusions about mechanism of the nickel-catalyzed reaction between organic nitriles and aryl halides were made.

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NEW METHOD OF SYNTHESIS OF BORONATED IMINES

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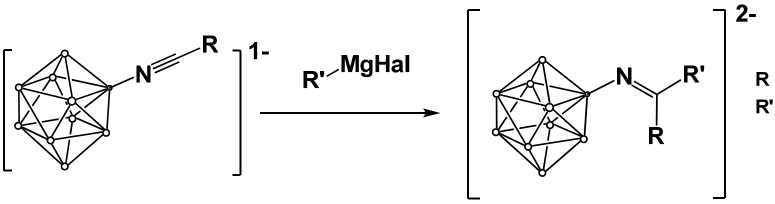
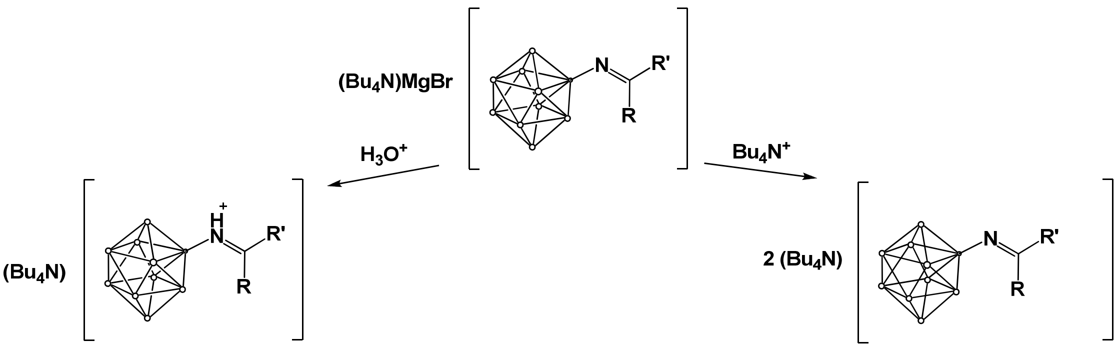
The interaction between nitrilium derivatives $[2\text{-}B_{10}H_9NCR]^-$ and organomagnesium compounds proceeds at room temperature in anhydrous ether solvent (THF, 2Me-THF) for 30-40 min. Imine-type products $[2\text{-}B_{10}H_9NCRR']^-$ are formed (Fig. 1).



R = CH_3, C_2H_5, $C(CH_3)_3$, C_6H_5
R' = C_2H_5, C_6H_5, 1-$C_{10}H_7$

Imino-*closo*-decaborate can be isolated in protonated or free form, depending on the method of isolation of the final product. Thus, when the reaction mixture is treated with an aqueous solution of hydrochloric acid, closo-decaborate derivatives with an imine exo-polyhedral group are formed. The interaction with an additional equivalent (Bu_4N) Br in an anhydrous medium leads to imino-clozo-decaborate (Fig. 2).



All obtained imino-*closo*-decaborate were characterized by physicochemical methods of analysis. On the basis of ^{11}B NMR spectra data for the resulting compounds, one can determine the substitution degree and the type of formed regioisomer (equatorial or apical substitution in the cluster). The spectrum of the anion $[2\text{-}B_{10}H_9NCRR']^-$ exhibits the following pattern: a signal of atom B (2) in the substituted position of the integrated intensity I = 1 in range of -12.7 ... -13.8 ppm and two signals of apical boron atoms in range of 1.6 ... 0.5 ppm [B (10), I = 1] and 0.1 ... -1.2 ppm [B (1), I = 1].

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OXYGEN PERMEABLE PHOTOLUMINESCENT MATERIALS BASED ON ORGANIC MATRICES AND OCTAHEDRAL MOLYBDENUM CLUSTERS

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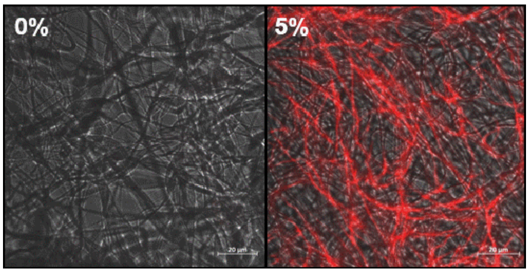

Molybdenum octahedral halide cluster complexes with general formula [$\{Mo_6X_8\}L_6$] (X = Cl, Br or I, L – apical ligand organic or inorganic nature) are interesting due to their high luminescent properties, namely quantum yields (up to 0.8) and lifetimes (up to several microseconds). One of the main way of quenching the luminescence is the interaction with triplet form of oxygen with formation of the singlet one. Such property allows us to use clusters in a lot of fields, namely oxygen sensors, or agents for bioimaging or photodynamic therapy. This work is aimed at obtaining oxygen sensitive materials for different applications.

Fluorinated polymer (copolymer of chlorotrifluoroethylene and 1,1-difluoroethylene, F-32) is oxygen permeable and capable to be stable at the temperature up to 180°C, in concentrated alkali or acid solutions. F-32 is also soluble in esters like ethyl acetate or butyl acetate. To form homogeneous material it was necessary to find ester-soluble clusters. It was experimentally noticed that clusters with fluorinated acid residue as apical ligands are soluble in esters and the longer carbon residue the higher solubility. In the framework of the work, the cluster complex $(Bu_4N)_2[\{Mo_6I_8\}(OOC(CF_2)_6CF_3)_6]$ was first time obtained. Compounds purity was confirmed by a number of modern analysis (^{19}F NMR, elemental analysis EDAX and mass-spectroscopy). The luminescence spectra were also recorded and the quantum yields were calculated. The data obtained are one of the highest for the molybdenum clusters. It was also confirmed that the cluster complex is well soluble in esters. So the materials with different concentrations of $(Bu_4N)_2[\{Mo_6I_8\}(OOC(CF_2)_6CF_3)_6]$ were obtained by dissolving of the cluster and the polymer in butyl acetate followed by drying at room temperature. Solubility of both components allowed obtaining materials of different morphology, *i.e.* films, fibers, and nano-sized particles. The morphology of the obtained materials was studied with scanning and transmission electron microscopy. Fibers were studied by the confocal microscopy (Fig.). By the luminescence we showed response of luminescence intensity and the presence of oxygen. Such response is reproducible and constant for a number of cycles. Material is fit to Stern-Folmer equation and calculated K_{sv} is 0.0725. Also, primary biological tests were made, which show the antibacterial activity of the materials due to the oxygen permeation of polymer and singlet oxygen formation of cluster complex.

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METAL–ORGANIC FRAMEWORK MIL-101 AS A NANOCARRIER FOR PHOTOACTIVE HEXAMOLYBDENUM CLUSTERS

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Octahedral molybdenum cluster complexes with the general formula $[\{Mo_6X_8\}L_6]^{2-}$ (X – Cl, Br or I; L – an organic or inorganic ligand) are gaining a lot of attention these days due to a considerable degree to their outstanding luminescence properties. Indeed, these complexes demonstrate bright red/near-infrared emission, which is characterized by high quantum yields and microsecond lifetimes under ultraviolet and X-ray irradiation. Recently, the $[\{Mo_6I_8\}L_6]^{2-}$ cluster complexes were shown to demonstrate the record values of the photoluminescence quantum yields (up to ~0.8) and lifetimes (up to ~360 μs) among all known transition metal cluster complexes. Furthermore, the bright red/near-infrared luminescence produced by such cluster complexes is able to generate singlet oxygen that can be used, for example, in photodynamic cancer therapy. The high quantum yields and ability to generate singlet oxygen make molybdenum cluster complexes attractive for biological and medical applications as bioimaging and biolabeling agents as well.

Though octahedral molybdenum cluster complexes possess such intriguing properties, the majority of the known $\{Mo_6X_8\}^{4+}$-based cluster compounds are insoluble in water and/or potentially react with physiological environments. This circumstance doesn't allow them to be used in biological and medical applications. To overcome these difficulties such octahedral metal-cluster complexes could be introduced into specific biocompatible matrices that can prevent a chemical interaction with physiological media of these cluster complexes. In this work, MIL-101 was used as matrix. MIL-101 is metal-organic framework (MOF) with general formula $[Cr_3F(H_2O)_2O(BDC)_3]$ (BDC – 1,4-benzenedicarboxylic acid), which is a good candidate as storage matrix due to its outstanding stability and mesoporosity.

In this contribution, we report the preparation of new inclusion compounds combining a $\{Mo_6I_8\}^{4+}$-based cluster complex and the nanosized MIL-101 using two alternative approaches, namely the direct introduction of the hexamolybdenum cluster complex into MIL-101 and the introduction of the cluster complex into preliminary pyrazine-modified MIL-101 (the post-synthetic modification approach). All compounds obtained were characterized by a number of physico-chemical methods. Also biological properties were investigated. The MTT study revealed a low cytotoxicity of pristine chromium metal-organic framework and molybdenum cluster inclusion compounds both with and without pyrazine. Furthermore, photoinduced reactive oxygen species generation in living cells by the released from MIL-101 cluster complexes was established. Also, we have demonstrated the ability of such a type of materials to apply in photodynamic therapy.

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SYNTHESIS OF COMPOUNDS BASED ON $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, Te) CLUSTER ANIONS AND CATIONIC COMPLEXES OF RARE-EARTH METALS

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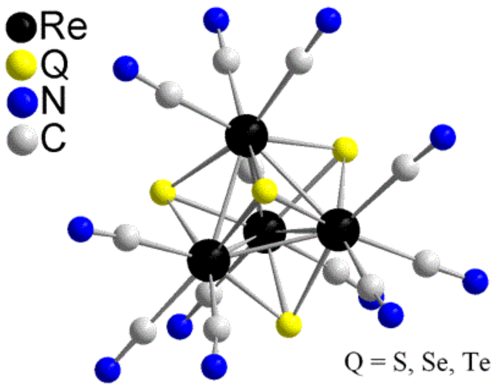

Design of self-assembled coordination polymers from pre-made building blocks which can be represented by large variety of metal ions/clusters and organic or inorganic linkers blocks is a facile route for rational generation of technological materials. Rhenium cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, Te) [1, 2] can be used as a building blocks due to large number of multidirectional accessible CN-groups and rigid geometry. The recent research has shown that rhenium chalcocyanide clusters anions $[Re_4Q_4(CN)_{12}]^{4-}$(Q = S, Se, Te) can be effectively used in reactions with transition metal cations for obtaining compounds with various geometry [3]. In our present work, we focused on the compounds, based on cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ and lanthanide complexes with 1,10-phenanthroline. 4*f* metal ions have large radii, high coordination numbers, and a wide variability of coordination environment as well the trivalent lanthanide ions also have useful physical properties as color-pure luminescence and large paramagnetism. Therefore, presence of rare-earth cations in the structure of compounds may cause magnetic and luminescence properties for resulting materials. It was shown that presence of organic ligand, particularly, 1,10-phenanthroline in the system $Ln^{3+}/[Re_4Q_4(CN)_{12}]^{4-}$ can influence on the structure and dimensionality of the resultant coordination polymer. Reactions between cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se or Te) and Ln^{3+} complex cations led to formation of compounds with ionic, oligomeric, chain-like or layered structures.

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SYNTHESIS AND PHYSICO-CHEMICAL PROPERTIES OF BINUCLEAR CLUSTER COMPLEXES OF VANADIUM AND NIOBIUM

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Binuclear sulphide clusters of the type $\{M_2(\mu\text{-}S_2)_2\}^{4+}$ (M = V, Nb) with a single direct M–M bond attract much attention due to the structural similarity of the $\{M_2(\mu\text{-}S_2)_2\}$ cluster core [1,2] and the $\{Fe_2S_2\}$ active center of the hydrogenase enzyme of bacteria of the genus *Clostridium*. However, the $\{M_2S_4\}$ complexes are stable in the solid state for months, unlike highly unstable in air bacterial enzymes, which makes them potential model systems for studying the work of bacterial hydrogenases and understanding the processes taking place in the active center of enzymes. Moreover heteroleptic complexes of formula $[Nb_2S_4(NCS)_6(R_2bpy)]^{2-}$ (R = H, C_9H_{19}, CO_2Me) containing bipyridine type ligands can act as optical limiters, with the nature of the bipy ligand exerting an influence on optical limiting merit [2]. $(Et_4N)_2[Nb_2S_4(NCS)_6(bpy)]$ coupled to TiO_2 P25 shows photocatalytic activity in hydrogen evolution reaction in the presence of 0.1 M Na_2S + 0.02 M Na_2SO_3 as sacrificial electron-donor [2].

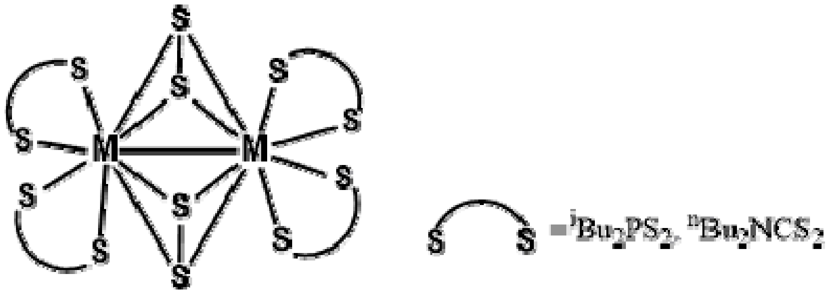

Fig. Schematic representation of $[M_2(\mu\text{-}S_2)_2(S\text{-}S)_4]$ molecules (M = V, Nb; S-S = $^iBu_2PS_2$, $^nBu_2NCS_2$)

In this work we report synthesis and detailed characterization of the series of complexes of general formula $[M_2(\mu\text{-}S_2)_2(S\text{-}S)_4]$ (M = V, Nb; S-S = $^iBu_2PS_2$, $^nBu_2NCS_2$) with chelate S-donor ligands (see figure). The characteristic feature of these complexes is that they demonstrate one or two steps of reversible one-electron oxidation process at mild potentials according to CV data. Chemical oxidation of $[M_2(\mu\text{-}S_2)_2L_4]$ using $(NO)BF_4$ allowed us to isolate and characterize $[M_2(\mu\text{-}S_2)_2L_4](BF_4)$ – products of one-electron oxidation. They are paramagnetic and their EPR spectra show fifteen and twenty lines of hyperfine splitting for V (I = 7/2 for ^{51}V) and Nb (I = 9/2 for ^{93}Nb) compounds, respectively, due to delocalization of the unpaired electron over two metal atoms.

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COORDINATION FEATURES OF THE FIRST BRD4(BD1) SELECTIVE INHIBITOR WITH BET-PROTEINS

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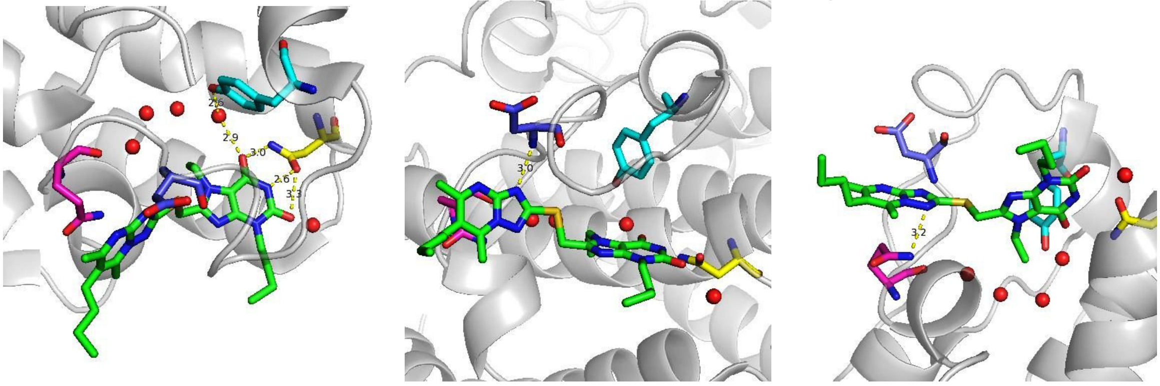
It is now well known that the coordination of BET-proteins with acetylated lysine residues of hystones plays an essential role in transcription of genes involving in cancer, that makes it a perspective target for anticancer therapy [1]. The last decade ligands, able to competitively coordinate with BET proteins, replacing acetylated lysine in its binding site, are actively developed. However, all of them have a common drawback: they coordinate with a similar affinity to all BETs due to a high level of similarity in binding sites of eight BET-members, that are presented by 4 isoforms (BRD2, BRD3, BRD4 and BRDT) and 2 domains (BD1 and BD2). The lack of selectivity may lead to potential side-effects in clinic.

In this study, key coordination features of the first known selective BET-inhibitors binding with BRD4(BD1) member of BET-family of proteins were investigated [2].



Three dimensional crystallographic structure of the ligand (green sticks) complexed with BRD4(BD1) obtained at 2.2 Å resolution showing the conserved N140 residue (yellow), Y97 residue (blue), D88 residue (violet), Q85 residue (purple) and five highly conserved water molecules (red spheres) located at the bottom of the cavity.

The crystal structure of the ligand in complex with BRD4(BD1) revealed the coordination with the protein by forming the canonical hydrogen bonds of N3,N7-dialkylated xanthine core with the conserved asparagines N140 and a water mediated hydrogen bond with Y97, that provide the pan-BET inhibition. Triazolo moiety allows the preferential inhibition of BET-BD1 domains forming a hydrogen bond with the conserved D88 residue. This BD1-conserved amino acid is replaced by larger residues such as arginine or lysine in the BD2 subfamily. Further condensation with pyrimidinyl moiety drives the corresponding triazolopyrimidinyl ligand to be selective toward BRD4(BD1) due to van der Waals interaction with the side chain of Q85. A steric clash prevents this interaction with the R54, its equivalent residue in BRDT(BD1), or the K present in the other BRDX(BD2) bromodomains. These key coordination features suggest a potential mechanism for the selectivity of BET bromodomains.

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SYNTHESIS AND REACTIVITY OF BIFUNCTIONAL DERIVATIVES OF *CLOSO*-DECABORATE ANION

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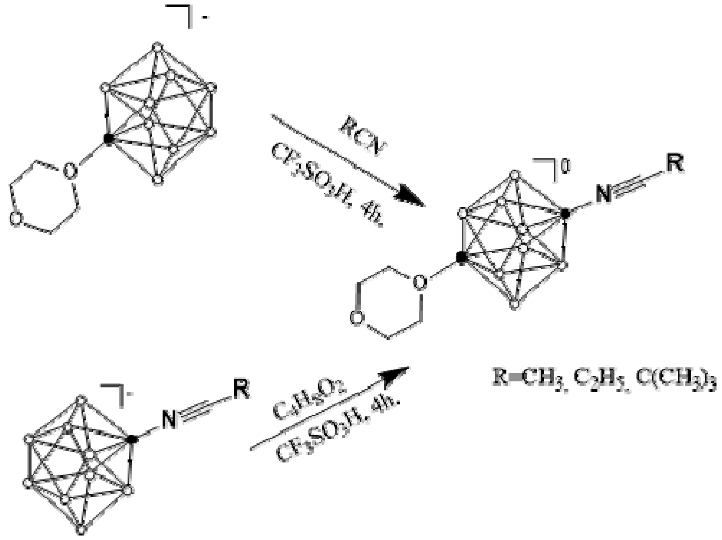
To date, a great number of *closo*-borate anion derivatives with *exo*-polyhedral boron-oxygen and boron-nitrogen bonds are well known. Among these compounds, oxonium and nitrilium derivatives of polyhedral boron hydrides are most studied. Firstly, this is connected with a variety of selective processes for preparing such compounds, and, secondly, with further modifications of introduced *exo*-polyhedral substituents.

The current research focuses on the development of approaches for the synthesis of bifunctional derivatives *closo*-decaborate anions with *exo*-polyhedral bonds B-O and B-N, based on the reaction of $[B_{10}H_{10}]^{2-}$ anions with organic nucleophiles in the presence of the CF_3SO_3H.

Initially, we observed interaction between $[B_{10}H_{10}]^{2-}$ anion and nucleophiles (ethers and nitriles) in the presence of one equivalents of triflic acid. Monosubstituted derivatives of *closo*-borate anion were formed. Than, interaction between monosubstituted derivatives of *closo*-borate anion and nucleophiles in the presence of electrophilic inducers were observed. Disubstituted derivatives of *closo*-borate anion anions with *exo*-polyhedral bonds B-O and B-N were formed. All obtained bifunctional derivatives were characterized by physicochemical methods of analysis.



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1′-PHTHALAZINYLHYDRAZONE OF ACETYLFERROCENE: STRUCTURE, PROPERTIES AND COMPLEXING ABILITY

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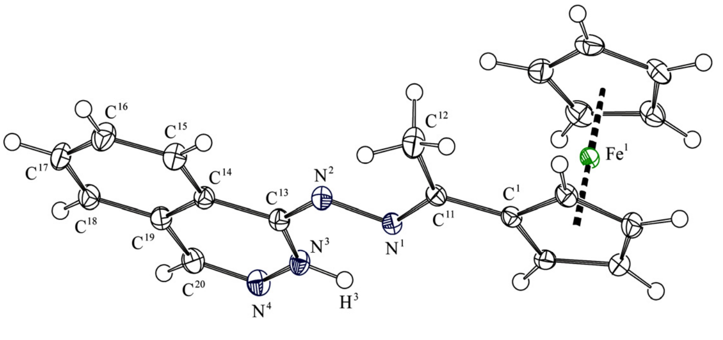
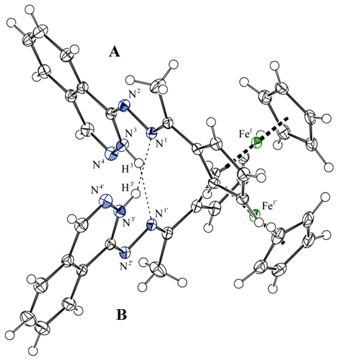
In continuation of studies on complexing properties of ferrocene-containing ligands we have synthesized and investigated 1′-phthalazinylhydrazone of acetylferrocene (**I**, HL). Compound **I** can exist in the form of two main tautomers: phthalazone **Ia** and hydrazone **Ib**. The IR and NMR spectral data of **I** suggest that compound exists in a phthalazone tautomeric form, which is also typical for other hydrazinophthalazine hydrazones. To prove this assumption we have performed quantum-chemical calculations of the electronic and spatial structure of tautomers at the density functional theory level (DFT/B3LYP/6-311G(*d*)) in the gas phase and in ethanol solution. The phthalazone form **Ia** is more stable than the hydrazone form **Ib**, and in ethanol the ΔE value decreases from 10.2 to 7.3 kcal/mol. The structure of compound **I** in the crystal was determined by XRD analysis. Compound **I** exists in the crystal in the phthalazone tautomeric form (see picture below). The unit cell contains two independent molecules, A and B, with close geometric parameters. In the crystal, the molecules A and B are linked by two intermolecular H-bonds and form dimers.





It should be noted that the results of quantum chemical simulation of the spatial structure of the phthalazone tautomer of compound **I** nicely agree with the XRD data. The best agreement with the experiment is observed for the geometry calculated in ethanol.

With Cu(II) and Ni(II) acetates, compound **I** forms complexes of the composition ML_2. IR spectroscopy data confirmed bidentate coordination of the ligand in deprotonated phthalazone form. Values of μ_{eff} at room temperature are 2.46 and 3.45 μB for Cu(II) and Ni(II) complexes, respectively. Such values are characteristic for tetrahedral complexes. It should be noted that the structure of the ligand excludes the possibility of formation of square-planar complexes due to steric hindrances.

Acknowledgements: This work was supported by an internal grant of SFedU No.213.01-07-2014/03PChVG.

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SYNTHESIS, STRUCTURE, OPTICAL AND ELECTROCHEMICAL PROPERTIES OF IRIDIUM (III) COMPLEXES WITH 2-ARYLBENZIMIDAZOLES AND VARIOUS β-DIKETONES

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Cyclometallated iridium(III) complexes possess intense phosphorescence and, therefore, are widely used as components of organic light-emitting diodes, catalysts for organic synthesis and sensors for oxygen.

In these Ir(III) complexes, ligands can be easily varied that affects immediately the optical properties of the complexes, including the absorption spectrum. In this regard, Ir(III) complexes are considered as photosensitizers (PS) for solar cells. For this reason, a number of requirements are imposed on the PS, including the presence of a ligand with an "anchor" group, a broad absorption spectrum, and high molar absorption coefficients in the visible region. Earlier in our laboratory we studied Ir(III) complexes with 2-aryl-1-phenyl-benzimidazoles and showed that compounds with these donor ligands can be used as PS. However, the complexes obtained had too high redox potentials and were positively charged. In order to lower the redox potentials, we chose β-diketones as the "anchor" ligands - derivatives of dibenzoylmethane (methyl 3-[3-oxo-3-(thiophen-2-yl) propanoyl] benzoate, 1-(3-methoxycarbonylphenyl)-3-phenylpropane-1,3-dione), which form neutral Ir(III) complexes.

The desired Ir(III) complexes ware synthesized in several steps. A dimeric intermediate complex was prepared from $IrCl_3 \cdot 3H_2O$ and appropriate 2-arylbenzimidazole. The reaction between the dimers and the "anchor" ligands resulted in the final complexes in moderate yields (60-70%).

As a result, two series of iridium (III) complexes with various electron-donor and acceptor substituents $[Ir(L)_2A]$, where L = 1-phenyl-2-(4-R-phenyl)benzimidazole (R = H, Cl, NO_2), 1-phenyl-2-(3,4-dimethoxyphenyl)benzimidazole, 2,5-diphenyloxazole, were prepared. All the ligands obtained were identified by ^1H and ^{13}C NMR spectroscopy. The final complexes were characterized by ^1H NMR, high resolution mass spectrometry (ESI-MS) and X-ray structural analysis.

The optical and electrochemical properties of the obtained series of Ir(III) complexes were studied. According to cyclic voltammetry, an increase in the electron-donor properties of substituents in 2-arylbenzimidazoles from -Cl to -OMe caused a decrease in redox potentials (Ir^{4+}/Ir^{3+}) of the complexes. The optical properties of the complexes vary nonmonotonically. An increase in the substituents electron-donor properties in 2-arylbenzimidazoles from -Cl to –OMe resulted in absorption maximum shifts to the long-wavelength region, but an even bathochromic shift of the absorption maximum was observed for the ligand with the acceptor NO_2-group. An analysis of both luminescence and absorption spectra disclosed absorption bands which lead to a transition to the triplet state.

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ELECTROCHEMICAL STUDY OF TRINUCLEAR PHENYLVINYLIDENE CLUSTERS CONTAINING RHENIUM, IRON, PLATINUM OR PALLADIUM

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Redox properties of trinuclear phenylvinylidene clusters $\mathrm{CpReFePt(\mu_3\text{-}C{=}CHPh)(CO)_5LL'}$ [L = CO, L' = $\mathrm{PPh_3}$ (**1**), $\mathrm{P(OPr\text{-}\mathit{i})_3}$ (**2**); L = L' = $\mathrm{P(OPr\text{-}\mathit{i})_3}$ (**3**)], $\mathrm{CpReFeM(\mu_3\text{-}C{=}CHPh)(CO)_5(P\text{-}P)}$ [M = **Pt**, P-P = dppe (**4**), dppp (**5**); M = **Pd**, P-P = dppe (**6**), dppp (**7**)] were studied by cyclic voltammetry, classical polarography and controlled potential electrolysis at platinum, glassed carbon and dropping mercury electrodes in acetonitrile. The clusters were investigated by IR and NMR spectroscopy. The molecular structures of the compounds **3, 6, 7** were established by X-ray diffraction analysis. Redox transformation schemes for the clusters **1-7** were proposed.

It was shown that one-electron oxidation of **1-7** leads to unstable radical cations studied by EPR spectroscopy:

$$\mathrm{CpReFeM(\mu_3\text{-}C{=}CHPh)(CO)_5(P\text{-}P)} \;-e^- \;\leftrightarrow\; \mathrm{CpReFeM(\mu_3\text{-}C{=}CHPh)(CO)_5(P\text{-}P)^{+\bullet}}$$

The radical cations formed at the first stage of the oxidation undergo subsequent transformations into binuclear **ReM** complexes and **Fe**-containing fragments:

$$\mathrm{CpReFeM(\mu_3\text{-}C{=}CHPh)(CO)_5(P\text{-}P)^{+\bullet}} \rightarrow \mathrm{CpReM(\mu\text{-}C{=}CHPh)(CO)_2(P\text{-}P)} + \mathrm{[Fe(CO)_3]^{+\bullet}}$$

Controlled potential electrolysis study revealed that the final oxidation products in case of the **ReFePt** clusters were the binuclear **RePt** complexes and the [**Fe**$\mathrm{(CO)_3]^{+\bullet}}$ fragment whereas in case of the **ReFePd** clusters were **Fe$_2$Pd** clusters and a mononuclear complex Cp(CO)$_2$**Re**=C=CHPh:

$$\begin{aligned}&\mathrm{CpReFeM(\mu_3\text{-}C{=}CHPh)(CO)_5(P\text{-}P)} + \mathrm{[Fe(CO)_3]^{+\bullet}} \rightarrow\\ &\quad\rightarrow \mathrm{[CpReFe_2(\mu_3\text{-}C{=}CHPh)(CO)_8]^{+\bullet}} + \mathrm{[Pd(P\text{-}P)]_{solv}}\end{aligned}$$

$$\begin{aligned}&\mathrm{CpReFeM(\mu_3\text{-}C{=}CHPh)(CO)_5(P\text{-}P)} + \mathrm{[CpReFe_2(\mu_3\text{-}C{=}CHPh)(CO)_8]^{+\bullet}} \rightarrow\\ &\quad\rightarrow \mathrm{2Cp(CO)_2Re{=}C{=}CHPh} + \mathrm{[(CO)_6Fe_2Pd(P\text{-}P)]^{+\bullet}}\end{aligned}$$

Thus, the redox transformations of the clusters with **ReFePt** (**1-5**) and **ReFePd** (**6, 7**) metal cores were established to proceed in different pathways, depending on whether the Pt or the Pd atom is presented in the metal core.

Acknowledgements - *This work was supported by RAS (Complex Program of Basic Research of the SB RAS №. II.2П/V.44-13, "Integration and Development") and Krasnoyarsk Region Science and Technology Support Fund (on participation of students, graduate students and young scientists in conferences, scientific events and internships)*

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Poster Presentations

CARBON NANOBEADS SYNTHESIS USING FERROCENE AS CATALYST

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Carbon nanomaterials have been developed since the discovery of the fullerene by Kroto in 1985 [1] and the carbon nanotubes by Iijima in 1991 [2]. These materials present unique properties and characteristics. Carbon nanobeads (CNBs) are one of the secondary products obtained in the synthesis of carbon nanotubes by chemical vapor deposition; in recent years this material has also focused the research interest. Carbon nanobeads are principally used due to its specific surface areas and conductivity. Their applications include catalyst carriers, lubricants, drug delivery vehicles and high capacity batteries. The aim of this research was the carbon nanobeads synthesis using ferrocene as catalyst by chemical vapor deposition.

The synthesis was carried out in quartz reactor (0.6 m length and 0.03 m diameter) using benzene as organic precursor and ferrocene as catalyst precursor [3]. The experiments were held for one hour at 760 °C temperature with 85 ml/min argon flow. Different samples were taken for the substrate and the inner part of reactor. Morphological analysis was performed separately for CNTs and nanobeads by Field Emission Scanning Electron Microscopy.

Carbon nanobeads were founded into clusters around 500 nm and their individual size was about 34 nm. The carbon nanotubes diameters were around 60 nm and their lengths above 30 μm. Energy dispersive spectroscopy analysis for nanoparticles showed a carbon content above 96%; the oxygen content vary for the CNTs that contain 2.97 % and the CNBs (3.07 %). Both materials contain iron, notwithstanding, the CNTs 0.96 % and the CNBs 0.01%. X-Ray Diffraction analysis and the Scherer and Bragg equation were used to determine crystallite size and interplanar distance. The interplanar distance (002) for nanobeads was 0.341 nm and 0.339 nm for the CNTs. The crystal size for CNBs was 14.096 nm and for the CNTs 12.517 nm. The analysis was performed for all diffraction peaks; thus, demonstrating that the major crystal size corresponds to the carbon nanobeads. The carbon nanobeads synthesis is feasible through chemical vapor deposition using ferrocene as catalyst.

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[2] S. Iijima, *Nature,* **1991**, *354(6348)*, 56-58.
[3] F. G Granados-Martínez, L. Domratcheva-Lvova, N. Flores-Ramírez, L. García-González, L. Zamora-Peredo and M. D. L. Mondragón-Sánchez, *Materials Research*, **2016**, *19*, 133-138.

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SYNTHESIS AND CRYSTAL STRUCTURES OF CADMIUM 1D COORDINATION POLYMERS WITH SCHIFF-BASE N,N'-TYPE LIGANDS

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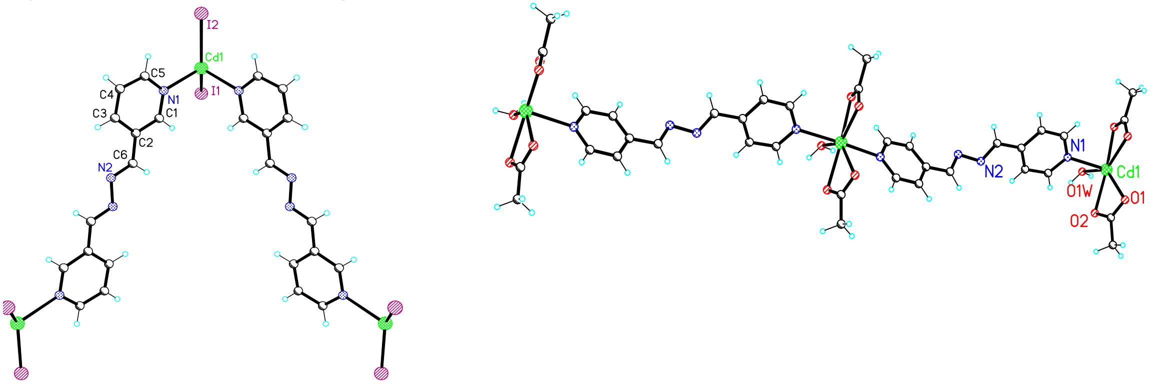
The rod-like bis-monodentate N,N'-type ligands, are a type of most widely used organic ligands in the field of supramolecular coordination chemistry because of their redox stability and easy modification. The infinite 1D chain structure is the simplest topology of coordination polymers, however, the complicated crystal packing modes of the 1D chains make their solid-state structures diversified thereof endow different potential applications. For instance, the 1D chains can stack in the crystal lattice in a parallel fashion which is the most common packing mode, but in many cases, the 1D chains were found to stack in a non-parallel fashion. In addition, if the 1D chains are not straightly linear, they can entangle with each other to form even complicated crystal structure [1].

We have long been interested in study of coordination polymers constructed from the ditopic rigid or flexible N,N'-type ligands which comprise the Py (pyridyl), terminal donor groups. We report a two 1D coordination polymers constructed from the rigid Schiff-base N,N'-type ligands (R–C=N–N=C–R) 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene (**N3Py**) and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (**N4Py**) namely $[Cd(3\text{-}bphz)I_2]_n$ (**1**) and $[Cd(4\text{-}bphz)(CH_3COO)_2(H_2O)]_n$ (**2**). The structures of compounds were determined using X-ray diffraction method (Fig.1).



$[Cd(3\text{-}bphz)I_2]_n$ (**1**)

$[Cd(4\text{-}bphz)(CH_3COO)_2(H_2O)]_n$ (**2**)

Fig.1. Molecular structures of compound **1** and **2.**

Single-crystal analysis reveals that complexe **1**, **2** crystallized in the orthorhombic crystal system. Complexe **1** display one-dimensional zig-zag chain structure, and the complex **2** display one-liniar chain structure. The node of compound **1** consists of a tetracoordinate Cd^{II} center bonded to two I–ligands and two 3-bphz ligands. In the second compound, the cadmium ion is heptacoordinated by two CH_3COO–ligands, two 4-bphz ligands and a water molecule.

[1] Qing Wanga, Bing Liangb, Jian-Yong Zhanga, Mei Pana, Bei-Sheng Kanga, and Cheng-Yong Su, Z. Anorg. Allg. Chem. 2007, 05, 2463-2469.

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27th International Chugaev Conference on Coordination Chemistry
4th Conference-School for Young Researchers "Physicochemical Methods in Coordination Chemistry"
October 2-6, 2017, N. Novgorod, Russia

COPPER(II) COORDINATION COMPOUNDS WITH *O*-VANILLIN SEMICARBAZONE: SYNTHESIS AND X-RAY DIFFRACTION STUDY

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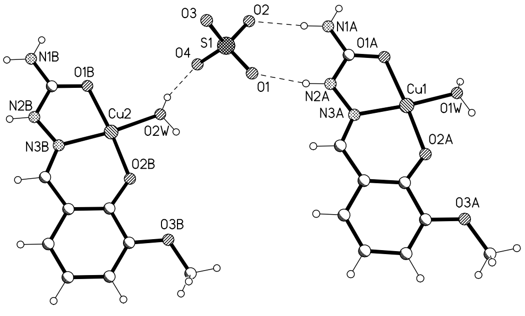
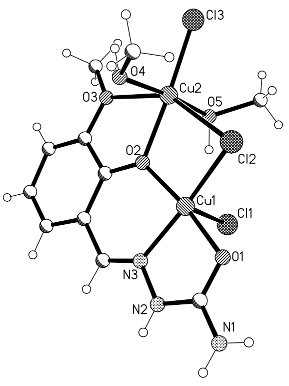
Semicarbazones present a wide range of biological activities, and their chemistry and pharmacological application have been extensively investigated. A series of publications report on biological activity of semicarbazones derived from aromatic and unsaturated carbonyl compounds. The biological properties of semicarbazones are often related to metal ion coordination and the metal complex can be more active than the free ligand. This work describes the preparation and structural characterization of two copper(II) complexes, mononuclear $[Cu(HL)(H_2O)]_2(SO_4)\cdot5.25H_2O$ (**1**) and binuclear $[Cu_2(HL)Cl_3(MeOH)_{1.5}(H_2O)_{0.5}]\cdot0.5MeOH\cdot0.5H_2O$ (**2**), where H_2L – *o*-vanillin semicarbazone.

Compound **1** was synthesized as a result of $CuSO_4\cdot5H_2O$ interaction with *o*-vanillin semicarbazone (H_2L) in 1:1 molar ratio in distilled water. Making the reaction with the use of $CuCl_2\cdot2H_2O$ in 2:1 molar ratio in methanol afforded binuclear complex **2**. In **1** the monodeprotonated ligand coordinates to copper ion in tridentate mode through the phenolic and carbonyl oxygen atoms, and azomethine nitrogen atom. One molecule of water, additionally coordinated to each Cu(II) ion, define the square planar geometry of the complex cation. The positive charge of each coordination cations is neutralized by dinegative sulphate anion in external sphere.



Molecular structure of $[Cu(HL)(H_2O)]_2(SO_4)$

In the crystal of compound **2**, there are actually two complex compounds with the formula $[Cu_2(HL)Cl_3(MeOH)_2]$ and $[Cu_2(HL)Cl_3(MeOH)(H_2O)]$ in a 1: 1 ratio. A molecule of monodeprotonated ligand is coordinated to two atoms of copper(II). The first atom of Cu(II) is bonded through the phenolic, hydrazinic nitrogen atom and carbonyl oxygen atom; the second is coordinated through oxygen atoms of hydroxy- and methoxy- groups. So, the ligand acts as a tridentate [O,N,O] donor to one metal centre and bidentate [O,O] donor to other metal with phenolic oxygen acting as a bridge. Three chlorine ions are coordinated differently: one Cl^- serves as bridge between two ions of Cu(II), and other two Cl^- ions are coordinated to each of Cu(II). It should be noted that the first metallic centre is five coordinated, while the other – six coordinated, due to the supplementary coordinated molecules of methanol and water. As a result, two coordination geometries are formed: distorted square pyramidal for Cu1 and octahedral for Cu2.



Molecular structure of $[Cu_2(HL)Cl_3(MeOH)_2]$

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OXIDATION COPPER PORPHYRIN BY BENZOYL PEROXIDE IN SOLUTION

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It is known that metalloporphyrins are unique coordination compounds. They are very effective catalysts of different processes, for example controlled ring-opening polymerization of various heterocyclic monomers [1]. So a great interest is the study of metalloporphyrin interaction with organic peroxides. In present work the oxidation of copper 5,10,15,20-tetra(4-methoxyphenyl)porphyrin by benzoyl peroxide in chloroform was studied using spectrophotometric method. It was found that in an excess of benzoyl peroxide, isoporphyrin is formed. Typical spectral changes are shown in Fig. 1.

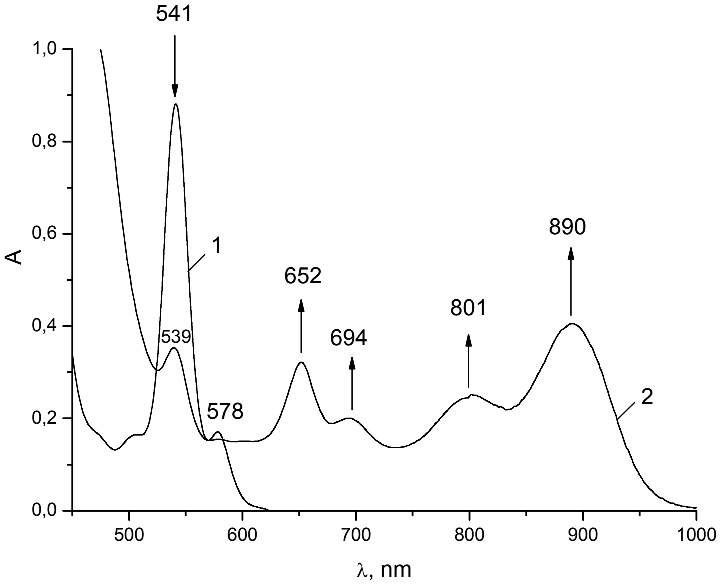

Fig. 1. Change of the electronic absorption spectra of CuTpMPP ($5{,}2\cdot10^{-5}$ mole/l) (1) in $CHCl_3$ during oxidation by benzoyl peroxide (0,021 mole/l) (2) at 25°C (τ = 3 h 20 min).

The rate constants of copper 5,10,15,20-tetra(4-methoxyphenyl)porphyrin oxidation by benzoyl peroxide were calculated. The reactivity of other metalloporphyrins with benzoyl peroxide was compared. The role of metal in these processes is shown.

[1] M. Glazkova, T. Ageeva, V. Alexandriyskiy, O. Koifman, *Macroheterocycles*, **2011,** *4(1)*, 22-25.

Acknowledgements - Work is carried out within the framework of the State task (project part), project №4.1929.2017/4.6

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PECULIARITIES OF IMIDAZOL-SUBSTITUTED PORPHYRINS COMPLEXATION WITH COBALT ACETATE

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Metallporphyrins are extremely interesting objects for the creation of supramolecular systems of diverse structure exhibiting unique photophysical, catalytic, sensory properties [1, 2]. Nitrogen-containing extraligands (pyridine, imidazole, pyrazole) form stable metallporphyrins extracomplexes. The introduction of imidazole, pyridyl fragments as peripheral substituents into the structure of tetrapyrrole macroheterocycles allows to obtain stable polymeric and oligomeric structures based on metallporphyrins. To construct coordination porphyrin-polymers, mono- and di-substituted tetrapyrrole macroheterocycles containing imidazole substituents in *meso*-positions at the periphery of a molecule have been synthesized. Oligometallporphyrins were isolated in addition to monomeric products after completion of complexation reaction of mono- and di-imidazolyl-porphyrins with cobalt acetate (Fig. 1).

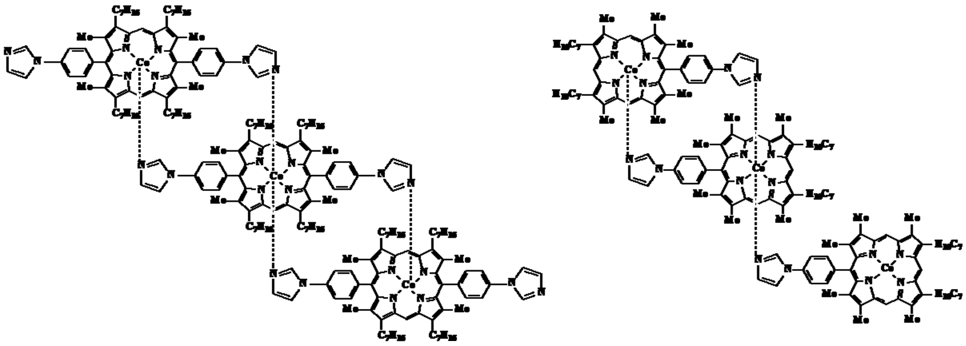

Fig.1. Oligomeric coordination-bound porphyrins metal complexes.

The formation of coordination-bound porphyrin-polymers was due to the extracoordination of the nitrogen atom of imidazole substituent in *meso*-position of a macrocycle with a central metal atom of the other macrocycle. These structures in contrast to the monomeric metalcomplexes lose solubility in many organic solvents. When pyridine is added to a coordination porphyrin-polymer, the destruction of the extracoordination of imidazole groups by cobalt to monomeric porphyrins metal complexes has been observed.

[1] F. Hajjaj, Z.S. Yoon, M.-C. Yoon, J. Park, A. Satake, D. Kim and Y. Kobuke, *J. AM. CHEM. SOC.*, **2006**, *128*, 4612-4623.
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OLEFIN METATHESIS CATALYSTS WITH FLUORINATED TRICYCLIC NHC-LIGANDS

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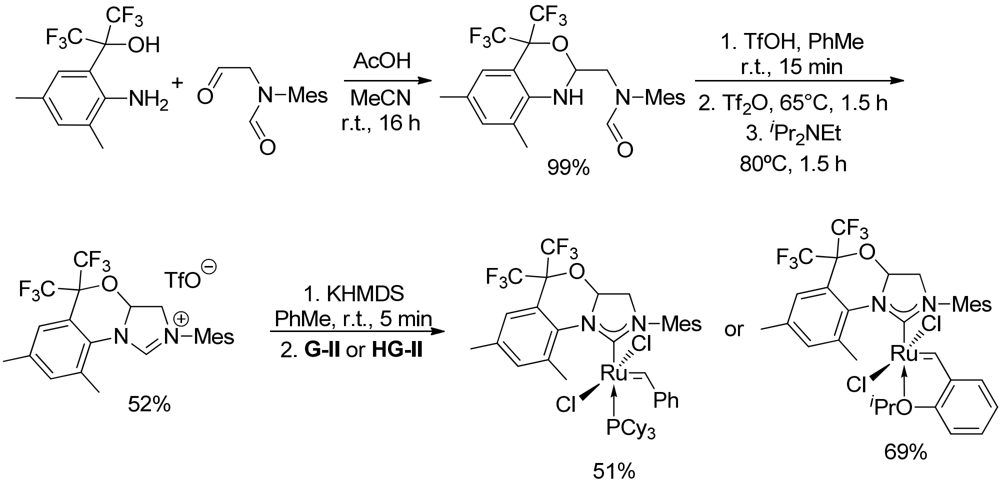
N-heterocyclic carbenes (NHC) are widely used as ligands in homogeneous metal catalysis. Among them, unsymmetrical NHCs attract a particular attention due to a unique possibility to perform a fine-tuning of their reactivity in different types of catalytic transformations. For instance, the incorporation of an additional anionic center on one of the nitrogen atom in vicinity of the carbenic center influences the catalyst stability, reactivity, and selectivity [1].

We have recently developed an efficient access to novel ruthenium carbene complexes bearing unsymmetrical NHC-ligands equipped with sterically demanding *ortho*-hexafluoroisopropoxy groups in one of the *N*-aryl substituents and demonstrated their successful utilization in ring-closing metathesis (RCM) and cross-metathesis (CM) reactions [2, 3]. Now we report on an efficient synthetic pathway to olefin metathesis catalysts containing fluorinated tricyclic oxazine-derived NHC ligands as well as a preliminary evaluation of their catalytic activity in RCM of unsaturated derivatives of malonic acid.



[1] S. Kress, S. Blechert, *Chem. Soc. Rev.*, **2012**, *41*, 4389-4408.

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[3] S.M. Masoud, M.A. Topchiy, A.S. Peregudov, T. Roisnel, P.H. Dixneuf, C. Bruneau and S.N. Osipov, *J. Fluor. Chem.*, **2017**, *200*, 66-76.

Acknowledgements
This work was financially supported by the Russian Scientific Foundation (grant RSF № 16-13-10364).

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FORMATION OF NICKEL(II) COMPLEXES WITH DI-,TRI- AND POLYAMINES IN WATER AND SODIUM POLYSTYRENESULFONATE SOLUTIONS

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Complexation of metal ions with water-soluble polymers underlies the modeling of interaction of metalcomplex with macromolecules, as well as polymer-enhanced ultrafiltration of industrial wastes. In such processes, polyethyleneimine (PEI), capable of forming strong complexes with transition metal ions in weakly acidic media, can be used. Addition of polyelectrolytes to metal complex solutions can also influence the equilibrium between complexes of various composition and charge. Thus in this work the complexation of nickel(II) ions with di-, tri- and polyamines in water and in solutions of water-soluble polymers of sodium polystyrene sulfonate (PSS) and polyvinylpyrrolidone (PVP) was studied using NMR-relaxation and spectrophotometry.

The nickel(II)ions were found to bind completely withPEIin solutions with pH >4. Comparison of the absorption spectra ofnickel(II) complexes with ethylenediamine (En) and diethylenetriamine (Dien)revealed two possible options for coordination of PEI to nickel(II) ions as a function of the pH of aqueous solutions: at pH 4-6 four amino nitrogens, as well as at pH>6additional two nitrogen atoms are coordinated per onemetal ion. The presence of six nitrogen atoms in the first coordination sphere of the PEI nickel complex in a neutral medium was confirmed by the NMR relaxation method according to the saturation curve.

Addition of the anionic polymer, PSS, as well as its mixtures with the non-ionic PVP polymer, do not affect the stability, spectral and relaxation characteristics of the all three Ni(II) complexes with En(M:L = 1:1, 1:2 and 1:3). Although this complexesdistinct in composition, they have the same charge+2 (as hasnickel aqua ions), thatprovides an equal interaction with the anionic polymer. Nevertheless, there is difference between Ni-En complexes in interaction with PSS. While $[NiEn]^{2+}$exists in polymer solution, the bis- and tris-complexes spontaneously prepicitatedfrom the solutions, forming correspondinglycoloured solids.Images of that solid samples of associates of Ni-Encomplexes with PSS were made using electron microscopy (SEM and TEM). According to the distribution of elements and elemental analysis, complete replacement of sodium ions in PSS by ions of $[Ni(En)_n]^{2+}$ complexes was confirmed.

The spectral parameters of the Ni(II)-Diencomplexes with M:L = 1:1 and 1:2 are specified with the coordination of three and six nitrogen atoms, respectively. According to the NMR relaxation data, the mixtures of polymers PSS and PVP do not affect the complexation of Ni(II) with Dien for the same reason as for Ni-Encomplexes.

Acknowledgements -Thanks for KFU Interdisciplinary Center "Analytical Microscopy" for SEM and TEM images.

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THE INFLUENCE OF PYRIDINE AND ITS DERIVATIVES ON THE EFFICIENCY OF Cu-MEDIATED RADIOFLUORINATION OF ARYL PINACOLE BORATES

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Copper-mediated radiofluorination of arylboronic acids pinacol esters (arylBPin) using $Cu(OTf)_2(py)_4$ catalyst has been shown to be a promising approach for introducing ^{18}F-label into electron-rich arenes [1]. Minimizing amounts of K_2CO_3 in the preparation of the $[^{18}F]KF/K_{2.2.2.}$ complex allows to further improve fluorination efficiency of diverse arylBPin precursors [2]. The $Cu(OTf)_2(py)_4$ catalyst employed can be also generated *in situ* from unstable copper triflate with excess of pyridine [3]. In this study we investigated if the addition of pyridine or its derivatives would have an accelerating effect on the $Cu(OTf)_2(py)_4$-mediated fluorination of 4-biphenylboronic acid pinacol ester (**I**) under “low base” conditions.

Fluorine -18 ($T_{1/2}$ 110 min) in a form of $[^{18}F]$fluoride was produced *via* $^{18}O(p,n)^{18}F$ nuclear reaction in water cyclotron target. To the mixture of an aqueous solution of Cs_2CO_3 (160 μg, 0.49 μmol) and K_{222} (270 μg, 0.72 μmol) in MeCN were added 20-25 MBq of $[^{18}F]F$- and 1.5 mL of MeCN. The solvents were evaporated; the residual water was removed by azeotropic driying (2×1 mL MeCN) under a stream of compressed air. The residue was taken up in a solution of **I (**5 mg, 17.9 μmol), $Cu(OTf)_2(py)_4$ (3.6 mg, 5.3 μmol) and pyridine or its derivative (159 μmol) in 0.4 mL of DMF. Fluorinations were performed at 110°C for 20 min. The reaction was quenched by adding 1 ml of 95% EtOH. Radiochemical conversion (RCC) was determined by radioTLC. Each run was carried out at least in triplicate.

In the absence of pyridine radiofluorination of **I** proceeded in a moderate RCC of 56±3%. The addition of pyridine RCC resulted in substantial increase of RCC up to 83±4%. In the less extent the enhanced fluorination effect was found in the presence of 2-dimethylaminopyridine, 2-methoxypyridine, 2,6-lutidine and 4-methoxypyridine (57±2, 61±5, 65±7 and 66±7%, respectively). However, the use of 4-cyanopyridine, 2-nitropyridine, 2-methylpyridine, 4-methylpyridine, 4-dimethylaminopyridine and 2,6-diaminopyridine had a negative effect on the RCC (50±5, 38±6, 24±1, 24±2, 29±2 and 4±1% respectively). To our surprise, no fluorination was observed when 2-cyanopyridine, 2,2'-bipyridine and 1,10-phenanthroline were added into reaction media.

To conclude, from the series of pyridine derivatives, the addition of pyridine has found to have the highest accelerating effect on the $Cu(OTf)_2(py)_4$-mediated fluorination of arylBPin precursor **I** as a model compound**.** The feasibility of this approach will be further investigated for its potential application in the preparation of clinically relevant radiotracers for positron emission tomography (PET).

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[2] B.D. Zlatopolskiy et al., *Chem. Eur. J.*, **2015**, *21(5)*, 5972-5979
[3] A.V. Mossine et al., *Org. Lett.*, **2015**, *17(23)*, 5780-5783

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SYNTHESIS, STRUCTURE AND PHOTO-SWITCHABLE PROPERTIES IN SOLUTION OF NEW CARBOXYLIC AZODERIVATIVES OF THIACALIX[4]ARENE ADOPTED IN 1.3-ALTERNATE CONFORMATION

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A lot of last efforts in supramolecular chemistry are concentrated on the preparation of new architectures exhibiting the responsiveness on the exterior stimuli [2]. Light driven photo-switchable systems are very promising for design of new materials with controlled properties (porosity, luminescence etc). Calix[4]arenes containing azo-groups present attractive molecular organic receptors for building new photoresponsive assemblies in solution as well as in the solid state. Here we report the synthesis of new low rim tetrasubstituted thiacalix[4]arene azoderivatives adopting *1,3-alternate* conformation and containing four carboxyl groups as coordinating sites (fig 1). The ability of these compounds to form nanoassociates in solution with metal cations (Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Gd^{3+}, Tb^{3+}, Er^{3+}) at the room temperature as well as under UV-irradiation (table 1) have been studied by UV-spectroscopy (fig.2) and Dynamic Light Scattering (DLS) (table1).

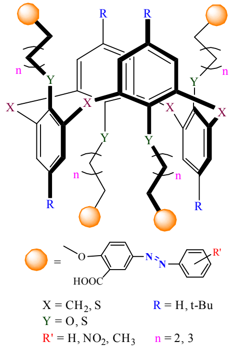


Figure 1

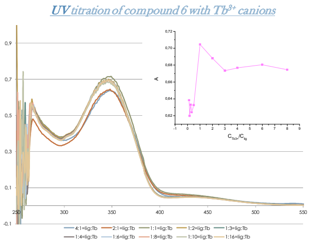


Figure 2

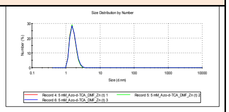
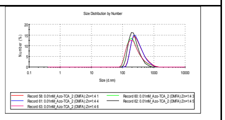
	Number
1:3=**lig 1**:Zn PDI = 0.808	
1:3=**lig 2**:Zn PDI = 0.284	

Table 1

[1] (a) Modrow, A.; Zargarani, D.; Herges, R.; Stock, N. *DaltonTrans.,* 2011, **40**, 4217; (b) Ko, C.-C.; Yam, V. W.-W. *J.Mater.Chem*., 2010, **20**, 2063; (c) Qu, D.-H.; Wang, Q.-C.; Zhang, Q.-W.; Ma, X.; Tian, H. *Chem. Rev.,* 2015, **115**, 7543;

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CF_3-PYRAZOLE CONTAINING SCHIFF BASE IN THE SYNTHESIS OF BINUCLEAR COPPER(II) COMPLEX

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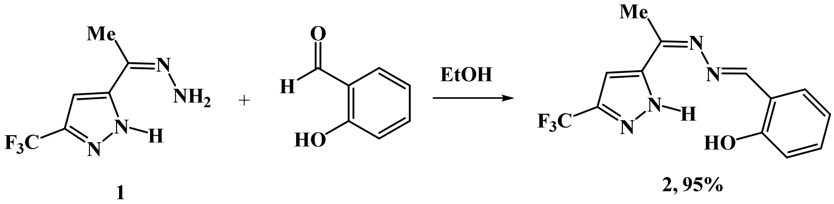
Schiff bases represent a well-known family of ligands with the strong coordination ability. Their biological activity, fluorescence and electroluminescent properties have been extensively studied. In addition, Schiff bases can form both mono- and polynuclear metal complexes exhibiting catalytic and magnetic properties.

Previously CF_3-pyrazole, containing amino-azomethyne fragment, has been synthesized through several steps starting from commercially available reagents [1,2]. We found that the interaction of CF_3-pyrazole **1** with salicylic aldehyde resulted in the formation of Schiff base **2** in good yield (Scheme 1). Product **2** is N_2O-ligand which affords binuclear complex **3** under the treatment with copper(II) chloride in methanol (Figure 1).



Scheme1. Synthesis of novel N_2O-ligand

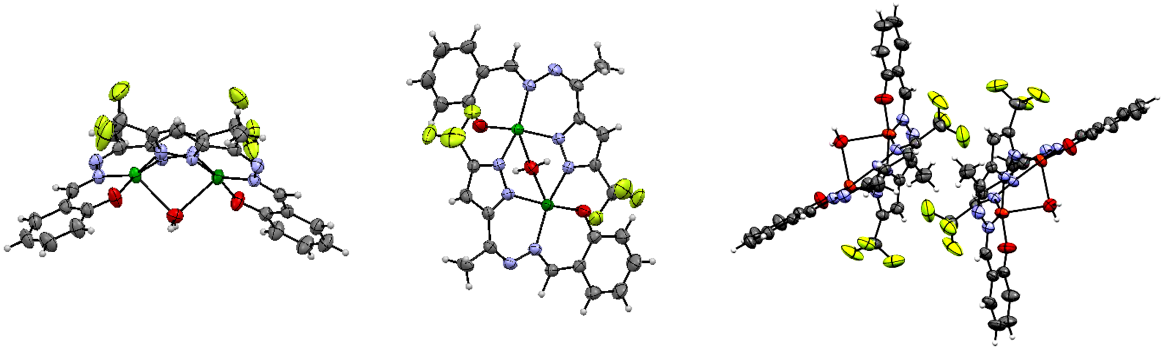


Figure 1. Different views of binuclear copper(II) complex **3** synthesized from Schiff base **2**

[1] D.N. Bazhin, D.L. Chizhov, G.-V. Roeschenthaler, Y.S. Kudyakova, Y.V. Burgart, P.A. Slepukhin, V.I. Saloutin and V.N. Charushin, *Tetrahedron Lett.,* **2014**, *55*, 5714-5717.

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NOVEL GALLIUM HIDRIDE COMPLEXES WITH ACENAPHTHENE-1,2-DIIMINE LIGAND

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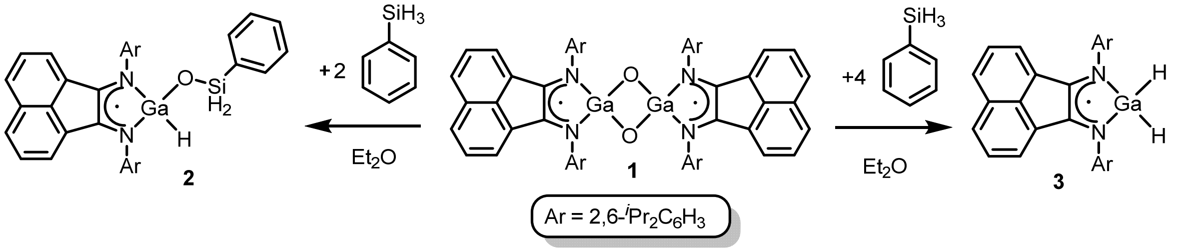
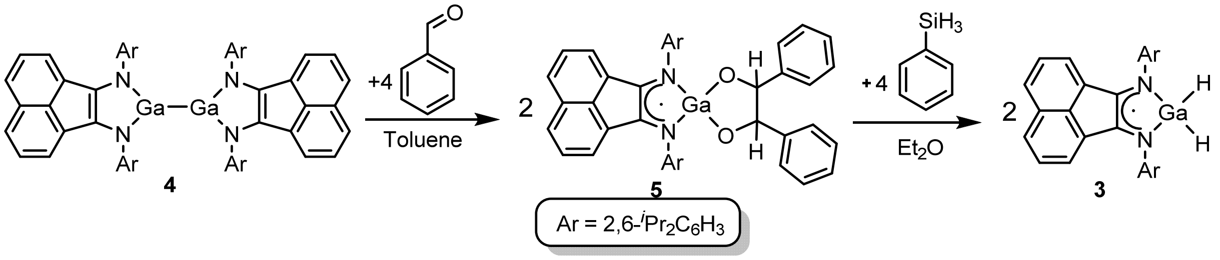
Gallium hydride derivatives are stabilized by bulky ligands have been attracted an attention of researchers recent year. Here we report the synthesis and characterization of gallium hydride complexes with dpp-bian (dpp-bian = 1,2-bis[(2,6-diisopropilphenil)imino]acenaphthene) ligand.

The treatment of [(dpp-bian)GaO]$_2$ (**1**) of two equivalent of phenylsilane in diethyl ether leads to formation of complex [(dpp-bian)Ga(H)OSiH$_2$Ph] (**2**). The reaction of **1** with phenylsilane of the reagent ratio 1:4 results to [(dpp-bian)GaH$_2$] (**3**). Both compounds **2** and **3** contain radical-anion diimine ligand.



The compound **3** was synthesized by reaction of [(dpp-bian)Ga]$_2$ (**4**) with four equivalent of phenylsilane in the preset four equivalent of benzaldehyde. The intermediate compound [(dpp-bian)Ga(OCH(Ph)CH(Ph)O)] (**5**) have been prepared by reaction of **4** with four equivalent of benzaldehyde. The compounds **2** and **3** are the first paramagnetic structurally characterized hydrides.



Complexes **2, 3** and **5** have been characterized by EPR- and IR-spectroscopy and element analysis. Molecular structures of these compounds have been determined by single crystal X-ray diffraction.

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ISOSTRUCTURALITY IN SERIES OF VOLATILE Co-, Ni-, Cu-, AND Pd(II) COMPLEXES WITH β-IMINOKETONES

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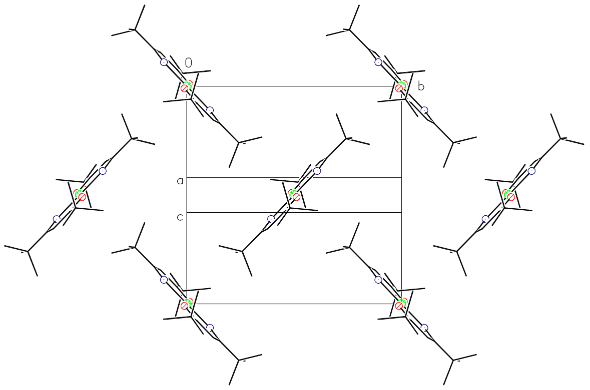
Volatile Co-, Ni-, Cu-, and Pd(II) complexes have been studied crystallochemically as precursors for preparing film oxide and metallic various coatings by the CVD method. Applying of β-iminoketones as ligands is one technique for preparing monomeric complexes to exhibit a noticeable vapor pressure at relatively low temperatures (150-300° C).

A study of the crystal structures is of interest not only for crystal chemistry but gives also important information for understanding processes taking place at sublimation. An influence of substituent nature on the crystal structure is of importance to study volatility and to search and synthesize novel volatile compounds. In this work, we have studied Co-, Ni-, Cu-, and Pd(II) β-iminoketonates of the general formula $M(L)_2$, where $L = (R^1\text{-C(O)CH-C(N-}R^3)\text{-}R^2)_2$, R^1 and $R^2 = CH_3, CF_3, C(CH_3)_3, C(OCH_3(CH_2)_2$ in various combinations, $R^3 = H, CH_3$.

All compounds studied belong to the molecular type and are built of the molecules of monomeric chelate complexes $M(L)_2$ bound by Van der Waals interactions. A most of complexes has the *trans*-configuration. The central metal atom has a square coordination with a different distortion degree. Replacing of the hydrogen imine atom by the methyl group results in the change of the coordination node, namely, the square distorts to the flattened tetrahedron and the *trans*-angles decrease from the ideal 180° to 145.5°. In methoxy-ketominates, the intramolecular hydrogen bond is realized to promote the flattening of the molecule. The molecules of the complexes are packed in stacks and layers with hydrogen and fluorine atoms of the terminal substituents on the external surfaces.

A comparative crystal chemical analysis showed that isoformular Co-, Ni-, Cu-, and Pd(II) complexes with ketoimine - $M(i\text{-acac})_2$ and with a nitrogen analog of dipivaloylmethane, $M(i\text{-thd})_2$, are isostructural. For fluorinated ketoiminates, the Cu and Ni complexes are isostructural.

$M(i\text{-thd})_2$



In $M(i\text{-thd})_2$ complexes, the square parquet nets form a pseudocell with four M...M distances lying in the layer between 7.40 and 8.72 Å.

In the $M(i\text{-acac})_2$ structures, the molecules of the complexes are packed into linear associates (bands) to be situated on the pseudoaxes 6^3 with the M...M distances of 5.67 and 5.74 Å. Such bands form the (011) layers with d = 7.52 Å.

The data obtained about the isostructurality of the complexes and isostructural series resulted are important for synthesis of more complex compounds and solid solutions to exchange metals of the stoichiometry given

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HOMO AND HETEROMETALLIC LANTHANUM COMPLEXES BASED ON 2-(2-BENZOXYAZOL-2-YL)PHENOLATE LIGAND. SYNTHESIS AND LUMINESCENT PROPERTIES

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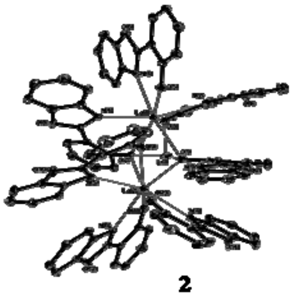
Phosphorescent metal complexes are widely used in bioimaging, photocatalysis, optical sensors, detectors and other optoelectronic devices. At present, most of the phosphorescent metal complexes are compounds of d metals such as iridium, rhenium, platinum, which are very expensive. Therefore, our attention was attracted to the complexes of lanthanum, lithium and sodium, which are substantially lower in cost and have a variety of coordination capabilities. In attempt to synthesize new phosphorescent materials the complexes $[La(L)_3]_2$ (**1**), $La_2Li(L)_7(DME)_2$ (**2**), $LaNa(L)_4(DME)_2$ (**3**), $[La(L)_3]_2(bipy)$ (**4**), $La(L)_2(Cp)(DME)$ (**5**), Li(L) (**6**) и Na(L) (**7**), where HL = 2- (2-hydroxyphenyl) benzoxazole were prepared.



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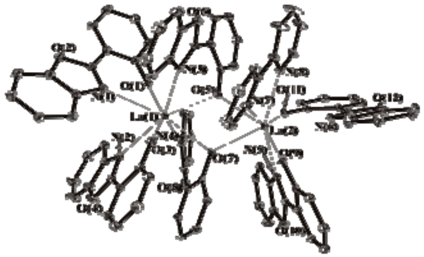

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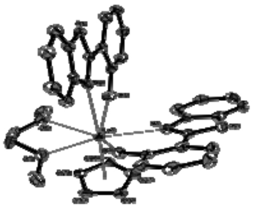
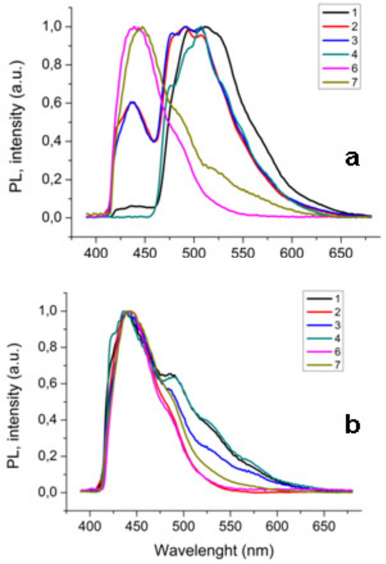


5

The PL spectra of compounds in the solid state at 300K and 77K as well as in THF or DME solution at 300 K are identical and contain a superposition of intense fluorescence signals with λ_{max}=435 nm and a weak phosphorescence with λ_{max}=510 nm. In a solution at 77K all derivatives showed a long phosphorescence with lifetimes from 3.5 to 95.8 ms. The high intensity and shorter lifetime of phosphorescence of **1** - **4** compared with **6** - **7** is explained by the presence in the molecules the metal atoms with a strong spin-orbit interaction, which increase the probability of intercombination conversion and the $^3T_1 \rightarrow {}^1S_0$ electronic transition.



Fluorescence and phosphorescence spectra of complexes in THF solutions at 77 K (a) and 300 K (b).

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FERROCENE-CONTAINING NONTRANSITION METAL COMPLEXES BASED ON QUINOID TYPE LIGANDS

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In recent years, ferrocene and its derivatives attract considerable interest due to their wide aplication. The uniqueness of the molecular geometry, the ability to the reversible oxidation, as in the case of redox-active quinoid type (capable of reversible oxidation or reduction in the metal coordination sphere) ligands, makes ferrocene to be promising object for the study of electron transfer processes. Complexes containing such redox-active centers in one molecule are potential objects to study intramolecular electron transfer between the *o*-quinone ligand and ferrocene.

Our interest in this subject led us to synthesize and research two type compounds, where ferrocene moiety locates immediate in redox-active ligand (fig. 1) or in auxiliary ligand coordinated to the metal central (fig. 2).

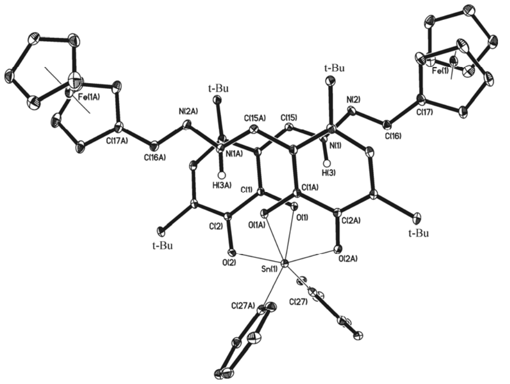

Figure 1

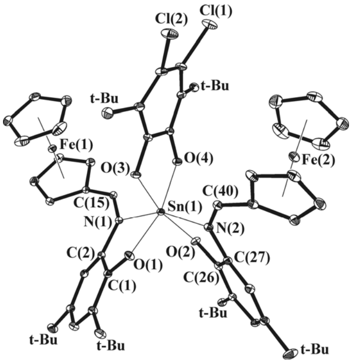

Figure 2

The first series of novel tin(IV) and antimony(V) complexes based on redox-active quinonato-type ligand with a ferrocenyl group linked by a conjugated –CH=N–N=CH– bridge were synthesized and characterized by IR spectroscopy; ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy; elemental analysis; and cyclic voltammetry. Generally the presence of such (–CH=N–N=CH–) group at the 6-position of the catecholato ligand results in the formation of stable complex structures with anionic metal–catecholato moieties and hydraziniumylidene counterions.

The other type complexes containing ferrocene fragment in ancillary ligand are tin(IV) complexes based on Schiff ligands containing ferrocene-aldimine substituent and variety o-benzoquinone(o-iminobenzoquinone) derivatives.

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NEW IONIC AND POLYMERIC COMPLEXES OF COBALT, NICKEL AND COPPER WITH 3,3',5,5'-TETRAMETHYL-4,4'-BISPYRASOLE

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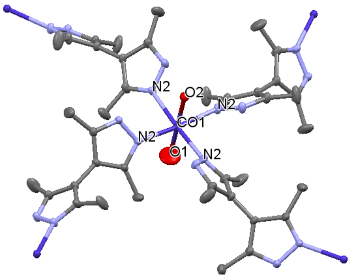
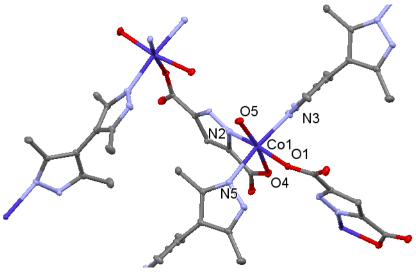
One-, two- or three-dimensional coordination polymers are of great interest for different fields of chemistry and material science. On the one hand polymeric complexes are chemically more stable and could be used in catalysis, on the other hand their structures contain pores with different shapes and sizes. The substitution of them by *guest*-molecules results in the change of the properties of the polymer. Of particular interest are three-dimensional polymers of the MOF (metalorganic frameworks) type.

The ligand 3,3',5,5'-tetramethyl-4,4'-bispyrazole (**4,4'bpz**) used in this work is of interest as a synthetically accessible compound (2 stages from acetylacetone) and is the basis for such ligands as 3,5 -Me_2Pz-R-3,5Me_2Pz, where the bridge varies between p-C_6H_4, 4,4'-biphenyl, C≡C, etc. Actually 3D and 1D complexes of some transition metals (Co, Ni, Cu, Zn) with 4,4'-bpz have been described [1-2]. These compounds have either a neutral or a charged (protonated (H_2Bpz^{2+}) or deprotonated) ligand. The complexes were synthesized in water-alcohol solutions at room temperature and in an autoclave; this allowed to obtain compounds with different structures.

In the present work we studied complexes of Ni^{2+}, Co^{2+} and Cu^{2+} with 4,4'-bpz in HCl and $HClO_4$ solutions, as well as in presence of an additional anionic ligand – pyrazole-3,5-dicarboxylic acid (**H_2Pdc**). The latter ligand was chosen as a chelating dianionic ligand; its two carboxyl groups cause the formation of polymeric structures.





Crystalline structures of three new Co complexes $[H_24,4'bpz][CoCl_4]*H_2O$ (**1**), $\{[Co(4,4'bpz)_2(H_2O)_2](ClO_4)_2*2EtOH\}_n$ (**2**), $[Co(4,4'bpz)(Pdc)(H_2O)]_т$ (**3**) were determined. The first one is an ionic crystal, the two other are plane coordination polymers. The replacement of the perchlorate-anion by 3,5-pyrasoledycarboxylate leads to the change of the coordination environment of Co (picture #). For Cu and Ni the compositions of the complexes were established $\{[Ni(4,4\text{-}bpz)(H_2O)_2](ClO_4)_2\}_n$ (**4**) and $\{[Cu(4,4\text{-}bpz)(H_2O)](ClO_4)_2\}_n$ (**5**). We assume a polymeric structure on the basis of data on solubility, chemical analysis, and IR spectra. All the compounds were characterized by a number of methods: DTA, XRD, IR, Raman, UV-VIS spectroscopy. Magnetic susceptibilities were also studied at different temperatures.

[1] A.Tăbăcaru, C.Pettinari, I.Timokhin et all.. // *Cryst. Growth. Des.* **2013**, *13*, 3087-3097.
[2] L.Hou, L.Jia, W.Shi et all. // Dalton Trans. **2013.** 42. 6306-6309

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NIR LUMINESCENT ATE COMPLEXES OF LANTHANIDES CONTAINING PERFLUORINATED 2-MERCAPTOBENZOTHIAZOLATE LIGANDS

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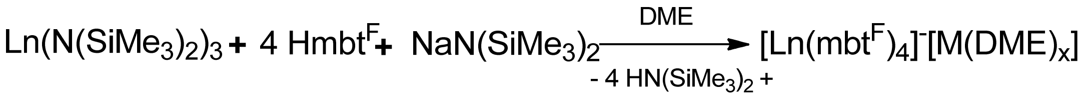
Lanthanide compounds, due to the unique luminescent properties of these metals, are widely used in optoelectronic devices and biomedicine. To obtain highly luminescent complexes, a sensitization of the lanthanide luminescence with organic chromophore groups is required. The use of perfluorinated ligands leads to an increase in the quantum yield of photoluminescence (PL) and the lifetime of the excited states of lanthanides, especially which are luminescent in near infrared (NIR) region, due to the absence in these compounds of luminescence quenchers – C-H, O-H and N-H groups. New perfluorinated lanthanide complexes with pefluorated thioketone 4,5,6,7-tetrafluoro-1,3-benzothiazole-2(3H)-thione ($\mathrm{Hmbt^F}$) were synthesized, their structure and luminescent properties were investigated. The luminescent properties of obtained complexes in NIR region were insufficient because of presence coordinated THF molecules. To remove THF molecules containing C-H bonds from coordination sphere of lanthanide we have synthesized new ionic ate complexes $\mathrm{[Ln(mbt^F)_4]^-}$ $\mathrm{[M(DME)_x]^+}$ (scheme 1). Studying of PL properties of lanthanide ate complexes revealed the enhancement of emission in NIR region from $\mathrm{Nd^{3+}}$, $\mathrm{Er^{3+}}$ and $\mathrm{Yb^{3+}}$ ions as compared with neutral counterparts. The molecular structure of some complexes was determined by X-ray analysis (Fig. 1).



$$\mathrm{Ln(N(SiMe_3)_2)_3 + 4\ Hmbt^F + \ NaN(SiMe_3)_2} \xrightarrow[\text{- 4 HN(SiMe}_3\text{)}_2\text{ +}]{\text{DME}} \mathrm{[Ln(mbt^F)_4]^-[M(DME)_x]}$$

Ln = Ce, Nd, Tb, Er, Yb; M = Na; x = 3
Ln = Yb; M = Li; x = 2

Scheme 1

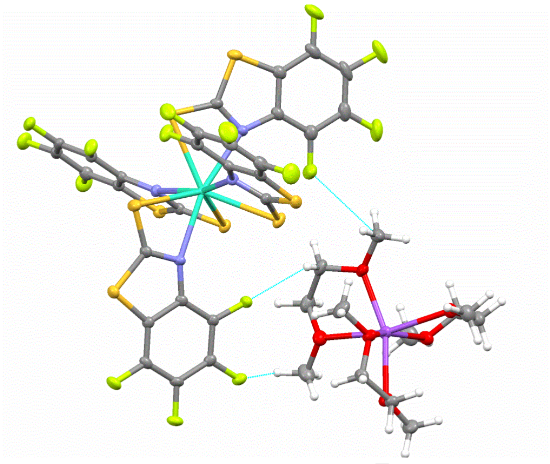


Figure 1. Molecular structure $\mathrm{[Tb(mbt^F)_4]^-[Na(DME)_3]^+}$

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NEW COMPLEXES OF COPPER(II) AND LANTHANIDES(III) WITH 4-(PYRIDIN-2-YL)METHYLENEAMINO-1,2,4-TRIAZOLE

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Organic molecules containing heterocyclic pyridyl and triazolyl rings are promising ligands for synthesis of metal complexes having unique luminescent and/or magnetic properties. In the case of lanthanide compounds the presence of pyridyl and triazolyl fragments provides effective energy absorption that is necessary for luminescence intensity increase. The presence of triazolyl bridges in complexes of magnetically active metals promotes the exchange coupling between paramagnetic ions through M–N–N–M channel. In the present work we investigated the interaction of copper(II) and lanthanides(III) with multidentate ligand 4-(pyridin-2-yl)methyleneamino-1,2,4-triazole (L), which was used for synthesis of Cd^{II} and Ag^{I} coordination polymers earlier [1, 2].

By the reactions of $Ln(NO_3)_3$ with L the series of isostructural compounds $[Ln(NO_3)_3(H_2O)_3]\cdot 2L$ (Ln = Eu (**1**), Gd (**2**), Tb (**3**), Dy (**4**)) was obtained. In the structures **1**–**4** Ln^{III} atom coordinates three nitrate anions and three water molecules. In crystal every $[Ln(NO_3)_3(H_2O)_3]$ molecule is bound to six L molecules due to H-bonds. The investigation of optical characteristics of compounds **1** and **3** showed the presence of metal-centered luminescence of Eu^{3+} и Tb^{3+}. According to magnetic measurements data the compound **4** exhibits single-ion magnet (SIM) behaviour in the temperature region 2–6.5 K ($\Delta E/k_B = 71$ K).

The interaction of $Cu(NO_3)_3\cdot 3H_2O$ with L in aqueous solution leads to formation of bis(pyridin-2-yl-methanol)-4-amino-1,2,4-triazole (H_2L^1) and 1-amino-4*H*-1,2,4-triazole (L^2), which can be coordinated to Cu^{2+} ions. Slow diffusion of MeOH into reaction aqueous solution results in formation of unusual 12-nuclear complex $[Cu_{12}(L^1)_4(L^2)_6(NO_3)_6(MeOH)_2(H_2O)_6]\cdot 10NO_3\cdot 3MeOH\cdot 11H_2O$ (**5**), while in the case of EtOH and MeCN the 1D-coordination polymer $\{[Cu_3L^1(L^2)_2(NO_3)_2(H_2O)_2]\cdot 2NO_3\cdot 1.5H_2O\}_n$ (**6**) crystallizes. The structures of compounds **5** and **6** are formed by similar trinuclear Cu^{II} fragments, linked with each other by triazolyl rings of H_2L^1 ligand. The behavior of the $\chi T(T)$ dependence for compound **6** indicates the domination of antiferromagnetic exchange coupling between Cu^{II} atoms in trinuclear fragments (calculated J_{ex} values are –149 and –175 cm^{-1}).

[1] D.-B. Dang. M.-M. Li, Y. Bai, R.-M. Zhou, *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.*, **2013**, *103*, 101–107.
[2] Ch.-W. Yeh, Ch.-H. Tsou, H.-T. Lee, H.-A. Tsai, M.-Ch. Suen, *Polyhedron*, **2015**, *92*, 12–21.

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DINUCLEAR CYCLOMETALLATED IRIDIUM(III) COMPLEXES WITH BRIDGING 2-(2-HYDROXYPHENYL)BENZIMIDAZOLE-CONTAINING LIGAND

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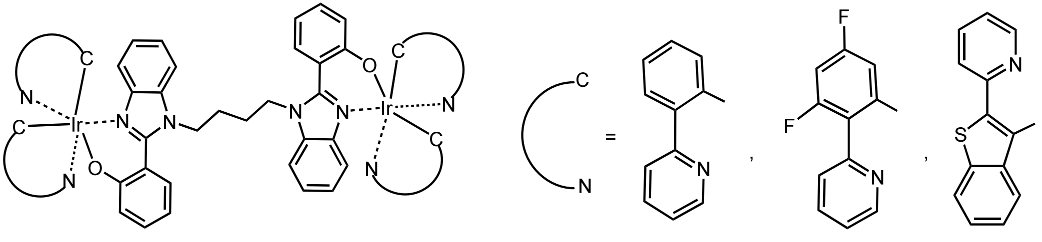
New 2,2'-(butane-1,4-diylbis(1*H*-benzo[*d*]imidazole-1,2-diyl))diphenol ligand was synthesized in high yield and characterized by NMR, FTIR and elemental analysis. On the base of the synthesized bridging ligand three new neutral cyclometalated iridium(III) homodinuclear complexes were obtained.



1 2 3

Dinuclear complexes were characterized by NMR, FTIR and elemental analysis. Compounds **1**-**3** revealed intense photoluminescence (PL) of green, bluish-green and red colors. The emission bands (Fig. 1) are attributed to metal-to-ligand charge transfer (MLCT) transitions mixed with ligand-centered (LC) transitions. The PL quantum yields in dichloromethane solution at room temperature were found to be 20-30%. Electroluminescent (EL) properties of the complexes were investigated. OLEDs with the configuration of ITO/PVK:**Ir-complex** (5% weight) (40 nm)/BATH(30 nm)/Alq_3 (30 nm)/Yb (150 nm) were fabricated. The compounds generated green, bluish-green and red electroluminescence for **1**, **2** and **3** respectively.

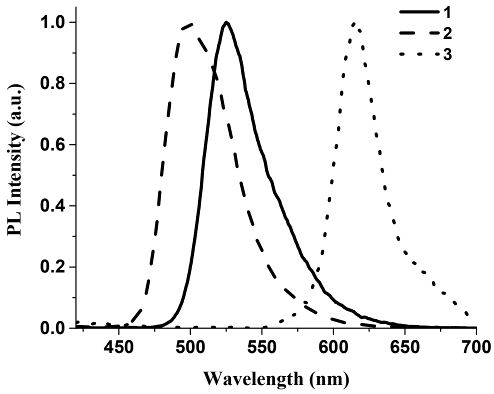


Fig. 1

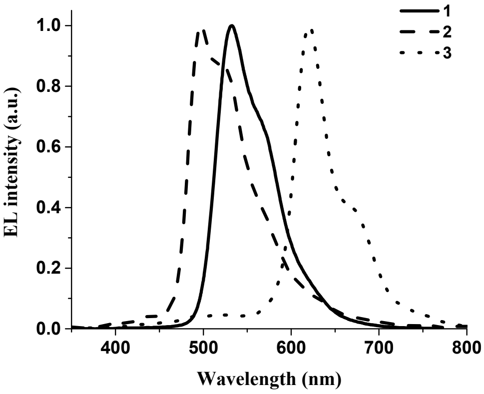


Fig. 2

The EL spectra of the complexes (Fig. 2) are similar to their PL spectra and contain the emission bands which can be assigned to MLCT/LC transitions. The highest brightness (7314 cd/m^2 at 26 V) was achieved for complex **1**.

Acknowledgements - this work was supported by the Russian Foundation for Basic Research (Project No 15-03-02467-a).

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Ln(III) COMPLEXES (Ln = Sm, Eu, Tb, Dy) WITH CHIRAL LIGAND CONTAINING 1,10-PHENANTHROLINE AND NATURAL TERPENE FRAGMENTS: SYNTHESIS, STRUCTURE AND PHOTOLUMINESCENCE

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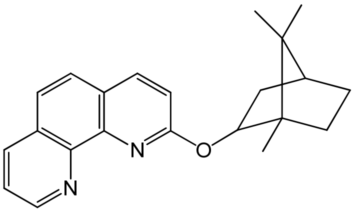
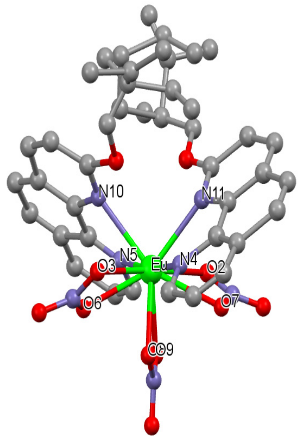
The ligand 1,10-phenanthroline is one of the best antenna which has been employed for the synthesis of various high luminescent Ln(III) complexes [1, 2]. The introduction of a chiral substituent into the 1,10-phenanthroline can lead to design of high luminescent chiral lanthanide complexes which combine both optical activity and impressive photophysical and magnetic properties. Particularly, the phenanthroline derivatives containing fragments of the naturally occurring optically active terpenes are one of the perspective chiral ligands for the synthesis of remarkable luminescent Ln(III) complexes.

A series of the lanthanide(III) complexes based on the new chiral ligand L, which contains 1,10-phenanthroline and borneol terpene fragments, namely $[LnL_2(NO_3)_3]$ (Ln = Sm (1), Eu (2), Tb (3), Dy (4)), have been synthesized and structurally characterized. The X-ray diffraction analysis shows that the crystal structure of 3 is formed by molecules of the mononuclear complex. The complex 3 comprises a 10-coordinate Ln^{3+} ion with two bidentate N,N-donor ligands (L) and three bidentate chelating nitrate groups. According to the X-ray phase analysis data the complexes 1–4 are isostructural.



L



The complexes 1–4 exhibit the metal-centered orange (Sm^{3+}), red (Eu^{3+}), green (Tb^{3+}) and yellow (Dy^{3+}) luminescence, respectively, in solid state at room temperature. The luminescence quantum yield for the solid samples increases in the order 2 > 3 > 1 > 4.

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[2] Z. Pan, G. Jia, C.-K. Duan, et al., *Eur. J. Inorg. Chem.,* **2011**, *5*, 637−646.

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EFFECT OF HETETOATOM IN TRIDENTATE LIGANDS ON STRUCTURE OF THEIR COPPER(II) COMPLEXES

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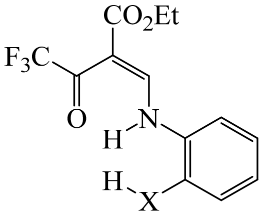
Tridentate ligands are popular building blocks for mono- and polynuclear metal complexes synthesis including ones with promising properties [1-3]. We have obtained two types of tridentate ligands based on ethyl 2-ethoxymethylene trifluoroacetoacetate and aromatic diamines. In case of *o*-phenylenediamine N_2O-ligand (H_2L^1) was synthesized whereas the use of *o*-aminophenol led to NO_2-ligand (H_2L^2) (Fig. 1). These ligands were found to form different complexes with copper(II) chloride: N_2O-ligand (H_2L^1) resulted in mononuclear complex Cu_2L^1Cl (Fig. 2) while NO_2-ligand (H_2L^2) gave binuclear complex $Cu_2L^2_2$ (Fig. 3). Obviously, the difference of the ligands behavior is due to the presence of oxygen atom in H_2L^2, which is more electronegative compared with nitrogen atom in H_2L^1.



H_2L^1 (**X = NH**),
H_2L^2 (**X = O**)

Fig. 1. Structure of tridentate ligands

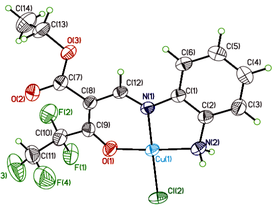


Fig. 2. Structure of mononuclear copper(II) complex Cu_2L^1Cl

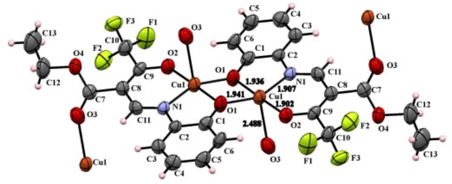


Fig. 3. Structure of dinuclear copper(II) complex $Cu_2L^2_2$

[1] E. Hahn, A. Casini, F. Kühn, *Coord. Chem. Reviews*, **2014**, 276, 97-111
[2] L. Hammarström, O. Johansson, *Coord. Chem. Reviews*, **2010**, *254*, 2546-2559
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Acknowledgements - This work was financially supported by Program of UB RAS (project 15-21-3-7) and the State Program for Supporting of Leading Scientific Schools of the Russian Federation (grant no. NSh-8922.2016.3).

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MIXED LIGAND COPPER(II) AND ZINC(II) COMPLEXES OF 1,10-PHENANTROLINE AND 2,2’-BIPYRIDINE WITH TRIDENTATE N, N, S MERCAPTOPYRAZOLE CONTAINING SCHIFF BASE

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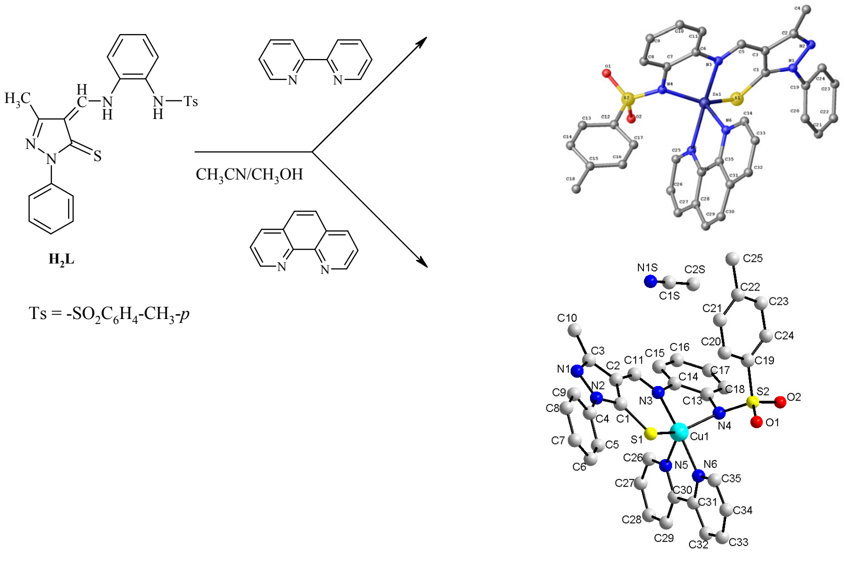
The electrochemical synthesis of novel adducts of 1,10-phenantroline (L^1) and 2,2’-bypiridine (L^2) in Zn(II) or Cu(II) chelates of the N,N,S- tridentate basic form of the tridentate Schiff base N-[2-[[3-methyl-1-phenyl-5-thioxo-pyrazole-4-ylidenemethyl]amino]phenyl]-4-methylbenzenesulfonamide (H_2L) with common formulae $[M(L)L^1]$ or $[M(L)L^2]$ were performed by using the corresponding metal as a sacrificial anode (Scheme). The compounds were characterized by elemental analysis, IR and ^1H NMR spectroscopy, and magnetic measurements. The crystal structures of all complexes have been determined by X-ray diffraction.



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SYNTHESIS, STRUCTURE AND PHOTOLUMINESCENCE PROPERTIES OF ZINC(II) COMPLEXES WITH 2-(N-TOSYLAMINOBENZILIDENE)-2'-IMINOALKYLPYRIDINES

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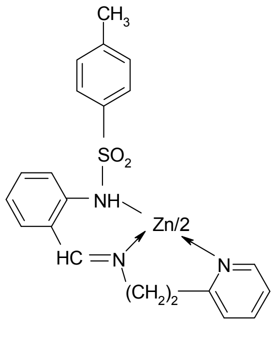
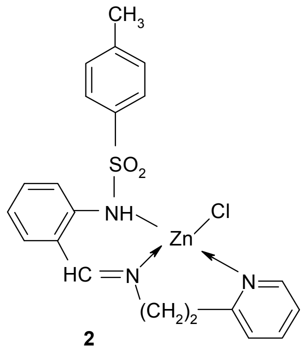
Zinc complexes of azomethine ligands are the matter of interest as active layers for OLED devices owing to their thermal stability, and high vitrification temperatures, easy sublimation during deposition of thin amorphous films, variability of structures, promising photo-and electroluminescent properties and electron-transfer characteristics.

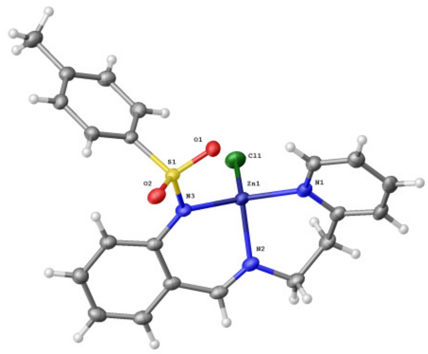
2-(N-tosylaminobenzilidene)-2'-iminoalkylpyridines have been used as precursors to novel zinc complexes (**1, 2**, correspondingly) that have been synthesized by chemical and electrochemical methods and thoroughly investigated by IR, UV-vis, NMR ^{1}H spectroscopy.



1 n=1, 2



2



The crystal structure of complex **2** has been determined by X-ray diffraction. The doubly deprotonated L^{2-} acts as a tridentate chelating specie means of amino- and imino-nitrogen atoms. The fourth coordination position is occupied by the nitrogen of pyridine ring.

The DMSO solutions of complexes **1** and **2** exhibit photoluminescence in the blue spectral region with the maxima located at 451 nm for **1** (n = 1) and 435 nm (n = 2) and 435 nm for compounds **2**.

The quantum yields of fluorescence of **1** (n = 1, 2) and **2** are ranged from 0.22 to 0.31.

Acknowledgements -
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INTERACTION OF PLATINUM METALS IONS WITH LIGANDS ATTACHED TO SILICA SURFACE

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Sorption is considered now as a main tool in hydrometallurgy of platinum metals (PMs) and silica with chemically attached ligands serve as sorbents in real technologies for selective extraction and separation of PMs. Here we present the results of our study of the interaction of palladium(II), platinum(II,IV), rhodium(III) and iridium(III,IV) ions in chloride solutions with following N-, S- and N,S-ligands attached to silica surface:

$SiO_2)$-$(CH_2)_3NH(CH_2CH_2NH)_nH$ (**I**, n = 0, 1, 4, 12-15);
$SiO_2)$-$(CH_2)_3OCH_2CH(OH)CH_2SR$ (**II**, R = CH_2CH_2OH, CH_2COOH);
$SiO_2)$-$(CH_2)_3OCH_2CH(OH)CH_2(SCH_2CH_2)_nN(C_2H_5)_2$ (**III**, n = 1, 2).

Various silicas with specific surface area 100-400 m^2/g were used as a support. The quantity of attached ligands reached 1 mmole/g.

Sorbents with N-ligands **I** showed high affinity for PMs ions which increased with the elongation of ethylenimine chain. Sorption proceeds in wide range of HCl concentration (0.1-6 M) with the following row of selectivity: Rh(III) ~ Ir(III) > Pt(IV) ~ Ir(IV) > Pd(II) > Pt(II), however, the selectivity is not high enough for separation of PMs. Among ions studied only Pd(II) forms complexes with attached ligands at ambient temperature, the sorption of all other ions is caused by ion exchange – the interaction of corresponding chloride complexes with protonated amino groups of the sorbent. Sorbents with S-ligands II extracted only Pd(II) due to complex formation, sorption of other PMs at ambient temperature was insufficient. This allows selective separation of Pd(II) from other PMs. Sorbents with N,S-ligands **III** occupy intermediate position between sorbents **I** and **II**. They have high affinity to Pd(II) due to its complex formation with attached ligands, but at the same time they effectively bind chloride complexes of other PMs by ion exchange. So, sorbents **III** are at least interest for PMs extraction among sorbents studied.

The greatest problems in sorption processing of PMs arrive from desorption. We have studied a big set of eluents: solutions of mineral acids and salts, ammonia, thiourea, etc. Although most of PMs bind to sorbents **I** and **III** by ion exchange mechanism their desorption by concentrated salt or acid solutions is rather ineffective and requires big volumes of eluent. The use of complexing eluent is more promising. Ammonia solutions destroy the complexes of Pd(II) with ligands I and II thus leading to complete desorption. For elution of Pt(IV) solution of thiourea in preferable. Thiourea forms complexes with Pt(IV) thus reducing the charge of its chloride complexes and facilitating their desorption. For inert Rh(III) and Ir(III) elevated temperatures are needed. Consistent use of appropriate eluents leads to complete separation of PMs.

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NEW POLYMORPHS OF THE ACETYLUREA COMPLEX WITH PRASEODYMIUM BROMIDE

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Attempts to synthesize the earlier reported complex of praseodymium bromide with acetylurea (AcUr) $[Pr(AcUr)_2(H_2O)_5]Br_3$ (**1**) [1] resulted in preparing its polymorph **2**. On cooling compound **2** down to 100 K, another polymorph **3** was found. DSC shows the beginning of the transformation **2** → **3** at ~232 K. Polymorph **2** is characterized by IR spectra.

The crystals of all three polymorphs include complex cations $[Pr(AcUr)_2(H_2O)_5]^{3+}$ (coordination number 9) and uncoordinated bromide ions. The AcUr molecules are coordinated via the bidentate mode through the oxygen atoms. The deviations from coplanarity of the AcUr ligands differ for **1**–**3**: the dihedral angles between two NCO planes in the ligands are 5.70°, 8.97° in structure **1** [1], 12.95° in structure **2** and 11.19–16.48° in structure **3**. The main difference of **2** and **3** from **1** is the arrangement of AcUr. The angle between the mean planes of two chelating acetylurea molecules are 34.50°, 56.83° and 54.74–56.70° for **1**–**3**, respectively. So, they can be considered as various conformers.

Structure **3** can be regarded as a superstructure relating to structure **2**. Unit cells of **2** and **3** include 2 (1 independent) and 8 (4 independent) formula units, respectively. Crystals of **2** are monoclinic, space group $C2$; a =18.3895(5), b = 7.8206(2), c = 7.6444(2) Å, β = 113.398(2)°, V = 1008.99(5) Å^3. Complex cations are arranged on straight lines parallel to the unit cell axes. In **3**, arrangement of complex cations is slightly irregular; the Pr–Pr–Pr angles vary in the 175.96–179.42° range. As a result, two pairs of independent formula units form two sub lattices similar to the lattice of structure **2**. Crystals of **3** are monoclinic, space group $P2_1$, a = 7.4972(2), b = 31.1736(9), c = 16.8265(6) Å, β = 91.7410(10)°, V = 3930.8(2) Å^3. Crystal density of **3** is slightly larger as compared to **2** (2.247 and 2.221 $g{\cdot}cm^{-3}$, respectively) and significantly larger than for **1** (1.983 $g{\cdot}cm^{-3}$) [1].

Quantum-chemical simulation allowed comparing stabilities of various conformers of $[Pr(AcUr)_2(H_2O)_5]Br_3$.

[1] L. Yu. Alikberovaa , D. V. Al’bov, A. S. Bushmeleva, G. A. Fedorova and V. V. Kravchenko, *Rus. J. Coord. Chem.*, **2014**, *40*, 918–924.

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COORDINATION INTERACTION AS A KEY FOR CATALYSIS INVOLVING METALLOPHTHALOCYANINES USE

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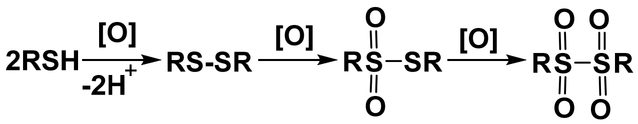
Materials consisting of transition metal coordination compounds with phthalocyanine ligands exhibit high catalytic efficiency within nature and model systems. Such materials are applied as catalysts of redox processes upon homogeneous and heterogeneous conditions [1-2]. Increase of manufacturability of the materials and selectivity of their action depends on mechanism of reaction using them. An electron transfer from oxidant to substrate within the systems is caused by formation of intermediate complex of the phthalocyanine.

Mechanism of disulfide formation from monomeric derivatives involving d-metal sulfo-acids of phthalocyaninate as catalysts is considered in the work. Oxidation of mercaptanes upon harsh conditions is multi-step process accompanied with formation of various compounds:



$$2RSH \xrightarrow[-2H^+]{[O]} RS\text{-}SR \xrightarrow{[O]} R\overset{O}{\underset{O}{S}}-SR \xrightarrow{[O]} R\overset{O}{\underset{O}{S}}-\overset{O}{\underset{O}{S}}R$$

The use of two-charged metal phthalocyaninates, primarily cobalt and iron ones, allows carrying out of reaction upon mild conditions reaching high selectivity toward non-oxidized disulfide formation as a main product.Use of water-alkali mediums for the process contribute existence of substrate in ionic form instead of molecular one that promotes interaction with central metal cation having uncompensated positive charge containing in macrocycle.

We have found out [3] transformation to radical form stably interacting with the macrocycle to take place upon electron transfer from substrate to phthalocyanine macrocycle. Further coordination of oxygen into sixth coordination position of metal cation stabilizes the system.

$$RS^{\bullet}\cdot M^{II}Pc\cdot O_2^{-} + Solv \rightleftarrows RS^{\bullet} + Solv\cdot M^{III}Pc\cdot O_2^{2-}$$

Kinetic study carried out shows the replacement of substrate-radical to solvent, which inherently is triple complex destruction, to limit the entire process. Competing between water and hydroxide-ions for entrance into macrocycle coordination unit is observed in water-alkali systems. Stability of such complexes determines catalyst efficiency.

[1] A. Sorokin, *Chem. Rev*, **2013**, *113*, 8152-8191.
[2] A. Vashurin, V. Maizlish, et al., *J. Porphyrins Phthal.*, **2017**, *21*, 37-47.
[3] A. Vashurin, I. Kuzmin, et al, *J. Serb. Chem. Soc.*, **2016**, *81*, 1025-1036.

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COPPER(II) HALIDE COMPLEXES WITH 1-*TERT*-BUTYL-1,2,4-TRIAZOLE: SYNTHESIS AND CRYSTAL STRUCTURE

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Copper(II) halide complexes with heterocyclic ligands show a variety of supramolecular assemblies. Realization of specific structural types of cupric halide complexes is strongly dependent on the structure of heterocyclic ligands. To date, complexation of 1-*R*-1,2,4-triazoles with cupric halides has been investigated to a small extent. As to complexes with the most simple 1-alkyl-1,2,4-triazoles, only two compounds, namely dichloro-bis(1-ethyl-1,2,4-triazole)-copper(II) [1] and dibromo-tetrakis(1-butyl-1,2,4-triazole)-copper(II) [2], have been structurally characterized.

The present study is devoted to the investigation of complexing behavior of 1-*tert*-butyl-1*H*-1,2,4-triazole (btr). The target triazole was prepared in 82% yield by alkylation of 1,2,4-triazole with *tert*-butanol in perchloric acid. Complexation of btr with copper(II) chloride or bromide was carried out in several solvents, such as ethanol, 2-propanol and 1,2-dichloroethane. As a result, complexes of two types, namely $[Cu(btr)_2X_2]_n$ and $[Cu(btr)_4X_2]$ (X = Br, Cl), were isolated depending on the ratio of reagents.

According to X-ray analyses, in all the complexes, btr acts as a monodentate ligand coordinated by Cu(II) cations *via* the heteroring N^4 atoms. The complexes $[Cu(btr)_2Cl_2]_n$ and $[Cu(btr)_2Br_2]_n$ are isotypic, and present 1D coordination polymers, formed at the expense of single halide bridges between neighbouring copper(II) cations, which show distorted square pyramidal coordination (Figure 1). These complexes are the first described coordination polymers of copper(II) halide with 1-R-1,2,4-triazoles. The isotypic complexes $[Cu(btr)_4Cl_2]$ and $[Cu(btr)_4Br_2]$ reveal mononuclear centrosymmetric structure, with Cu(II) cations having octahedral environment (Figure 2).

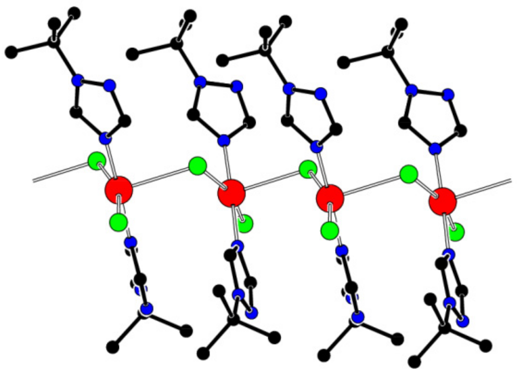

Figure 1. Coordination polymeric chain in the crystal structure of $[Cu(btr)_2Cl_2]_n$, running along the *c* axis. H atoms are omitted for clarity.

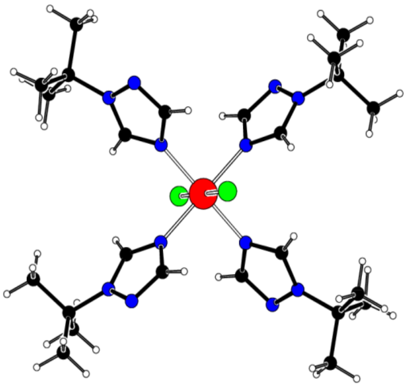

Figure 2. Complex molecule in the crystal structure of $[Cu(btr)_4Cl_2]$.

[1] Yu. L. Slovokhotov, Yu. T. Struchkov, A. S. Polinsky, V. S. Pshezhetsky and T. G. Ermakova, *Cryst. Struct. Commun.*, **1981**, *10*, 577–582.
[2] K. F. Wang, F. F. Jian, R. R. Zhuang, *J. Braz. Chem. Soc.* 2010, *21*, 614-619.

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1-(1,2,4-TRIAZOL-3-YL)TETRAZOLES: COMPLEXATION AND COPPER-ASSISTED TETRAZOLE RING DISCLOSURE

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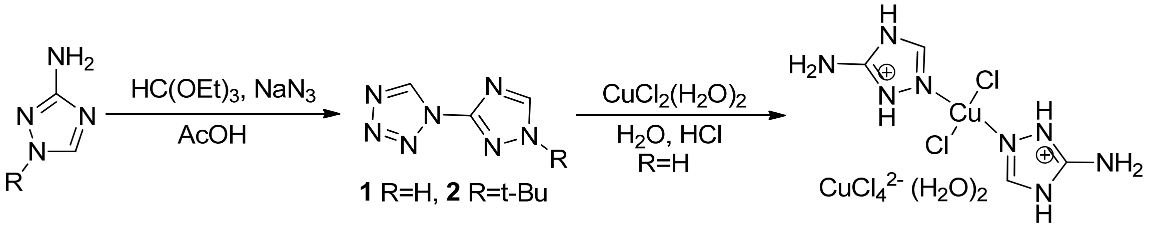
[b]*Belarusian State University, Minsk, BELARUS.*

Compounds including both tetrazole and triazole moieties are of interest as high-energetic and gas-generating agent as well as multidentate nitrogen-containing ligands [1]. The present work is devoted to 1-(1,2,4-triazol-3-yl)tetrazoles and their complexes. Crystal structures of all synthesized complexes were determined by single crystal X-ray analysis.

Here, we prepared 1-(1,2,4-triazol-3-yl)tetrazole (**1**) and its *tert*-butyl derivative **2** by heterocyclization of corresponding amines with triethyl orthoformate and sodium azide, and studied their complexation towards copper(II) chloride. Interaction of ligand **1** with copper salt in 15% aq. HCl was found to lead to 3-amino-1,2,4-triazolium complex **3**. Formation of **3** can be explained by copper assisted disclosure of the tetrazole ring with generation of nitrogen and N-(1,2,4-triazol-1-yl)cyanamide. The latter undergoes hydrolysis to give amine.



1 R=H, **2** R=t-Bu

3

Interaction of **1** with copper(II) chloride in ethanol in the presence of few drops of conc. HCl was found to result in 1D coordination polym er $[CuCl_2L(H_2O)]_n{\cdot}nH_2O$ (**4**), where L is 1-(1,2,4-triazol-3-yl)tetrazole (Figure 1). Butylated ligand **2** reacts with copper salt in ethanol giving 2D coordination polymer $[CuCl_2L]_n$ (**5**), where L is 1-[1-(*tert*-butyl)-1,2,4-triazol-3-yl]tetrazole (Figure 2). Surprisingly, coordination compounds of 1-(1,2,4-triazol-3-yl)tetrazoles have not been reported till now.

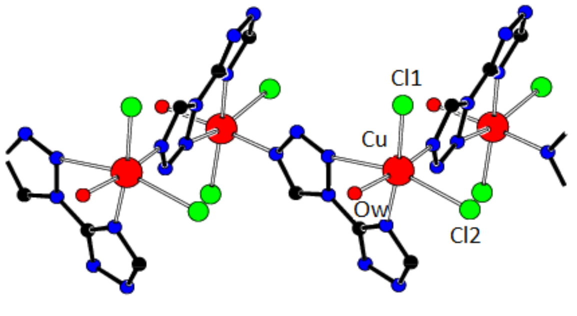


Figure 1. Fragment of coordination polymeric chain in complex **4**. Hydrogen atoms are omitted for clarity.

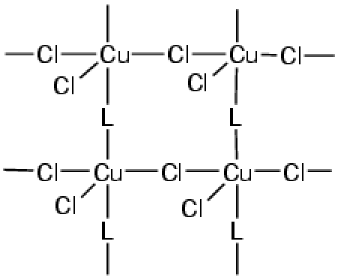


Figure 2. Schematic representation of polymeric layer in complex **5**.

[1] D. Srinivas, V. D. Ghuleb and K. Muralidharan, *RSC Adv.*, **2014**, *4*, 7041–7051.

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RHODIUM(III)-CATALYZED TRIFLUOROMETHYL-CARBENOID FUNCTIONALIZATION OF ARYL PURINES

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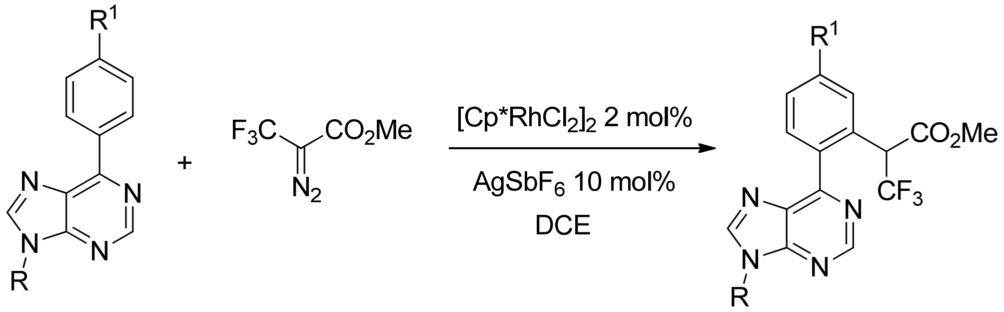
6-Arylpurines have been identified with a variety of valuable biological properties, such as anti-mycobacterial, cytostatic, and anti-HCV activities [1]. Therefore, selectively constructing functional 6-arylpurines is significant for emergency. It is well-known, the transition-metal-catalyzed functionalization of the C–H bond has emerged as one of the most efficient synthetic methods in terms atom-economy to construct diverse organic molecules from simple starting materials [2]. However, metal-catalyzed direct C-H functionalization of 6-arylpurines is rare. Previously, we have elaborated an efficient approach for direct CF_3-carbenoid C-H functionalization of (hetero)arenes, indoles and indolines using readily available methyl-3,3,3-trifluoro-2-diazopropionate as a cross-coupling partner under chelation-controlled Ru(III)-catalysis [3]. Herein, we wish to disclose our recent results on the direct Rh(III)-catalyzed CF_3-carbenoid functionalization of 6-aryl purines.



R = *i*-Pr, Bn

R^1 = H, Me, OMe, F

55-68 %

[1] (a) L.-L. Gundersen, J. Nissen-Meyer, B. Spilsberg, *J. Med. Chem.*, **2002**, 45, 1383-1386; (b) M. Hocek, P. Naus, R. Pohl, I. Votruba, P. A. Furman, P.M. Tharnish, M. J. Otto*, J. Med. Chem.*, **2005**, 48, 5869–5873; (c) A. K. Bakkestuen, L.-L. Gundersen, B.T. Utenova, *J. Med. Chem.*, **2005**, 48, 2710-2723.

[2] (a) Moselage, N. Sauermann, S. C. Richter, L. Ackermann, *Angew. Chem. Int. Ed.* **2015**, *54*, 6352; (b) Z. Chen, B. Wang, J. Zhang, W. Yu, Z. Liu, Y. Zhang, *Org. Chem. Front.,* **2015**, *2*, 1107.

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*P**-CHIRAL BISDIAMIDOPHOSPHITE LIGANDS FOR Pd- AND Rh-CATALYZED ASYMMETRIC REACTIONS

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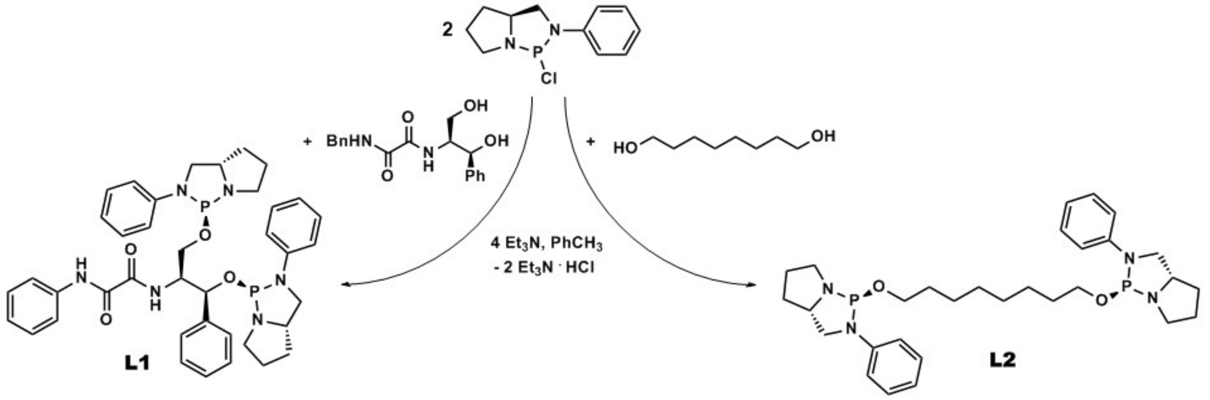
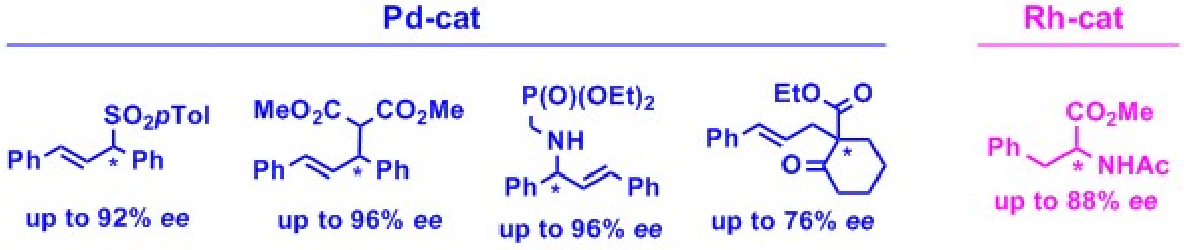
Bisdiamidophosphites **L1** and **L2** were synthesized in one step by condensing the phosphorylating reagent (2 equiv) with the corresponding diol in toluene in the presence of an excess of NEt_3 as a base. The new ligands were purified by flash chromatography on Al_2O_3 and isolated in good yields as white solids. Both compounds could be prepared on a gram scale. The elemental analyses as well as ^{1}H, ^{13}C, and ^{31}P NMR spectra are consistent with the expectation for these bisdiamidophosphites. During the phosphorylation, the exclusive formation of the stereoindividual bisdiamidophosphites **L1** and **L2** with an (*R*)-configuration at the asymmetric phosphorus atoms occurred.



With these bisdiamidophosphites in hand, initial studies were carried out with **L1** and **L2** as stereoselectors for Pd-catalyzed allylic sulfonylation of racemic (*E*)-1,3-diphenylallyl acetate with *p*-$TolSO_2Na$ as the S-nucleophile, alkylation with dimethyl malonate as the C-nucleophile and amination with diethyl aminomethylphosphonate as the N-nucleophile ($[Pd(allyl)Cl]_2$ was a palladium source). Next, we tested novel ligands in the Pd-catalyzed allylic alkylation of cinnamyl acetate with ethyl 2-oxocyclohexane-1-carboxylate, this is a challenging transformation where a quaternary stereogenic center is generated in the nucleophile. In order to further investigate the potential of readily available bisdiamidophosphites **L1** and **L2**, they were tested in the Rh-catalyzed enantioselective hydrogenation of (*Z*)-methyl 2-acetamido-3-phenylacrylate ($[Rh(COD)_2]BF_4$ was a rhodium source). Additional studies highlighting the potential of these ligands in other asymmetric reactions are currently in progress in our laboratory.



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SYNTHESIS OF LUMINESCENT Cu_4I_4 – COMPLEXES WITH 10-(ARYL)PHENOXARSINES

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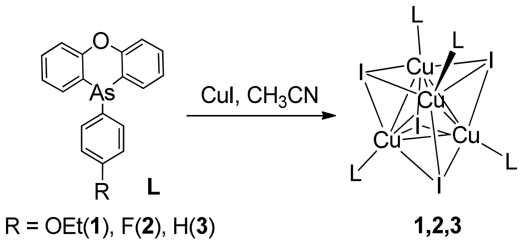
The complexes of copper (I) halides have been of great interest due to the large variety of their photophysical properties associated with the ability of copper (I) halides to form various types of structures [1]. The composition and structure of the complexes depend on the geometry and steric factors of the ligand, type of solvent and ligand to metal ratio [2]. It is known that the Cu_4I_4 clusters with various pnictogen ligands demonstrate luminescent properties [3,4].

This report is devoted to the synthesis of Cu (I) iodide complexes of 10-(aryl)phenoxarsines with a tetrameric Cu_4I_4-core and the study of their luminescence in the solid state.

Complexes **1-3** of the composition $Cu_4I_4L_4$ are obtained by the reaction of 10-(aryl)-phenoxarsine ligands (**L**) with copper iodide in the equal molar ratio in acetonitrile (Scheme 1). The structures of **1** and **2** were analyzed by the X-ray crystallography (Figure 1). Phenoxarsine ligands are As-monodentate. In Cu_4I_4-core four copper atoms occupy the vertices of a tetrahedron, each of them is connected via three bridging iodides. Each copper atom has the tetrahedral geometry.



Scheme 1

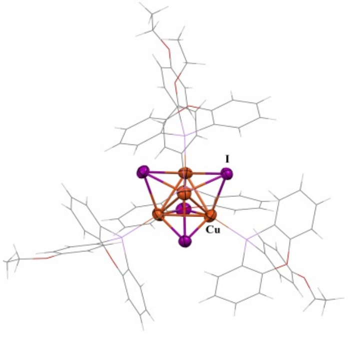


Figure 1

Complexes**1-3** exhibit intense green luminescence (λ_{max}=525-540 nm) under UV irradiation in the solid state with lifetimes 3.0-6.4 *μs*.

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α-HYDROXYCARBOXYLATES OF RARE EARTH, ALKALINE EARTH AND SOME TRANSITION METALS: SYNTHESIS, STRUCTURE AND OXIDE THIN FILMS DEPOSITION

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Nowadays the great attention is paid to developing of new techniques for fabrication of thin film functional materials. Among the large variety of physical and chemical methods the Metal-Organic Chemical Solution Deposition (MOCSD) is considered as the most flexible and promising. This method is characterized by the low cost, high reproducibility, technical simplicity and highly effective control of the composition and thickness of obtained films. However, MOCSD requires the precursor solution in polar and volatile organic solvents, mainly alcohols, to be developed for each metal. Moreover, in case of complex oxide thin films these precursors must be compatible to each other.

In the present work we have focused on rare earth, alkaline earth and some transition metal α-hydroxycarboxylates and their mixed-ligand complexes with N-donor ligands, monoethanolamine and diethylenetriamine. α-Hydroxycarboxylates (glycolates, lactates, etc.) are low-cost and environmental friendly compounds, which demonstrates sufficient stability in solution being formed by chelating ligands. Metal lactates are widely applied in medicine (e.g. as contrast agents for MRI), in lanthanide-actinide separation and household chemistry. Nevertheless, the detailed synthesis, crystal structure and thermal behavior of metal lactates as well as their application for thin film deposition have not yet been studied.

Here we reported the successful synthesis in aqueous solution of Ca, Sr, Ba, La-Lu, Y, Zr, Fe, Ni, Mn lactates and glycolates of general formula $[M(Carb)_n(H_2O)_m]$. Their composition, structure and thermal behavior were studied by TGA, IR spectroscopy, powder and single crystal XRD as well as DFT simulations. Several crystal structures have been reported for the first time. Lactate- and glycolate-anions always act as bi- and tridentate bridging ligands, capable of both forming 1D-polymeric chains and individual molecules linked together by hydrogen bonds with limited solubility in organic solvents.

The reactions with N-donor ligands allows to increase the solubility of metal α-hydroxycarboxylates due to formation of mixed ligand complexes with saturated coordination sphere of central ion. Moreover, the interaction of amine ligand with water traces under thermal treatment of precursor solution results in decreasing of it decomposition temperature. As a result a large variety of amorphous and crystalline homogeneous and uniform thin film were obtained: planarizing layers (Y_2O_3, La_2O_3), thermal barrier (ZrO_2:Y_2O_3), and functional ($LaNiO_3$, $LaMnO_3$, $LuFeO_3$) oxide thin films.

Acknowledgements – Theoretical simulations were performed within the resources of Supercomputing Center of Lomonosov Moscow State University.

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STRUCTURE, THERMODYNAMICS AND STEREOSELECTIVITY OF FORMATION OF HOMO- AND HETEROLIGAND ZINC(II) COMPLEXES WITH AMINO ACIDS

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Homo- and heteroligand complexes of zinc(II) with amino acids (Amac) are of great interest for bioinorganic chemistry as models of active centres of numerous zinc-containing enzymes, primarily hydrolytic ferments. It is equally important that the study of the zinc(II) complexes with enantiomeric amino acids makes it possible to identify stereoselective effects in complex formation and to conclude about the role of metal nature in the stereoselective processesfrom comparisonsuch effects for the zinc(II) complexes with the corresponding nickel(II) and copper(II) complexes.

In the present work thermodynamics and stereoselectivityof homo- and heteroligand complex formation in the binary and ternary systems zinc(II) –*L*/*D*/*DL*-amino acids (histidine, HisH; aspartic acid, $AspH_2$; serine, SerH; threonine ThrH; phenylalanine, PheH; tryptophan, TrpH; methionine, MetH; and cysteine, $CysH_2$) at 25.0°C in aqueous solutions with 1.0 mol dm^{-3} KNO_3 as backgroundhave been studied by the pH-metry method in combination with mathematical modeling using the program STALABS [1].In addition to *mono*- and *bis*-complexes, hydroxo-complexes of the compositions Zn(Amac)(OH), $Zn(Amac)_2(OH)$, and $Zn(Amac_1)(Amac_2)(OH)$were discovered and characterizedfor the first time. These hydroxo-complexes are of particular importanceformodelling active centres of zinc-containing enzymes.

Statistically significant stereoselective effects of complex formation were revealed in many studied binary and ternary systems.The most significant enantioselective effects were found for homoligand complexes $Zn(His)_2$, $Zn(Phe)_2$, and $Zn(Trp)_2$as well as forheteroligand complexes Zn(Met)(His), Zn(CysH)(His), and Zn(Trp)(His).

The interpretation of the revealedstereoselective effects was performedwith using quantum chemical computations of the various structures of possible isomers of some complexes by the DFT method with GAMESS program [2] at the CAM-B3LYP/TZVPlevel, taking into account the solvent effects in the polarizable continuum model (C-PCM).

From the comparison of the thermodynamic and quantum chemical computations data obtained it was shown that main factorscontrolling the stereoselectivity of formation of the zinc(II) amino acids homo- and heteroligandcomplexesare the following: *trans*effect,"softness" of ligand and central ion, inter-ligand hydrogen bonds formation, and*d*-π-interaction metal-ligand.

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SYNTHESIS OF HETEROGENEOUS CATALYSTS BASED ON OCTACARBOXYPHTHALOCYANINES OF COBALT AND COPPER

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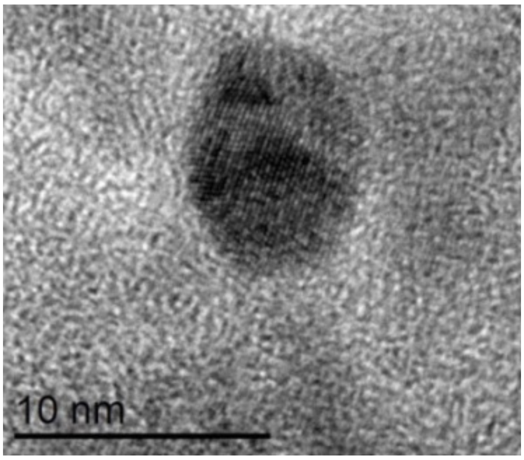
Metal-organic frameworks (MOFs) are highly porous materials containing metal cations coordinated with organic polydentate ligands, such as terephthalic acid. This type of compounds is intensively investigated as catalysts, effective sorbents ets. [1]. The metallophthalocyanines are synthetically available and more accessible in comparison with porphyrinates. These compounds demonstrated the high stability and perspective as building blocks for the development of new materials.



Photomicrograph sectional nanomaterial obtained based octacarboxyphthalocyanine of copper

Materials based on octacarboxyphthalocyanines of copper and cobalt with varying linkers were synthetized. The manganese and aluminum salts were used as linkers. The different properties of these compounds were investigated. Resulting materials are dark blue colored powders contained nano sized fibers (see Fig). The structure of materials depend on the structure of starting octacarboxyphthalocyaninate.

Is has been shown that octacarboxyphthalocyanine ligand containing complexes exhibit high catalytic activity in the reactions of oxidation of natural compounds by air oxygen. This opens perspectives for preparation of materials with specific properties and selectivity by changing of the nature of central and peripheral cations.

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CROWN-ETHER CONTAINING PHTHALOCYANINES IN LOW-MOLECULAR-WEIGHT HYDROGELS: PROPERTIES, MOLECULAR STATE, AND RELEASE

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Labile supramolecular ensembles of low- and high-molecular-weight gelators can act as excellent *hosts* for incorporating various *guests*, including nano materials. Bile acid salts (BS), among which sodium deoxycholate (SDC) and sodium taurodeoxycholate (STDC), belong to the class of natural surfactants with clear-cut features.

This study is devoted to (a) extending the range of natural surfactants suitable for solubilization of crown-containing phthalocyanines (Pc) in aqueous media and to exploring (b) the behaviour of new Pc in low-molecular-weight hydrogels based on BS, and (c) a process of active component, Mcr_xPc (x = 8, M = Mg, Zn; x = 4, M = Mg), release from the gel under the action of external influences such as heating or the addition of some amino acids. $Mgcr_8Pc$ in the monomeric form is responsible for fluorescent activity of the Pc-bearing supramolecular hydrogel [1]. The properties of the systems under study were characterized by absorption spectroscopy, scanning electron microscopy, Fourier transform infrared spectra, small-angle X-ray scattering, and others.

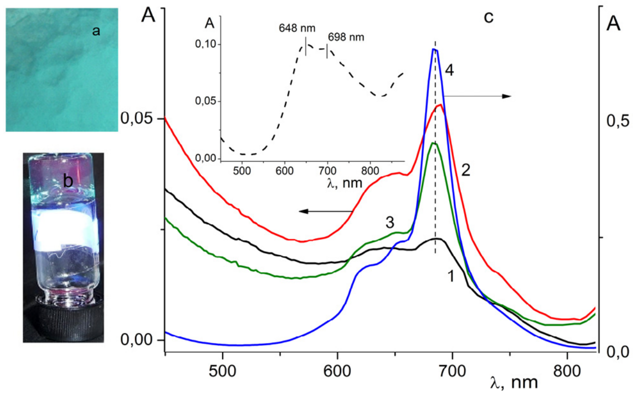

Fig. Photos of (a) $Mgcr_8Pc/SDC/lys{\cdot}HCl/NaCl$ gel and (b) $Mgcr_8Pc/SDC/lys{\cdot}HCl$ gel under illumination in the near-UV spectral range; and (c) absorption spectra of $Mgcr_8Pc/SDC/lys{\cdot}HCl$ (1), $Mgcr_8Pc/SDC/lys{\cdot}HCl/NaCl$ (2), $Mgcr_8Pc/SDC/NaCl$ gels (3) and of micellar solution of $Mgcr_8Pc/SDC/NaCl$ (4). Quartz slide was used as a substrate. For all gels, the [SDC]/[$Mgcr_8Pc$] ratio was around 800. In the insert: absorption spectrum of $Mgcr_8Pc$ film.

$Mgcr_8Pc$: magnesium octa[(4'-benzo-15-crown-5)-oxy]phthalocyanine; lys·HCl: lysine hydrochloride

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SYNTHESIS AND LUMINESCENT PROPERTIES OF MIXED-METAL LANTHANIDE 1,2,3-TRIAZOLEDICARBOXYLATES

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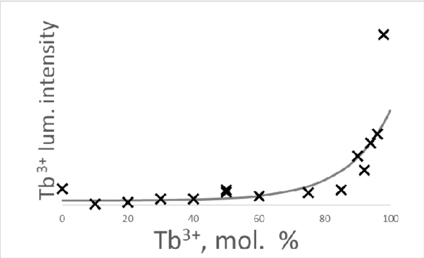
Metal Organic Frameworks(MOF) have been in the chemists' center of attention for the last decades. The structure of MOF contains bulk pores which are able to hold "guest molecules". This property allows usage of MOFs in catalysis, separation and storage of gases and sensors. Lanthanide-based frameworks are especially interesting due to luminescent and magnetic properties of rare-earth elements. Selective sorption of "guest molecule" by MOF-type substance can lead to luminescent sensoric response. Some of the described [1] MOFs based on mixed metal systems show an example of sensibilisation of one lanthanide's luminescence by the other. The change of this sensibilisation efficiency leads change in ratio of two lanthanides' luminescence intensity, which can be used as positive sensoric response

The current work consists of synthesis and research of mixed coordination compounds of Eu and Tb with 1,2,3-triazole-4,5-dicarbolic acid(H_3TDA) as ligand.

Synthetical availability, ability to sensibilize luminescence of both Eu and Tb and modification simplicity via the N1 atom makes H_3TDA a convenient model object. The complexes have been synthesized hydrothermally by heating aqueous solutions containing lanthanide salts, ligand and base in Teflon-lined stainless steel autoclave at 160*C for 48 hours.

The samples have been characterized with XRD, DTA, XPS-, IR- and luminescence spectroscopy. XPS-spectroscopy data confirmed the molar ratio of Tb and Eu ions used in synthesis. According to XRD pattern and IR-spectroscopy data, all obtained substances are isostructural to the one of formula $[Eu_2(TDA)_2(H_2O)_3]*5H_2O$ described earlier in paper [2]. IR-spectra consist of bands that match with only coordinated ligand, which confirms the absence of ligand as "guest molecule" in the structure of obtained MOF. The TDA shows that heating the substance up to 250*C leads to the loss of 10% of the mass, which can be the result of water molecules' exit from the inner coordination sphere of the metal. Heating at 400*C leads to full decomposition of the substance.



The color of samples' luminescence changes gradually from green, which corresponds to 100% of Tb, to red, which corresponds to 100% of Eu. Samples' emission spectra contain bands that correspond to f-f transitions of both Eu and Tb. Nevertheless, Tb luminescence intensity's dependence on its molar fraction has non-linear(exponential) type, greatly increasing from zero only at 90% of Tb. At the same time, even if the substance contains 2% of Eu, its luminescence intensity can be compared to the one of Tb in it. This fact confirms the presence of energy transfer that follows the scheme: $TDA^{3-} \rightarrow Tb^{3+} \rightarrow Eu^{3+}$, which allows us to recommend obtained substances as luminescent sensors.

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Ag^0@SiO_2 NANOPARTICLES IN OXIDATIVE CATALYSIS

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Metal nanoparticles have attracted considerable attention because of their novel physical properties and their potential applications in areas such as catalysis. Among various metal nanoparticles, silver nanoparticles attract special attention due to the fact that they can be employed as sensors, and also have high catalytic activity. In addition, silver nanoparticles in solution quickly aggregate, so they need stabilization. In solution media, these nanoparticles are usually stabilized by surfactants, organic acids or through the encapsulation within the polymer matrix. However, these methods lead to a partial loss of catalytic activity of metal nanoparticles. The most promising way of Ag (0) nanoparticles stabilization is through doping them inside the silica nanoparticles. Silica nanoparticles are characterized by biocompatibility, good dispersibility in the aquatic environment, and physico-chemical stability.

In this study, silica nanoparticles containing silver nanoparticles inside a polymer matrix were synthesized. Nanoparticles are characterized by TEM, UV and luminescence spectroscopy.

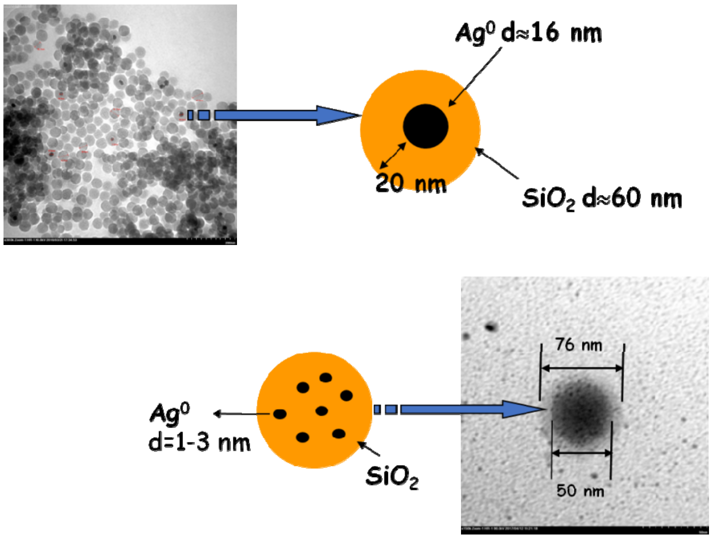

Fig. TEM-images of silica nanoparticles doped silver nanoparticles

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THERMODYMAMIC AND ELECTROCHEMICAL PROPERTIES OF COBALT(II), NICKEL(II), COPPER(II), ZINC(II) COMPLEXES FOR SOME AMINO ACIDS

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The electrodeposition of some metals and binary alloys is known to be normally used blocking out corrosion of steelwork. At present there is a growing interest in the application of electrolytes including various organic and inorganic ligands which form stable complexes under conditions of the electrolysis. But it is confronted with the difficulties in understanding of the electrochemical behavior of these complexes because there appears a lot of the ionic species which are capable of being electroactive. The limited type of the reliable reference data sources for the thermodynamic and electrochemical properties is powerless to provide the relations between the functions of the individual reactions in the multiconstituent systems. Comprehensive study of the electrolytes containing compounds with amino and carboxylic groups being able to form the chelate rings is the key to solving this problem.

This work presents results of calorimetric, potentiometric and spectrophotometric investigations of the acid-base interaction and cobalt(II), nickel(II), copper(II), zinc(II) complex formation processes in aqueous solutions of some amino acids. Among the objects investigated are homoserine, serine, threonine, taurine, glycine, alanine, valine and aspartic acid. Thermodynamic parameters (logK, ΔG, ΔH, ΔS) for the relevant equilibria have been determined at 298.15 K and ionic strength values from 0.1 up to 1.5 M. The influence of background electrolyte character and concentration on the protolytic and coordination equilibria has been discussed. The standard thermodynamic parameters (logK°, ΔG°, ΔH°, ΔS°) have been evaluated for the corresponding reactions. The results obtained were compared with the reference data on related compounds investigated earlier in this laboratory under the same experimental conditions. A plausible explanation of changes in these quantities has been proposed in view of the metal ion and ligand structures (type of coordination, denticity, presence of hydrophobic and hydrophilic fragments, solvation features of the zwitter ions).

The electrodeposition of zinc, nickel, cobalt and binary alloys of these metals from some amino acid solutions have been examined by cyclic voltammetry and polarization curve measurements in order to galvanize a 08KP steel. The influence of the competitive protolytic and coordination equilibria on the relevant processes occurred at the electrode surface was under consideration. The results were compared with the corresponding data for electrolytes containing some useful carboxylates, amines, aminoalcohols and complexones investigated earlier. A complex approach to the research of the solution equilibria and electrode processes allowed us not only to analyse precisely the information but to optimize the electrolytic bath compositions and electrolysis conditions, based on the analysis. New promising electrolytes have been suggested for plating with alloys of zinc-cobalt and zinc-nickel. The deposits obtained had excellent tribometric and anticorrosion characteristics.

Acknowledgements - The development of the galvanic bath electrolytes was specified by the Ministry of Education and Science of the Russian Federation. The study on thermodynamic properties of the amino acid complexes was partially supported by the Russian Foundation for Basic Research, project 14-03-00360-a.

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27th International Chugaev Conference on Coordination Chemistry
4th Conference-School for Young Researchers “Physicochemical Methods in Coordination Chemistry”
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THE SYNTHESIS OF NEW TRICARBONYLCHROMIUM DERIVATIVES OF 1,3-OXAZOLIDINES BY CONDENSATION REACTION

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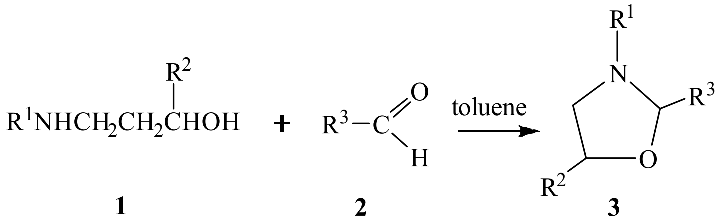
1,3-Oxazolidines are a large class of natural and synthetic heterocyclic compounds widely used in medicine, pharmacology, agriculture and other spheres. The aim of our research was the synthesis of new (η^6-arene)tricarbonylchromium derivatives of 1,3-oxazolidines by condensation reaction between β-substituted aminoalcohols (**1**) and aldehydes (**2**) (scheme 1):

Scheme 1



a: R^1= Ph[Cr(CO)$_3$], R^2=H, R^3=Me; **b**: R^1= Ph[Cr(CO)$_3$], R^2=Me, R^3=Me; **c**: R^1= Ph[Cr(CO)$_3$], R^2=H, R^3=H; **d**: R^1= Ph[Cr(CO)$_3$], R^2=Me, R^3=H; **e**: R^1=H, R^2=H, R^3= Ph[Cr(CO)$_3$]; **f**: R^1=Ph, R^2=H, R^3= Ph[Cr(CO)$_3$]; **g**: R^1= Ph[Cr(CO)$_3$], R^2=H, R^3=Ph; **h**: R^1=Ph, R^2=Me, R^3= Ph[Cr(CO)$_3$]; **i**: R^1= Ph[Cr(CO)$_3$], R^2=Me, R^3=Ph;

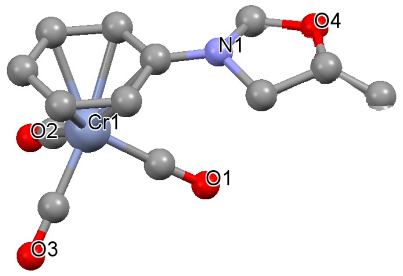


Figure 1. Molecular structure of chromium-containing 1,3-oxazolidine **3d**.

The synthesized 1,3-oxazolidines (**3**) were isolated and purified by column chromatography and crystallization from hexane - ethyl acetate and characterized by HPLC, UV-, IR-, ^{1}H NMR-spectroscopy, mass-spectrometry and X-ray diffraction analysis (Figure 1). Some characteristics of synthesized heterocyclic compounds are represented in Table 1.

Table 1. Some characteristics of 1,3-oxazolidines **3a-f**

1,3-Oxazolidine	Yield, %	M.p., °C	IR (ν(C≡O)), cm^{-1}	Mass Spectrum (EI, 70 eV), m/z (I_{rel} (%))
3a	31	71-72	1884, 1950	299 $[M]^+$ (10), 215 $[M\text{-}3CO]^+$ (48)
3b	22	84-85	1855, 1937	313 $[M]^+$ (50), 229 $[M\text{-}3CO]^+$ (30)
3c	47	126-127	1843, 1945	285 $[M]^+$ (30), 201 $[M\text{-}3CO]^+$ (100)
3d	30	131-132	1848, 1945	299 $[M]^+$ (30), 215 $[M\text{-}3CO]^+$ (28)
3e	40	-	1961, 1880	285 $[M]^+$ (31), 201 $[M\text{-}3CO]^+$ (93)
3f	39	-	1884, 1970	361 $[M]^+$ (8); 277 $[M\text{-}3CO]^+$ (48)

Thus, we obtained a number of new (η^6-arene)tricarbonylchromium complexes with N,O-heterocyclic ligands and found out that the presence of bulky Ph and Ph[Cr(CO)$_3$]-groups both aminoalcohol and aldehyde molecules prevents the condensation reactions: the formation of 1,3-oxazolidines **3g-i** are not observed.

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CATALYTIC ACTIVITY OF TETRA {PEROXODICHLOROPHOSPHINRHODIUM (III)} - CALIX[4] REZORCINE IN MODEL REACTIONS OF METHYL METHACRYLATE AND VINYL ACETATE POLYMERIZATION

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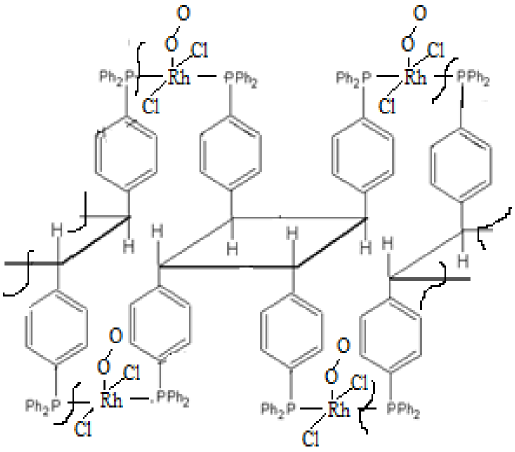

The results of studies of the catalytic activity of calix [4] resorcinol tetra-(peroxodichlorophosphin- rhodium (III)} (**1**) [1] are exemplified by model polymerization reactions of methyl methacrylate (MMA) and vinyl acetate (BA). Polymerization products MMA and VA - polymethyl methacrylate (PMMA) and polyvinyl acetate (PVA) are the most important and highly demanded polymers. The figure shows complex 1 - the upper rim of calix [4] resorcinol (rctt-conformer, trans-isomer) is shown as a plane of symmetry. The lower rim with aryl diphenylphosphine-new radicals being covalently associated with Rh (III) peroxodichlorocomplexes have been marked. The high catalytic activity of **1** is revealed due to peroxide radicals rapidly replacing the solvent molecules in the reaction mixture and the possibility of electronic redistribution between the coordination center and the calixresorcinic matrix owing to the transfer of one or two electrons.

For the purpose of testing the catalytic activity, the dependence of the reaction rate constant on the concentration of C_1 complex in the initiating mixture "benzoyl peroxide + 1" (PB + 1) and also on the ratio of solvents (formamide: dioxane,% by volume) were studied. In experiments with MMA and VA, catalytic activity of **1** was studied at $C_1 = 0.5 \cdot 10^{-4} \div 2.5 \cdot 10^{-4}$ mol/l, however, the kinetics of the initial stage could be fixed only for the ratios 10:90 and 20:80. With the increase in the volume content of formamide in the solvent mixture, the reaction mixture was stratified.

The velocities and reaction rate constants, as well as the order of reactions along the initiating mixture are calculated. The report discusses the effect of C_1 in the initiating mixture (PB + 1) and composition of the solvent on the polymerization rate and the molecular weight distribution (MWD) of the polymer samples. A comparative analysis of the effectiveness of the system (PB + 1) and previously described systems is carried out. It is shown that the use of the mixture (PB + 1) promotes an increase in the reaction rate constant by a factor of 10 and the preservation of narrow MWD polymer samples. There is a tendency to the formation of macromolecules with a low molecular weight is observed.

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DIRECT SYNTHESIS AND CRYSTAL STRUCTURE OF COPPER(II) THIOCYANATE COMPLEXES WITH N-*TERT*-BUTYLAZOLES

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Direct synthesis of coordination compounds from zerovalent metals has become an active area of chemical research owing to its potential ability to generate the complexes, being unavailable by traditional synthetic routes [1]. Recently, we showed that this approach was a facile and convenient tool toward coordination compounds with some tetrazole ligands. In particular, novel Cu(II), and heterobimetallic Cu(II)/Mn(II) and Cu(II)/Zn(II) complexes of different nuclearity were prepared [2].

Here we report direct synthesis of copper(II) thiocyanate complexes with 1-*tert*-butyl-1,2,4-triazole (btr) and 2-*tert*-butyltetrazole (btt). All the obtained complexes were characterized by single crystal X-ray analysis. We found that interaction of a copper powder with btr and ammonium thiocyanate in DMSO at a molar ratio Cu : btr : NH_4SCN = 1 : 2 : 2 gave compound $[Cu(btr)_2(SCN)_2]_n$ (**1**). Analogous reaction but using excess of btr (10 eq.) in toluene resulted in complex $[Cu(btr)_3(SCN)_2]$ (**2**). Interaction of a copper powder with thiocyanate and btt without any solvents allowed to obtain coordination compound $[Cu(btt)_2(SCN)_2]_n$ (**3**).

Complexes **1** and **3** was found to be 1D coordination polymers, formed due to bridging thiocyanate anions (Figure 1). They are isotypic, showing only very small difference in the crystal structures. Compound **2** presents a mononuclear complex, in which thiocyanate anions are coordinated by metal cations through the nitrogen atoms (Figure 2). In compounds **1**–**3**, btr and btt act as monodentate ligands coordinated by Cu(II) cations *via* the heteroring N^4 atoms.

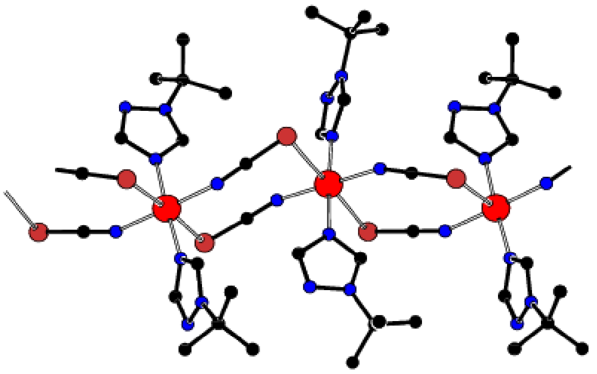

Figure 1. Coordination polymeric chain in the crystal structure of **1**. Hydrogen atoms are omitted for clarity.

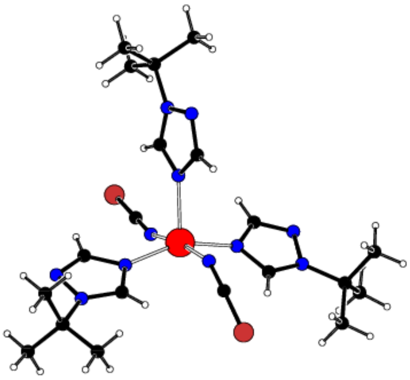

Figure 2. Complex molecule in the crystal structure of **2**.

[1] V. V. Skopenko, V. N. Kokozay, O. Y. Vassilieva, V. A. Pavlenko, Oxidative dissolution of metals and metal oxides in a liquid phase, in: A.D. Garnovskii, B.I. Kharisov (Eds.), Direct synthesis of coordination and organometallic compounds, Elsevier Science, Amsterdam, 1999.
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SYNTHESIS OF COMPLEX OF Bi(III) WITH CEFAZOLINE

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Cephalosporins are antibiotics used in the treatment of diseases caused by β-lactamases. Cephalosporins are chemically related to penicillins, which predetermines a similar mechanism of their antimicrobial activity, mechanism of resistance, and other properties. Many metal complexes of cephalosporins have toxicological and pharmacological properties but when these compounds are located in the organism, properties of the complexes can change. The metalloantibiotic complexes, for example bismuth compounds, can be used in medicine. In addition, bismuth compounds are used against bacteria *Helicobacter pylori*. The purpose of the paper is to study the synthesis of complexes of cefozaline with Bi(III) and discuss its physicochemical properties.

The compound was synthesized in the molar ratio of metal to ligand 1:1 in water medium, pH=2. A brown precipitate was formed in 4 hour. The product yield was 80-90%. The complex was determined by physicochemical, elemental and thermal analysis, IR, Raman and NMR spectroscopy, X-ray.

The compounds have the chemical composition of $[Bi(Cef)(H_2O)_2(OH)_2]$. The complex is soluble in DMSO and DMFA but it is insoluble in water and EtOH. The complex $[Bi(Cef)(H_2O)_2(OH)_2]$ is obtained in crystalline form. Cell parameters determined for the complex: a=12,063 Å, b=11,977 Å, c=10,114 Å, α =110,955°, β = 99,490°, γ=70,902°, V=1287,60 Å^3, space group symbol: $P2_1$, system group: centrosymmetric, space group number: 2.

To establish the type of coordination of cefazoline to metal ions, the FT-IR Raman and NMR spectra of sodium cefazoline and $[Bi(Cef)(H_2O)_2(OH)_2]$ were analyzed. Cefazoline has several donor atoms: oxygen atoms of carboxylate, lactam, and amide carbonyl group and sulfur atoms. In the IR spectrum of the complex, ν(C=O)-lactam vibration and symmetric and asymmetric stretching vibrations of COO^- group are shifted relative to spectrum of sodium cefazoline. This shows that the oxygen atoms of the lactam and carboxylate group are bound to the metal ion. A Sulfur atom of sulphanyl is coordinated to bismuth ions by the data of Raman and NMR spectra. This analysis is in agreement with previous studies where cefozaline is described as a polydentate ligand. In addition, a bismuth ion is bound with two water molecules and two hydroxy groups.

Authors express their thanks to the Centre for Equipment Joint User of Siberian Federal University, Institute of Chemistry and Chemical Technology SB RAS for technical support.

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A DIMETHYLSULFIDE OSMIUM(III,IV) COMPLEX SYNTHESIZED VIA THE MICROWAVE-ASSISTED INTERACTION OF $K_2[OsCl_6]$ WITH DMSO

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Attempted syntheses of dymethylsulfide osmium complexes via the interaction of $[OsX_6]^{2-}$ with dimethyl sulfide (hereinafter, dms) have remained unsuccessful so far. The only chlorodimethylsulfide osmium complex $[Os^{IV}Cl_4(dms)_2]$ was prepared by thermal treatment of $[H(dmso)_2]_2[OsCl_6]$ as a result of the dehydrochlorination and deoxygenation of dymethyl sulfoxide. Effects of microwave (MW) irradiation on the synthesis has been also unexplored.

A novel dimethylsulfide osmium complex $[Os^{III}Cl_2(dms)_4][Os^{IV}Cl_5(dms)]$ was isolated as orange red crystals from a reaction medium of $K_2[OsCl_6]$ $C_{Os} \sim 0.4$ M) in DMSO autoclaved at 100 °C for 10 min under MW irradiation at a power of 100 W. The product was washed with chloroform and water to remove dimethyl sulfone. MALDI mass spectrum of the product reveals a dominant isotope cluster with 790 m/z attributed to $[Os_2Cl_7S_5+H]^+$ cation. Mid-IR spectrum measured in the attenuated total reflection (ATR) mode with a ZnSe crystal reveals a set of bands clearly attributable to vibrations of CH_3-groups of DMSO at 981 and 1026 cm^{-1} $\rho(CH_3)$ as well as at 1298, 1324, and 1422 cm^{-1} $\delta(CH_3)$. Far-IR spectrum (diamond) is dominated by ν(Os-Cl) vibrations at 302 and 168 cm^{-1}. UV-Vis spectrum of an DMSO solution manifests absorption bands at λ_{max} = 367 and 430sh nm.

The molecular structure of the complex has been unambiguously established by single-crystal X-ray crystallography (see Figure). The complex is built of $[OsCl_2(dms)_4]^+$ cation and $[OsCl_5(dms)]^-$ anion. In both moieties, the coordination environment of osmium atoms can be described as distorted octahedra. In the cation, the chloride atoms are disposed in the *trans*-position to each other with four dimethylsulfide ligands of the equatorial plane adopting a propeller conformation. The Os←S coordination bonds in the cation (2.366(6)-2.393(2) Å) are somewhat shorter than those in the anion 2.429(3) Å. In contrast, the Os-Cl covalent bonds in the cation (2.407(4) Å) are somewhat longer than those in the anion (2.315(3)-2.331(2) Å).

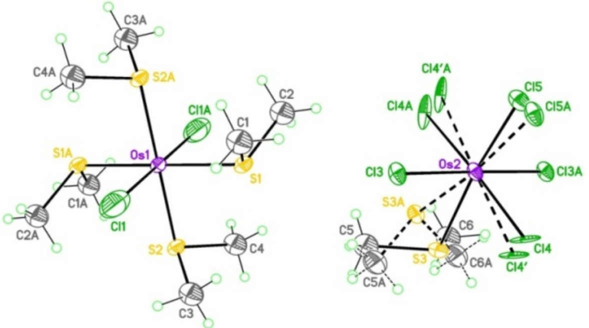

Figure. The Molecular structure of
$[Os^{III}Cl_2(dms)_4][Os^{IV}Cl_5(dms)]$

T, K	100(2)
λ, Å	0.98700
Singony	monoclinic
Sp. gr.	P2/c
Z	2
a, Å	7.8600(16)
b, Å	8.7250(17)
c, Å	19.630(4)
β, °	96.67(3)
α, γ, °	90
V, $Å^3$	1337.1(5)
$R_1 = 0.062$, $wR_2 = 0.160$	

It is of note that the complex reported has no close analogs among related compounds of noble metals. Only one structurally similar anion has been reported for Pt(IV).

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SYNTHESIS AND X-RAY STRUCTURE OF HYBRID BINUCLEAR TETRAPYRROLE-CAPPED TRIS-PYRIDINEOXIMATES

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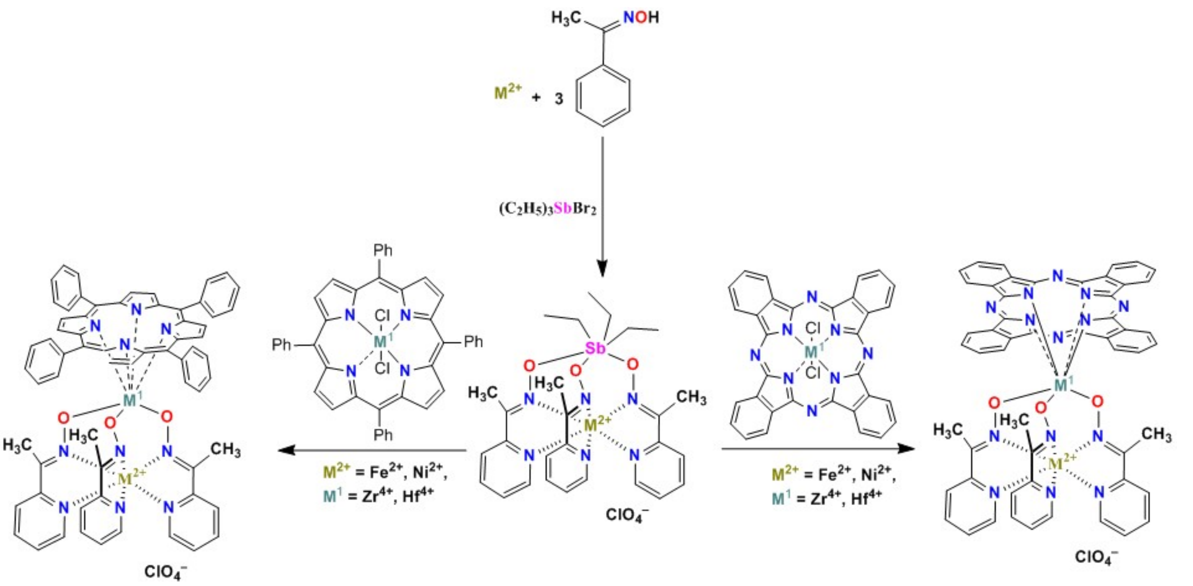
Pseudoencapsulating monocapped tris-azomethine 3d-metal complexes of the tripodal N_6-hexadentate ligands [1] possess unique spectral characteristics [2] and magnetic properties, including a single-molecule magnet behavior [3]. Hybrid metal(IV) phthalocyaninato- and porphyrinato-capped iron and nickel complexes of this type were obtained by Scheme 1 *via* transmetallation of their triethylantimony-cross-linked precursors using a Lewis acidity of zirconium and hafnium(IV) phthalocyaninates and porphyrinates.



Scheme 1

New polynuclear compounds were characterized using UV-Vis, MALDI-TOF MS, IR and multinuclear 1D and 2D NMR spectra, and by single crystal X-ray diffraction; their redox properties were studied using cyclic and differential pulse voltammetry methods.

[1] O.A. Varzatskii, L.V. Penkova, S.V. Kats, A.V. Dolganov, A.V. Vologzhanina, A.A. Pavlov, V.V. Novikov, A.S. Bogomyakov, V.N. Nemykin and Y.Z. Voloshin, *Inorg. Chem.*, **2014**, *53*, 3062-3071.
[2] M. Azarkh, L. Penkova, S. Kats, O. Varzatskii, Y. Voloshin and E. Groenen, *J. Phys.Chem. Lett.*, **2014**, *5*, 886-889.
[3] V.V. Novikov, A.A. Pavlov, Y.V. Nelyubina, M.-E. Boulon, O.A. Varzatskii, Y.Z. Voloshin and R.E.P. Winpenny, *J. Am. Chem. Soc.* **2015**, *137*, 9792-9795.

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SYNTHESIS, STRUCTURE, BIOLOGICAL AND MAGNETIC ACTIVITY OF Co(II), Ni(II) AND Cu(II) COORDINATION COMPOUNDS WITH HETEROCYCLIC POLYNITROGEN LIGANDS

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Complexes of 3*d* metals with heterocyclic polynitrogen ligands are of great interest to scientists, since such compounds have a significant biological activity and/or nontrivial magnetic properties. From this point of view, 1,2,4-triazolo[1,5-a]benzimidazoles, pyrimidines and pyridazines represent a promising classes of ligands for the synthesis of transition metal ions coordination compounds.

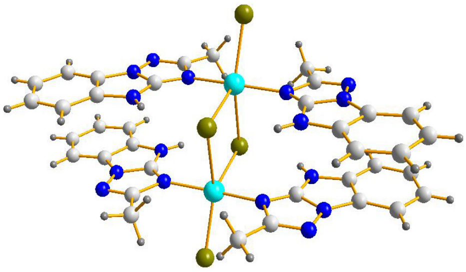
Fig. 1. Structure of $Cu_2(L^1)_4(\mu\text{-}Br)_2Br_2$

Co(II), Ni(II) and Cu(II) coordination compounds with 2-methyl- and 2,4-dimethyl-1,2,4-triazolo[1,5-a] benzimidazoles (L^1, L^2), 4-aminopyridazine (L^3) and 2-N-acetylaminopyrimidine (L^4) presented as $[Co(L^1)_2Cl_2]\cdot0,5H_2O$ (I), $[Ni(L^1)_2(H_2O)_4]Cl_2\cdot4H_2O$ (II), $Cu_2(L^1)_4(\mu\text{-}Br)_2Br_2$ (III), $Co(L^2)_2Cl_2$ (IV), $Cu(L^2)_2A_2$ ($A=Cl^-$, Br^-) (V, VI), $Cu(L^3)A_2$, ($A=Cl^-$, Br^-) (VII, VIII), $[M(L^4)_2Cl_2]\cdot2H_2O$ (M=Co(II), Ni(II)) (IX, X) and $Cu(L^4)_2A_2$ ($A=Cl^-$, Br^-, NO_3^-) (XI-XIII) have been synthesized. The compounds have been studied using elemental analysis and methods IR and UV/Vis spectroscopy, powder X-ray diffraction, and the static magnetic susceptibility. The crystal and molecular structures of I-V have been determined using a single crystal X-ray diffraction technique (Fig. 1).

A High Content Analysis was carried out to investigate the cytotoxic effect of ligands L^1, L^2, L^4 and complexes I, III-VI, IX-XIII exerted on human larynx carcinoma cell line (Hep-2). The investigation was performed using a method of double staining with fluorescent dyes Hoechst and Propidium Iodide, which allows one to isolate living, apoptotic and dead cells. The ligands showed an insignificant cell death (up to 10% at the final concentration 125 μM). However, the complexation of Cu(II) with the mentioned ligands allows one to obtain much more efficient compounds as to compare with free organic ligands. The effect of the complexes leads to a significant cell death to occur (IC_{50} = 17 and 18 μM for III and XI respectively). Thus, the study of the synthesized Cu(II) complexes as potential antitumor drugs is a promising direction of research.

Study of the dependence $\mu_{eff}(T)$ within the temperature range of 2-300 K have shown that there are antiferromagnetic exchange interactions between Cu(II) in the complexes VI, VII.

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COMPLEXES OF 14 AND 15 GROUP ELEMENTS BASED ON PHENANTRENE-9,10-DIIMINES

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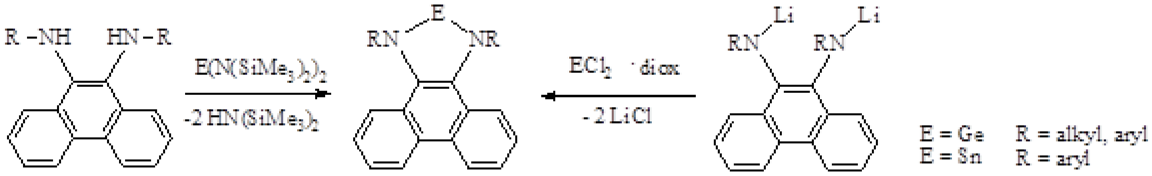
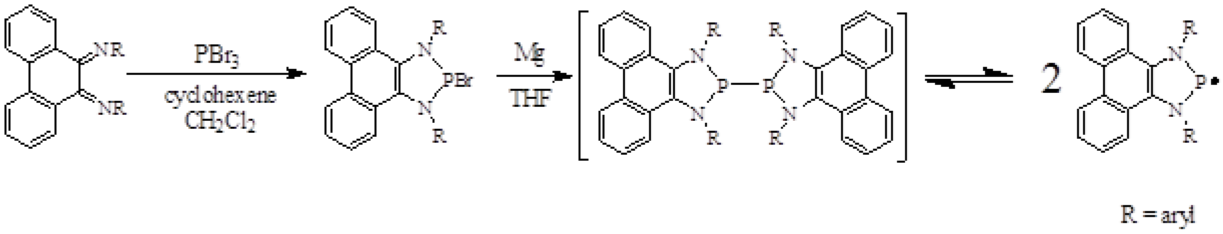
The set of donor-acceptor and steric characteristics of phenanthrene-9,10-diimine ligands allows to stabilize a low-valent derivatives of 14 group metals, also known as metallenes - N-heterocyclic analogues of carbenes. In this work a number of germylenes and stannylenes based on N,N'-diaryl-, N,N'-dialkyl- and N,N'-alkyl-aryl-substituted phenanthrenediimines were synthesized by two methods: a) exchange reaction between lithium salts of phenantrene-9,10-diimines and ECl_2 (E = Ge, Sn); b) treatment of phenantrene-9,10-diamines with $E(N(SiMe_3)_2)_2$.



Plumbylenes with any type of ligand and stannylenes with alkyl-substituted ligands are unstable and decompose during the reaction with the release of metals.

Also a new bromo-N-heterocyclic phosphanes and diphosphanes with a labile P-P bond from N,N'-diaryl-substituted phenanthrene-9,10-diimines were prepared. It were shown that this compounds undergo a dissociation to form phenanthrenediamides phosphorus-centered radicals which were detected by ESR spectroscopy.



All attempts to synthesize analogous antimony compounds were failed due to the instability of phenantrene-9,10-diamides antimony halide as well as analogous plumbylenes based on this type ligands.

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HETEROSPIN BIRADICALS BASED ON NITROXYL SUBSTITUTED o-QUINONE

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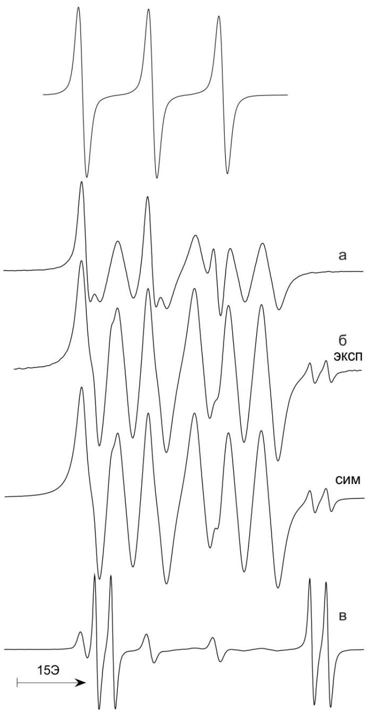
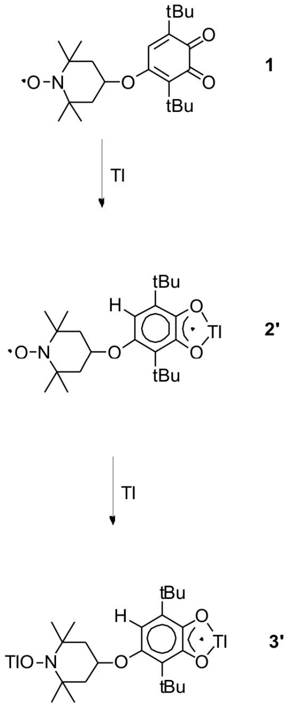
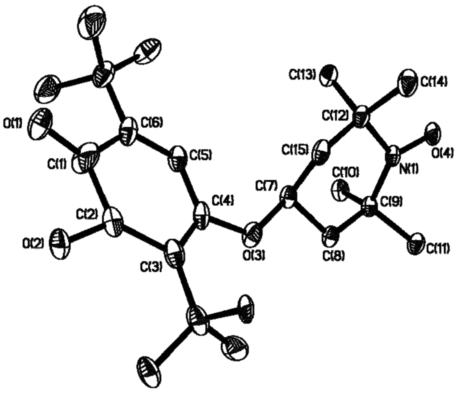
One of the directions in the molecular magnets design is searching of new bifunctional paramagnetic ligands for constructing multispin bi- and polynuclear metal complexes as well as coordination polymers. The nitroxyl (nitronyl-nitroxyl) and *o*-semiquinone derivatives are capable to form such heterospin ligands. In this work we synthesized new sterically-hindered quinine **1** containing 2,2,6,6-tetramethylpiperidine oxyl function by reaction 4-hydroxy-2,2,6,6-tetramethylpiperidine oxyl and 3,6-di-*tert*-butyl-*o*-benzoquinone. The structure of **1** were confirmed by EPR, IR, mass-spectroscopy and X-Ray analysis. It was shown the compound **1** to be a redox active in reaction with metallic potassium and thallium amalgam. The reduction of **1** with alkaline metals is accompanied by reaction color change from cherry red to green and formation of heterospin biradicals **2'** (a) with strong and fast exchange interactions between radical centers. Biraical 2' were detected by EPR spectroscopy. The subsequent reduction *o*-quinone **1** with alkaline metals leads to formation semiquinone derivatives **3'** (в). Then the signal of **3'** is disappeared, what confirms the formation of diamagnetic trianion metal salts.



EPR spectra of **1** with thallium amalgam (THF, room temperature. a – in 5 min after start of reaction, б – in 10 min., в – in 50 min).





Molecular structure of new *o*-quinone **1**

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MOLECULAR INDUSTRY OF CAGE METAL COMPLEXES FOR BIOCHEMICAL APPLICATION: THE SYNTHESIS AND PROPERTIES OF A SERIES OF THE RIBBED- FUNCTIONALIZED IRON (II) CLATHROCHELATE WITH TERMINAL PROTONO- AND IONOGENIC BIORELEVANT GROUPS

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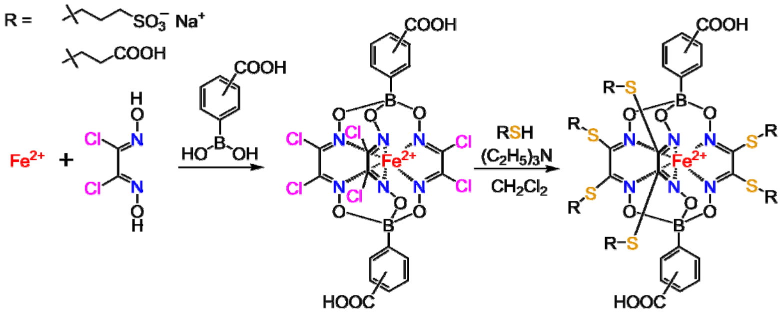
Modern trends in drug development lead to discovery of the new biological targets, including the hidden allosteric sites and(or) the interfaces of macromolecular interactions. The concept of topological drugs[1-2] suggest the use of three-dimensional species as rigid scaffolds for macromolecular binding that form multicentered supramolecular interactions in the vacant cavities of protein macromolecules and(or) their macromolecular complexes as well as on their surfaces. Based on the results of *in vitro* and ADMET tests, the biological activity of the clathrochelate complexes is limited by their insufficient bioavailability: for example, many of them have a very limited solubility in the aqueous buffer solutions at biological pH values.



Iron(II) clathrochelates having from six to eight protono- and(or) ionogenic terminal groups were prepared to ensure the higher bioavailability of such cage complexes. *One-pot* template condensation of dichloroglyoxime with the corresponding carboxyphenylboronic acids on an iron(II) ion as a matrix by Scheme was used for the synthesis at the *meta-* and *para-*substituted carboxyphenylboronic-capped hexachloroclathrochelates as the reactive macrobicyclic precursors. Clathrochelates with terminal carboxyl and sulfonate groups were obtained by nucleophilic substitution of the chlorine atoms of these apically functionalized precursors with the thiolate anions, the derivatives of mercaptoacetic acid and sodium mercaptopropanesulfonate, as *S*-nucleophiles using triethylamine as organic base to generate these anions (Scheme).

The complexes obtained were characterized using elemental analysis, UV-vis, IR multinuclear NMR spectroscopies, and by MALDI-TOF mass-spectrometry. The ribbed functionalized clathrohelate compounds were found to be a soluble in DMSO and water, thus allowing to study their biological activity as potent prodrugs.

[1] Y.Z.Voloshin, I.G.Belaya, R.Krämer, The encapsulation phenomenon: synthesis, reactivity and applications of caged Ions and molecules, Springer, 2016; Cage metal complexes: clathrochelates revisited, Springer, 2017
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UNUSUAL TETRAHEDRAL BIS-O-IMINOBENZOSEMIQUINONATO NICKEL(II) AND COBALT(II) COMPLEXES

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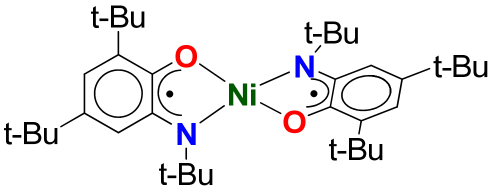
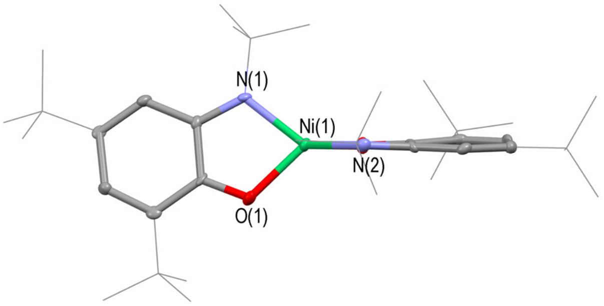
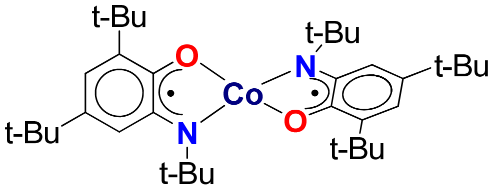
The new bis-*o*-iminosemiquinonate nickel and cobalt complexes $(imSQ^{t\text{-}Bu})_2M$ (M = Ni, Co), where imSQ is a radical anion of 4,6-di-*tert*-butyl-*N*-(*tert*-butyl)-*o*-iminobenzoquinone were synthesized and characterized in details. The molecular structures of **1** and **2** have been established by single-crystal X-ray analysis. The metal atoms in **1** and **2** have distorted tetrahedral environment, the dihedral angles between planes of two radical imSQ ligands are approximately 80° in both complexes.

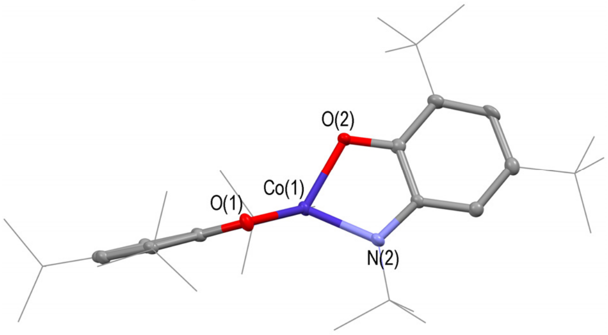


$(imSQ^{t\text{-}Bu})_2Ni$





$(imSQ^{t\text{-}Bu})_2Co$



According to the structural and spectroscopy data along with magnetic susceptibility measurements the electronic structure of the complexes should being definitely interpreted as high spin metal center Ni^{II} (d^8, S = 1) in **1** and Co^{II} (d^7, S = 3/2) in **2** bonded with two *o*-iminosemiquinonate radicals (S_{rad} = ½).

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EXTENDED NETWORKS BASED ON NICKELSILOXANE UNITS

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New family of bi-, tetra-, penta-, and hexanickel cage-like phenylsilsesquioxanes **1-3** (Fig.1) was obtained by self-assembling and transmetalation procedures. Their crystal structures were established by single crystal X-ray analysis; and features of crystal packing relevant to the networks formation were studied by a topological analysis.The geometry of metallosiloxane units **1** and **2** could be assigned to a distorted prism, with prominent shift of prism’ bases (silsesquioxane ligands) from the vertical axis. In turn, molecular architecture of compound **3** is regular prismatic one. Compounds **1-3** form extended networks in crystal via coordination bonds between alkali metals (Na, K, Cs) and oxygen atoms of siloxanolate moieties or coordinated solvent molecules (see, for instance Fig. 2). The investigation of magnetic properties revealed the presence of ferro- or antiferromagnetic interactions between Ni(II) ions giving rise in the most cases the presence of a slow relaxation of the magnetization, which can arise from the spin frustration.

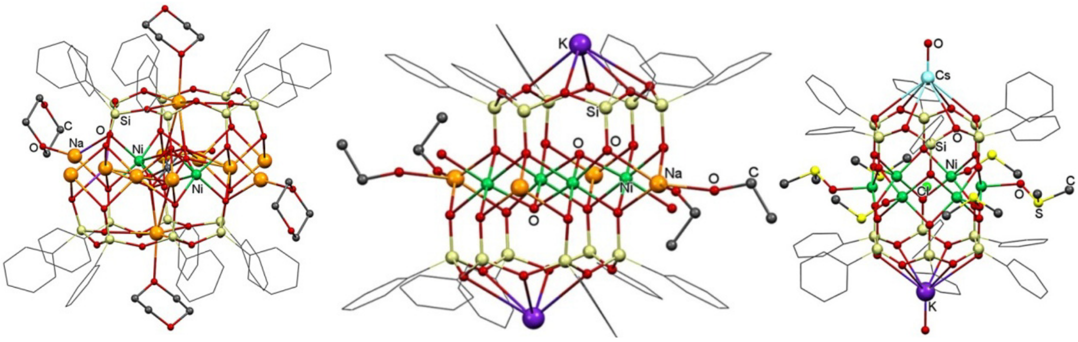

Fig. 1 Molecular structure of compounds **1**-**3**

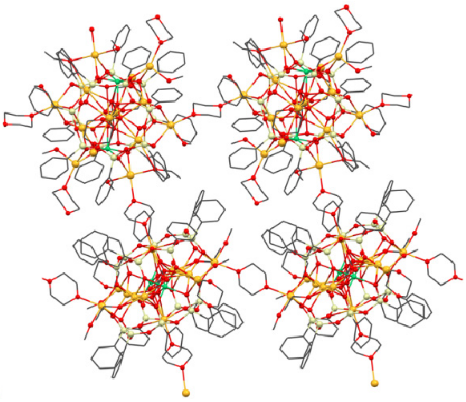

Fig.2 A view of the coordination polymer structure of **1**.

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TRIBOLUMINESCENCE AND CRYSTAL STRUCTURES OF THE COMPLEXES [LN $(NO_3)_3$ $(HMPA)_3$]. ROLE OF CLEAVAGE PLANES

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Studies of triboluminescence (TL) – light emission emerging upon crystal friction or destruction – is of urgent importance from as fundamental (search of the ways of transformation of the mechanical energy into the optical one) as practical points – the latter is concerned with development of highly sensitive optical sensors to be applied in different fields of science and technology. These sensors are promising in view of monitoring the size and location of microcracks in critical objects (aircrafts, automotive vehicles, bridges, cryogenic fuel or oxidizer tanks for space vehicle, etc.). Triboluminescent damage sensors comprising highly efficient triboluminescent materials could allow simple, real-time monitoring of both the magnitude and location of damage [1, 2].

One of the promising classes of triboluminophors includes intensively luminescent complexes of lanthanides. The photophysical properties of lanthanide-based compounds (their long lifetimes, narrow emission bands, large Stokes shifts, and high photostability) make them very promising candidates to be used in the receptor units of highly sensitive triboluminescent sensor detectors. In triboluminescent lanthanide complexes, the resulting emission can be absorbed by the ligands. Indeed, experiments with Gd (III) complexes show TL characteristic for the ligand, suggesting that the ligand is acting as an energy-harvesting antenna.

The report presents the data on interconnection between geometrical and electron structure of the rare-earth complexes [$Ln(NO_3)_3(HMPA)_3$] [where Ln = Eu(III), Tb(III), Sm(III), Dy(III) and HMPA = hexamethylphosphotriamide] and their luminescent and triboluminescent properties.

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Acknowledgements

The work was supported by the “Far East” Program for Fundamental Studies of the Far Eastern Branch of the Russian Academy of Sciences (grant 15-I-3-027 № 0065-2015-0017).

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THE SYNTHESIS OF NEW 1,3-OXAZINANES CONTAINING TRICARBONYLCHROMIUM GROUP

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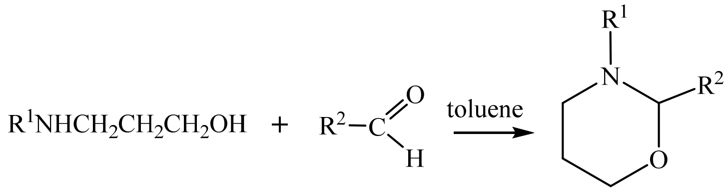
Nowadays, the reaction of condensation of aminoalcohols with carbonyl compounds is one of the easiest and available synthetic methods for achieving heterocyclic compounds containing nitrogen and oxygen atoms. Reactions between γ-aminoalcohols and different aldehydes lead to the formation of six membered heterocyclic products – 1,3-oxazinanes. These compounds are widely used in medicine, pharmacology and agriculture. The presence of antimicrobial and antiphlogistic activity makes it possible to use them also in cosmetic products [1].

The aim of our research was the synthesis of new 1,3-oxazinanes and its tricarbonylchromium analogs. We used 3-aminopropanol-1 (**1a**) and it metal-containing derivative (**1b**) as starting aminoalcohols. Paraformaldehyde (**2a**), acetaldehyde (**2b**), benzaldehyde (**2c**) and (η^6-benzaldehyde)tricarbonylchromium (**2d**) were carbonyl compounds. The reactions of condensation of γ-aminoalcohols and aldehydes were carried out in round-bottom flask with Dean-Stark apparatus and toluene acted as solution. The products of these reactions were 1,3-oxazinanes (**3**) (scheme 1):

Scheme 1



1a-b **2a-c** **3**

R^1= Ph(**a**), $PhCr(CO)_3$(**b**) R^2= H(**a**), CH_3 (**b**), Ph(**c**), $PhCr(CO)_3$(**d**)

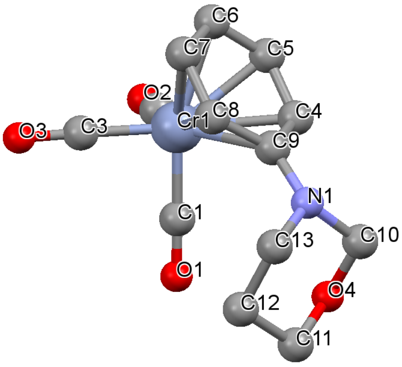


Figure 1. Molecular structure of chromium-containing 1,3-oxazinane.

The synthesized 1,3-oxazinanes were isolated and purified by column chromatography and crystallization from hexane - ethyl acetate and characterized by HPLC, UV-, IR-, ^{1}H NMR-spectroscopy, mass-spectrometry and X-ray diffraction analysis (Figure 1). It is found out that the increase of the size of R^1 and R^2-substitutes affected on the rate of condensation reactions and the yield of 1,3-oxazinanes. No products was observed in the case of reactions between compounds containing both bulky phenyl or (η^6- phenyl)tricarbonylchromium groups (**1b** and **2d, 1a** and **2d**, **1b** and **2c**).

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THERMAL INVESTIGATION OF NEW REDOX-ISOMERIC o-SEMIQUINONIC COBALT COMPLEX WITH NITROXYL-CONTAINING IMINOPYRIDINE LIGAND

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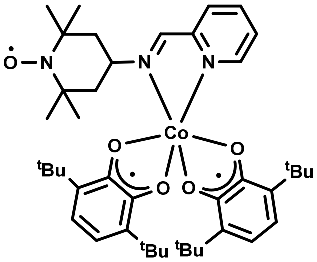
A novel complex (pyridine-2-yl-methylene)-4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl)-bis(3,6-di-tert-butyl-o-semiquinonato)cobalt(II)



possessing redox-isomerism was obtained and investigated by differential scanning calorimetry over temperature range 130-500 K with heating rate 10 K/min. Phase transition related with redox-isomeric transformation was observed, the experimental results of magnetic measurements and x-ray diffraction confirmed that complex in solid state undergo thermally driven redox-isomeric transformation.

It was revealed that interval of phase transition during first cooling is 205-225 K (T_{tr} = 218.5±0.3 K, ΔH = -4.3±0.1 kJ/mol). Following first and second subsequent heating show phase transition between 242 and 286 K (T_{tr} = 274.5±0.3 K, ΔH = 4.2±0.1 kJ/mol). Second cooling - in the interval 212-237 K (T_{tr} = 224.9±0.3 K, ΔH = -4.2±0.1 kJ/mol) (Fig.). Difference in T_{tr} for first and second cooling could be explained by changing of original crystal structure during first cooling.

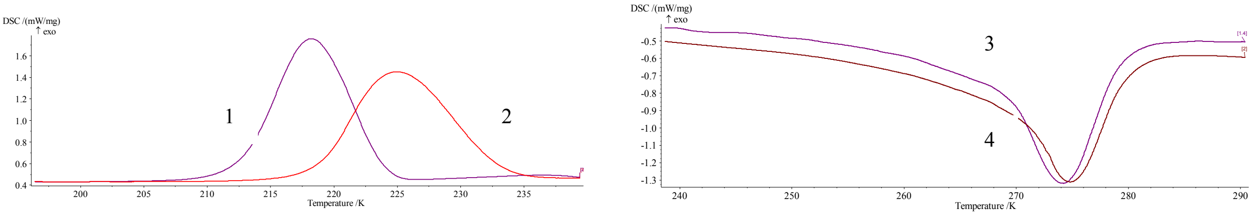


Figure. DSC-curves for first (1) and second (2) cooling, first (3) and second (4) heating

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AGGREGATION AND SOLUBILIZATION PROPERTIES OF SUPRAMOLECUAR SYSTEMS BASED ON GLUCAMINE-CONTAINING AMPHIPHILE: THE INFLUENCE OF ORGANIC SALTS ADDITIVES

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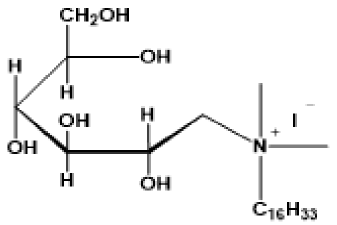

Fig. 1. CGI chemical structure.

In the framework of this study using tensiometry, potentiometry, spectrophotometry, dynamic and electrophoretic light scattering techniques supramolecular systems based on the novel cationic amphiphile bearing glucamine fragment (N,N-dimethyl-N-cetylglucamine iodide, CGI, fig. 1) and various organic salts additives (sodium salicylate NaSal, sodium benzoate NaBenz, sodium tosylate NaTos) have been investigated. In all three cases, in accordance with tensiometric data, addition of the salt induces decrease of aggregation thresholds of the system by one order of magnitude in comparison with individual surfactant solutions (cmc 0.7 mM): 0.035 mM for NaSal, 0.045 mM for NaTos, and 0.054 mM in the case of NaBenz. Using potentiometry technique it has been established, that tosylate and salicylate anions act as inorganic ones, increasing counterion binding degree β up to 95 % and 94 %, respectively (in the absence of salts $\beta = 78$ %). In the case of benzoate anion β value decreases down to 62 %. Addition of all three salts induces the morphological rearrangement of aggregates formed, that has been exhibited by dynamic light scattering method. Various salt additives in all three cases allows to regulate the size of aggregates from 2 nm (small micelle like associates) up to 100 nm (probably, layered or stacked structures). It has been shown, that selecting the salt and its concentration, the existence of positively and negatively charged aggregates could be reached in the range of ζ-potentials from -20 to +50 mV. Using spectrophotometry method on the example of sodium salicylate the effect of salt additives on solubilization characteristics of CGI towards hydrophobic dye Orange OT has been examined. Calculated values of solubilization power in the absence and in the presence of the salt are, respectively, equals to 0.014 $\text{mole}_{\text{Orange OT}}/\text{mole}_{\text{CGI}}$ and 0.01 $\text{mole}_{\text{Orange OT}}/\text{mole}_{\text{CGI}}$.

This work was financially supported by Russian Science Foundation (project № 14-23-00073).

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COMPARATIVE STUDY OF SPECTRAL AND ELECTROCHEMICAL PROPERTIES OF OCTAPHENYLPORPHYRAZINATES AND THEIR PERFLUORINATED DERIVATIVES

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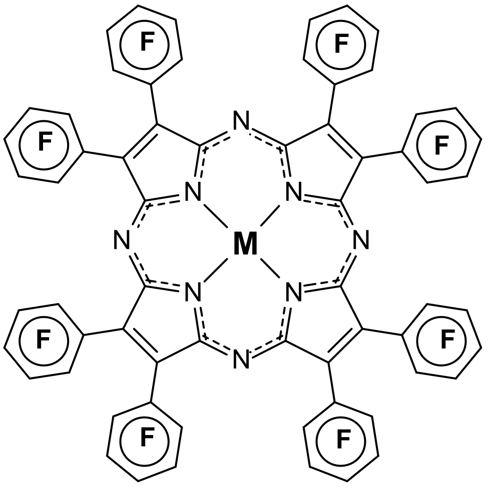
Fluorinated tetrapyrrolic macrocycles have been actively studied during the last two decades due to their various application potentialities. On one hand, the introduction of strongly electronegative fluorine atoms on the periphery of the porphyrinoid macrocycle remarkably changes its physical-chemical properties if compared with nonfluorinated species. The intrinsic fluorescence properties, photostability and improved solubility encourage the usage of fluorinated porphyrins in biomedicine (e.g. photodinamyc therapy and photodiagnosis of a cancer) [1a]. On the other hand, the click-reaction of nucleophilic aromatic substitution of the para–F atoms in pentafluorophenyl substituted porphyrins opens the wide opportunities for design of novel peripherally modified compounds [1b]. Skillful combination of fluorine substituents with other functional groups in their structures, including sugars led to novel molecules possessing outstanding phototoxicity [1].



$[MPz(F_5Ph)_8]$

M = Zn, Al(Cl), Ga(OH), In(OH)

Recently, we have prepared for the first time perfluorinated octaphenylporphyrazine ($H_2Pz(F_5Ph)_8$) [2]. Here we report on synthesis and physical-chemical properties of its complexes with zinc and with the aluminum subgroup metals. The influence of introduction of strong electron-acceptor fluorine atoms into porphyrazine macrocycle on the electron absorption and fluorescence spectral properties, electrochemical properties, bahaviour in acidic solutions is demonstrated by comparison with nonfluorinated analogs. In the case of zinc complex [$ZnPz(F_5Ph)_8$] the possibility of click-reaction of fluorine atom substitution with formation of water-soluble galactosyl derivatives with different degrees of substitution is shown.

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SYNTHESIS, ACID-BASE, COORDINATION AND FLUORESCENT PROPERTIES OF 5-PHENUL-*β*-ALKYLPORPHYRINE *MESO*-NITRODERIVATIVES

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Porphyrins play an exceptionally important role in the life of animals, plants and bacteria. The complexes of porphyrins with metals cation perform the most important key functions in the processes of photosynthesis and provide vital activity to humans and animals. This causes an interest in the structure and synthesis of new porphyrin ligands with predetermined properties. The targeted use of new tetrapyrrole compounds and their metal complexes is difficult in practice because of the lack of complete data on the relationship between the structure of the porphyrins and their coordination properties towards to metal cations. The study of the mechanisms responsible for the formation of the optical responses due to the interaction of porphyrins with metal cations is an important component of the directional change in their coordination, physico-chemical and acid-base properties, as well as the development of highly selective analytical methods for the determination and separation of metal ions. In the present work, the 10,15-dinitro-5-phenyl-2,3,7,8,12,13,17,18-octamethylporphyrin, 10,15,20-trinitro-5-phenyl-2,3,7,8,12,13,17,18-octamethyl porphyrin and 10,15,20-trinitro-5-(4-nitrophenyl)-2,3,7,8,12,13,17,18-octamethyl porphyrin have been synthesized and their acid-base, coordination and fluorescent properties have been investigated by means of UV-Vis, IR and ^{1}H NMR spectroscopy. Geometry of these porphyrins have been optimized using quantum-chemical method PM3 (HyperChem program, version 7.02). The set of obtained spectral-luminescent studies shows that the chemical modification of the macrocycle can lead to a directed change in the acid-base and fluorescence properties of macroheterocyclic ligands, and the change in the composition of the medium, along with the structural and electronic effects of the substituents, can be a powerful tool for controlling of the tetrapyrrolic macrocycles reactivity.

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SYNTHESIS, COORDINATION AND ACID-BASE PROPERTIES OF *MESO*-DINITROSUBSTITUTED DERIVATIVES OF 5,15-DIPHENUL - β - OCTAALKYLPORPHINE.

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Porphyrins and metalloporhpyrins are widely extended in nature and have significant biological value. Investigation of unique properties of porphyrins may promote solving of not only fundamental problems (mechanisms of energy transformation upon photosynthesis, obtainment of synthetic oxygen carriers and etc.) but also practically useful ones (creation of sensory and catalytically active materials of novel generation). Diversity of useful properties of porphyrins and their structural analogues (porphyrazines, phthalocyanines) relates to their structure features. In this way, successful fundamental research and practical application of such compounds directly depend on optimization of porphyrins synthesis and chemical modification of macroring periphery. Introduction of substituents of various natures allows varying physical and chemical properties of porphyrins-kind compounds in wide range. However, substituents themselves exhibiting electron-donor or electron-acceptor properties are able to impact the rate of complexation and also change stability of ionized forms of tetrapyrrolic ligand. Presented work shows results of original synthesis and spectrophotometric researches on properties of meso-dinitrosubstituted derivatives: 10,20-dinitro-5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethyl-porphine and 10,20-dinitro-5,15-bis(4-nitrophenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethyl-porphine in comparison with 2,8,12,18,3,7,13,17-octaethylporphyrin and 2,3,7,8,12,13,17,18-octaethyl-5,15-dinitroporphyrin. Distortion of porphyrin macrocycle planarity leads to increase of basic, as well as acid properties of deformed porphyrins compared to their planar analogues. Rate of porphyrins complexation with zinc acetate is found to be significantly increased upon transfer from molecular to dianionic ligand forms. Decrease of reaction activation energy is obviously caused by absence of energy costs for deformation and reaction center N–H bond destruction and also by higher polarization of the molecule and hence higher solvation degree of anionic porphyrin forms of intermediate state.

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A REDOX-ACTIVE RU(II) COMPLEX WITH TRIDENTATE 1,9-DIOXOPHENOXAZINATE LIGANDS

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It has been found that the reaction of 2,4,6,8-tetrakis(tert.-butyl)-9-hydroxyphenoxazin-1-one with $RuCl_3$ performed in DMFA affords a bis-chelate complex bis-(2,4,6,8-tetrakis(tert.-butil)-1,9-dioxophenoxazinate Ru (II) $Ru(DOPO)_2$, which being reduced by Zn amalgam in pyridine solution gives rise to the Ru(II) complex **I** with one of the chelate ligands substituted by three pyridine molecules (fig. 1.).

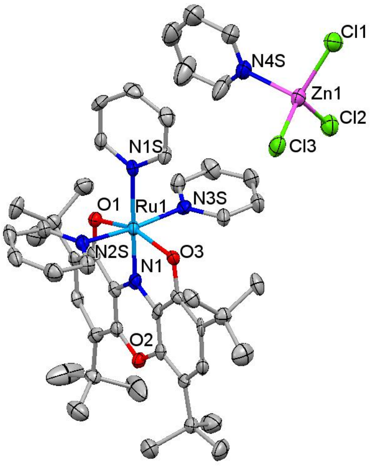

Fig. 1. X-ray determined molecular structure of **I**

The further reduction of **I** with Zn amalgam in toluene solution leads to the formation of its radical-anion determined by ESR. The redox-active properties of **I** have been studied using cyclic voltamperometry that allowed to register a series of reversible one-electron redox reactions corresponding to conversion of the ligand to its radical-anion and then to the dianion form and also to the Ru(II)/Ru(III) transformation (fig. 2.).

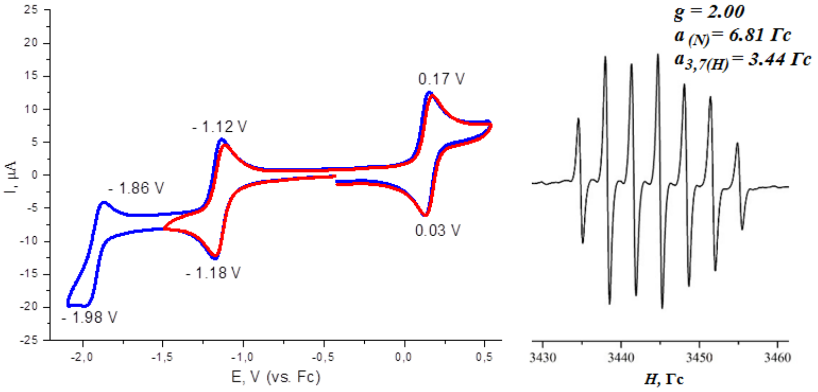

Fig. 2. Cyclic voltamperometry (in acetonitrile) and ESR spectrum of radical-anion of **I**.

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CARBON-CHAIN POLYMERS CONTAINING COPPER(I) COMPLEXES WITH HETEROCYCLIC LIGANDS AS EMISSIVE MATERIALS FOR OLED

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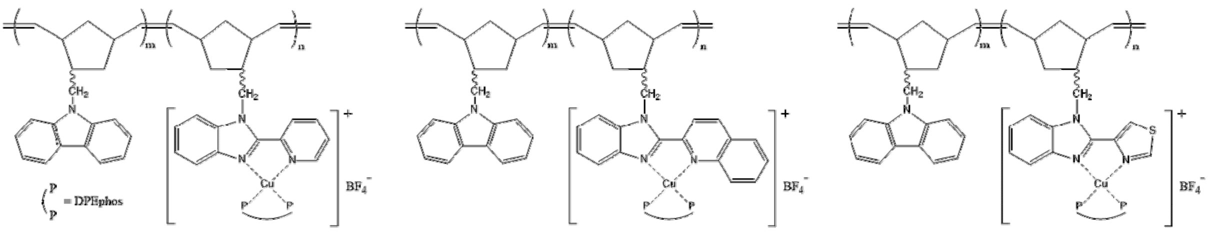
Luminescent metal-containing polymers are promising emitting materials for OLEDs. In this work new copper-containing copolymers with different charge-transporting and luminescent groups have been prepared via ring-opening metathesis polymerization:



The prepared polymers were isolated as yellow solids stable in air, readily soluble in THF, CH_2Cl_2 and $CHCl_3$. The copolymers were characterized by elemental analysis, GPC, TGA, UV-vis, IR, and NMR spectroscopies. Electroluminescent properties of the copper-containing copolymers were studied using model OLED devices of the ITO/Cu-polymer/BATH/Alq_3/Yb configuration: the ITO (indium oxide doped with tin oxide) layer acted as the anode; the copper-containing polymers were used as the emission layer; 4,7-diphenyl-1,10-phenantroline (BATH) and aluminum tris(8-oxyquinolinate) (Alq_3) were used as the hole-blocking and the electron-transporting layers, respectively; finally, ytterbium metal was used as the cathode. Depending on the nature of heterocyclic ligand the OLEDs showed luminescence of orange (2-(quinolin-2-yl)-1*H*-benzoimidazole), yellow (2-(pyridin-2-yl)-1*H*-benzoimidazole) and green (4-(1*H*-benzoimidazol-2-yl)thiazole) colours. The highest luminance efficiency was observed in the case of copolymer containing equimolar amounts of the carbazole groups and the copper(I) pyridylbenzimidazole complex. The non-optimized OLED device generated yellow light with maximal luminance of 629 cd/m^2.

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CRYSTALS OF POLYNUCLEAR COMPLEXES GROWN FROM THE IONIC LIQUID – COPPER(II) SALT – WATER SYSTEMS

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In recent years ionic liquids (ILs) draw attention as green chemistry solvents, because they have many valuable properties, such as low volatility, high thermal stability, high ion density, high ionic conductivity, broad temperature range of liquid state, *etc*. It is a great deal of interest in the application of the ionic liquids as catalysts, extraction solvents, and stationary phases for chromatography. Crystal grown from ionic liquids and from water or organic solvents in the presence of ILs is also important for modern chemistry. In the previous work [1] we reported the synthesis of the complexes crystals, containing products of C-H bond activation of ionic liquid cation, from the 1-ethyl-3-methylimidazolium acetate ([Emim]AcO) – copper(II) acetate – water – air system.

In the present work the crystals of the $([Emim][Cu_2(AcO)_5])_n$ coordination polymer and $[Emim]_2[Cu_2(AcO)_4(H_2O)_2][Cu_2(AcO)_6]\cdot 2H_2O$ compound have been grown from the same system and investigated by X-ray diffraction method. Both compounds consist of "chinese lantern" like units $Cu_2(AcO)_4$. In the coordination polymer those units are bind together through the acetate residues to form 1D polymeric chains. The second compound consists of two different "chinese lantern" units which also form polymeric chains due to hydrogen bonding between water molecule of the one "lantern" and acetate residue of the other. The complexes $[Emim]_2[Cu_2(AcO)_4Cl_2]$ and $([Emim][Cu_2(AcO)_4Cl])_n$ have been synthesized from the 1-ethyl-3-methylimidazolium acetate – copper(II) chloride – water and 1-ethyl-3-methylimidazolium chloride – copper(II) acetate – water systems. Crystals of these compounds consist of "chinese lantern" like units with chloride ions which are bridging in the last complex (Fig. 1). New interesting crystals, similar with described [3], were synthesized from the 2-(3-methylimidazol-3-ium-1-yl)acetate – copper(II) salt – water systems.

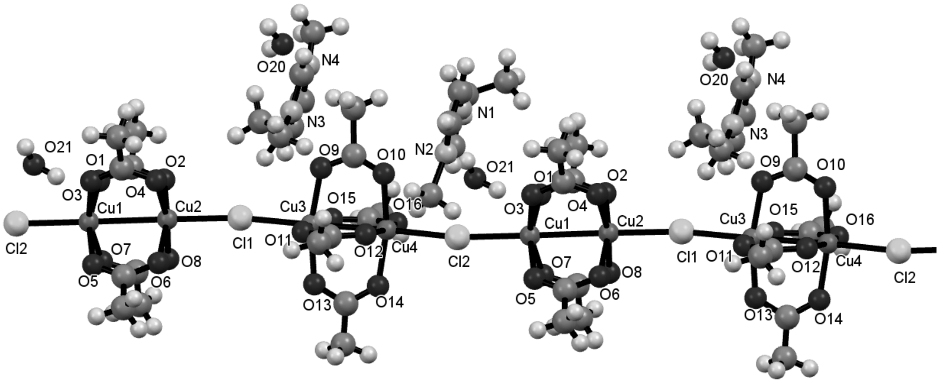

Fig. 1. Crystal structure of the $([Emim][Cu_2(AcO)_4Cl])_n$ complex.

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DFT SIMULATION OF SOLVENT INFLUENCE ON SAT-INTERMEDIAT OF Zn-PORPHYRIN COMPLEX FORMATION

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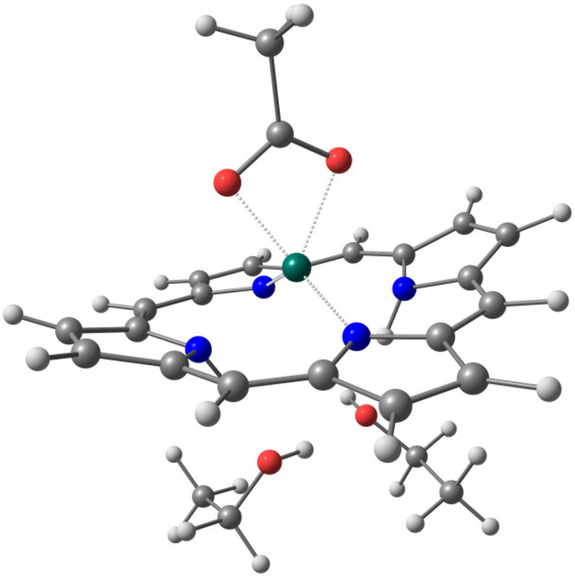
The problems of specific solvation of macroheterocyclic compounds are extremely important for both biological and synthetic porphyrins, phthalocyanines and their analogues which are widely used for the creation of new functional materials. The metalloporphyrin formation reaction is an important process related to the biochemistry. The mechanism by which a metal is inserted into a porphyrin has been extensively investigated via kinetic methods and a “sittingatop” (SAT) reaction intermediate has been suggested by many researchers.



Theoretical studies on solvates of SAT complexes (transition states of the complexation process) were carried out. The influence of ethanol molecules number on the SAT-complex stereochemistry and redistribution of electron density of nitrogen atoms was established. The macrocycle acoplanarity intensification and H-bonds and coordination bonds strengthening were show at the increase of alcohol molecules number in the first solvate shell.

A "push-pull" effect responsible for the stabilization of the SAT complex was discovered. It consists of the expulsion of hydrogen atoms by the $Zn(OAc)^+$ ion and in the stretching of the N-H bond at nucleophilic solvation. Based on the results of kinetic studies and quantum chemical calculations of SAT-complexes, conclusions were drawn about the limiting stage of the formation of SAT-complexes during the complexation of porphyrins with zinc acetate under the conditions studied.

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COPPER COMPLEXES OF 1,2,3-THIADIAZOLYL-SEMICARBAZIDES IN PLANT PROTECTION

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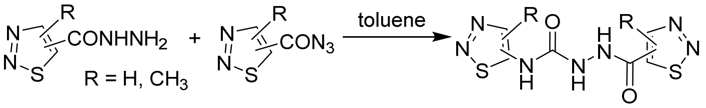
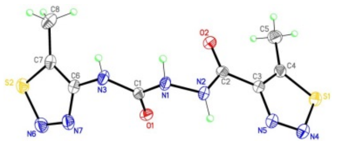
Chemistry of 1,2,3-thiadiazoles derivatives has become one of the focuses in the investigation of new agrochemicals because commercial pesticides containing 1,2,3-thiadiazole often possess simple structure and unique active mechanism. For example, thidiazuron, a cotton defoliant, has been found to exhibit more significant plant growth regulative activity than 6-benzyladenine and zeatin. Benzothiadiazole was the first commercial plant activator. Tiadinil was an excellent plant activator. Many 1,2,3-thiadizole derivatives have been reported with antiviral, antitumor, antibacterial, fungicidal, and insecticidal activities.

In view of these facts and also as a part of our continuous study on the bioactive heterocyclic compounds, the synthesis, characterization, binding properties and biological study of a series of 1,2,3-thiadiazole-containing semicarbazide derivatives and their copper complexes are reported herein.

The synthesis route of the semicarbazide derivatives is outlined in the Scheme.



The structures of the ligands were confirmed by elemental analysis, IR, ^{1}H, ^{13}C NMR, MS spectra and X-Ray analysis.



The binding properties of the compounds towards Cu(II) were studied using spectrophotometric method. The stoichiometric composition of the complexes in the solution was determined by the molar ratio and Job’s methods. Fungicide and antibacterial activity of the ligands and their metal complexes towards *Alternaria solani*, *Fusarium solani*, *Rhizoctonia solani*, *Phytophthora infestans*, *Colletrotrichum coccodes*, *Candida albicans*, *Pectobacterium atrosepticum, Staphylococcus aureus, Escherichia coli* and *Bacillus subtilis* was evaluated.

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OPTICAL PROPERTIES THE FILMS OF ANISOMETRIC SAMARIUM (III) AND EUROPIUM (III) COMPLEXES

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Unique luminescent properties of coordination lanthanide compounds open the possibility of their using as materials for optoelectronics. In contrast to organic luminescent materials and semiconductors, lanthanide compound emission spectra exhibit narrow luminescence lines, their position being determined by the central metal atom and practically independent of its coordination environment. This causes high purity of the emitted light and accurate colour rendition. However, the structure of complexes can significantly affect to the intensity of the luminescence. Therefore, the obtaining and investigation of new lanthanide complexes with effective luminescence is an actual and practically important task.

At the present work describes the new tris(β-diketonate) Ln(III) complexes with a variety of 1,10-phenanthroline derivatives. The structures are shown on Fig. 1.

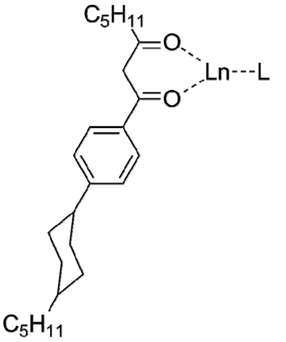
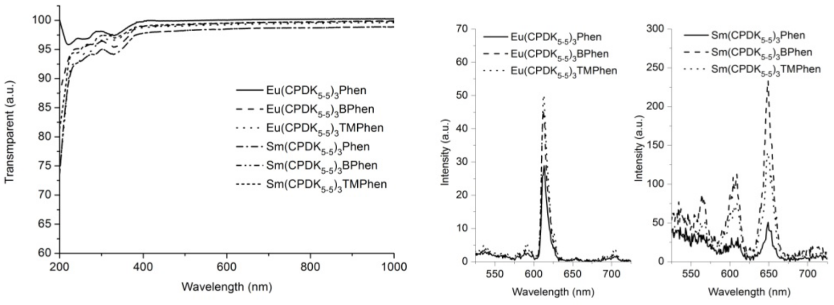


Fig. 1 - The structures of complexes, where Ln = Eu; Sm, L = 1,10-phenantroline; 4,7-Diphenyl-1,10-phenanthroline; 3,4,7,8-Tetramethyl-1,10-phenanthroline.



a b

Fig. 2 - The transmission (a), excitation and fluorescence (b) spectra of films of complexes Sm(III) and Eu(III) with derivatives of 1,10-phenanthroline

The films of the complexes were obtained by spin-coating from a solution in toluene at a concentration of $1x10^{-3}$ mol / l. It is shown that the introduction of chain hydrocarbon and cyclohexane substituents into the structure of the complex makes it possible to obtain films of lanthanide (III) complexes with high transmittance of the light (up to 98%) in the entire visible and near infrared region (Fig. 2a). The obtained complexes have effective luminescence in the orange and red regions of the visible spectrum (Fig. 2b) and can be used as emitting components of luminescent materials.

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HALOCHROMIC BEHAVIOUR OF WATER-SOLUBLE Eu(III) - Cu(II) POLYNUCLEAR METALLAMACROCYCLIC 15-MC-5 COMPLEX BASED ON PHENYLALANINEHYDROXIMATE LIGANDS

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Water-soluble Ln(III) - Cu(II) 15-MC-5 metallacrowns (MC) represented an exceptional class of polynuclear metallamacrocyclic complexes with unique structures and properties [1]. In these complexes the neutral ring consists of five [Cu(II)–N–O] repeat units, and the five hydroximate oxygen atoms encapsulate a Ln^{3+} ion within the central cavity that structurally resembles crown ethers.

In this work we synthesized the metallacrown on the basis of phenylalaninehydroximate ligand (Phalaha) and investigated its spectroscopic properties. The electronic absorption spectra of the Eu[15MC$_{\mathrm{CuPhalaha}}$-5] complex in aqueous solution demonstrate a broad band with a maximum at 577 nm which is assigned to a d–d transition of the copper(II) ion. The original blue color of the Eu[15MC$_{\mathrm{CuPhalaha}}$-5] aqueous solution disappears upon addition of acids (HCl, HNO$_3$, CH$_3$COOH) but this is reversibly returned by addition of a base, so that the Eu[15MC$_{\mathrm{CuPhalaha}}$-5] complex possesses halochromic properties. Accordingly, the visible absorption spectrum of the Eu[15MC$_{\mathrm{CuPhalaha}}$-5] complex change reversibly over the pH range 3.3–12.4 (Fig. 1).

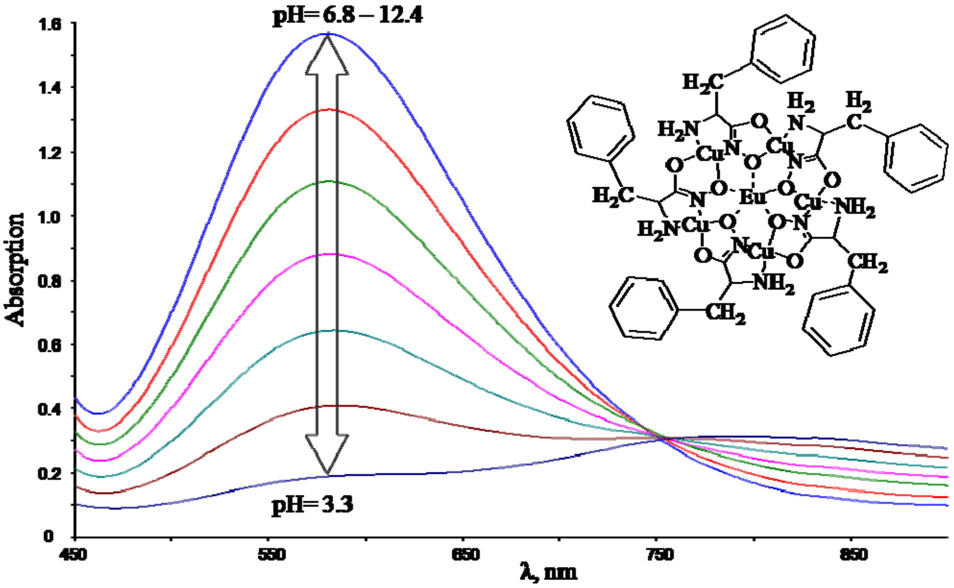

Fig. 1. The pH dependent visible spectra of the Eu[15MC$_{\mathrm{CuPhalaha}}$-5] complex.

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Acknowledgements - This work was partially supported by the RFBR (projects № 15-43-02285). G.Z. and G.Z. thank RSF for support of the spectroscopic investigations (project 17-73-20287).

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INVESTIGATIONS ON THE CONDITIONS OF THE LUMINESCENT COMPLEXES FORMATION OF GOLD(I), SILVER(I), COPPER(I), AND PLATINUM(II) WITH 2-MERCAPTO-5-BENZIMIDAZOLESULFONIC ACID IN SOLUTION AND ON THE SILICA SiO_2-PGMG SURFACE

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Nowadays, luminescence of metal complexes with organic ligands fixed on the silica surface is under a great interest. Complexes of Au(I), Ag(I), Cu(I), and Pt(II) with sulfur-containing ligands have an intense luminescence at 77 K when are irradiated with the UV-light. The absence of a sorbent matrix own color makes it possible to investigate the processes of complexation of metal ions with ligands fixed directly on the silica surface by the luminescent method of analysis. Complexations of Au(III), Ag(I), Cu(II), and Pt(II) with 2-mercapto-5-benzimidazolesulfonic acid (MBI) in aqueous solutions and with MBI non-covalently fixed on the silica surface are investigated in the present work.

The complex compounds of Cu(II), Ag(I), Au(III), and Pt(II) with MBI, that formed in aqueous solutions in the 6M-pH7 range, have a yellow-orange luminescence at 77K (Cu, Ag, Au) and red (Pt) at 77 K when are irradiated with the UV-light. The luminescence of Ag(I) complexes with MBI is observed in the 4-7 pH range. Au(III) and Cu(II) ions reduce to Au(I) and Cu(I) during the complexation. The luminescence excitation spectra of Au(I), Ag(I), Cu(I), and Pt(II) complexes with MBI are broad bands with maxima at 330, 335, 365, and 310 nm, respectively. The luminescence spectra of metal complexes with MBI in 1 M HCl are wide non-structural bands in the range of 400-750 nm with a maxima at 490 nm (Au), 510 nm (Cu), and 610 nm (Pt). The maximum of the luminescence spectrum for the Ag(I) complex with MBI at pH 4 is at 520 nm. The luminescent complex compounds are formed during the sorption of Au(III), Ag(I), Cu(II), and Pt(II) on the surface of SiO_2-PGMG-MBI in a liquid nitrogen at 77 K when are irradiated with UV-light. The shape of spectra, and the peak position of the luminescence excitation and the luminescence spectra for the Au(I), Ag(I), Cu(I), and Pt(II) surface complexes with MBI are identical to the luminescence characteristics of the complexes with MBI in aqueous solutions.The band corresponding to the charge transfer (CT) from a d level of a metal to the ligand ($d \rightarrow S^1$) in the absorption spectra is observed. The ratio of the reacting components (metal cation/MBI) is determined by the equilibrium shift method in the luminescent and photometric variants (over the CT band): 1:4 for Au(III), 1:5 for Cu(II), 1:4 for Pt(II), and 1:2 for Ag(I). That allows us to conclude that complexes of different stoichiometry are formed in solutions and on the sorbent's surface: 1:2 for Au(I), 1:4 for Cu(I), 1:4 for Pt(II), and 1:2 for Ag(I).Two MBI molecules reduce Au(III) cation to Au(I) and two molecules participate in the complexation reaction. For Cu(II), one molecule is used for the reduction and four are coordinated.

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RARE EARTH ISOVALERATES AND THEIR MIXED-LIGANS COMPLEXES WITH AMINES AS PRECURSORS FOR CHEMICAL DEPOSITION OF MIXED-OXIDE THIN FILMS

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Since the rare earth (RE) complex oxides in a form of thin films have a huge number of application as functional materials the development of chemical solution deposition method (MOCSD) of such thin films is currently under high interest. Mixed-ligand complexes of RE carboxylates with amines are considered as promising metal-organic precursors. Here we present synthesis, composition, structure and thermal behaviour of RE isovalerates and their mixed-ligand complexes with monoethanolamine (MEA) and diethylenetriamine (DETA).

RE isovalerate hydrates of general formula $[Ln(^{i}Val_3)(H_2O)_n]$ (Ln = La, Gd, Y, Lu; x = 0-2) were synthesized for the first time by 4 methods based on ligand-exchange reactions in water and organic solvents. The composition of products was studied by TGA, IR and XRD methods. Syntheses in water solutions give high yields for light RE (La-Gd), whereas reactions in organic solvents give higher yields for Y and heavy lanthanides. A new crystalline structure of $[Gd(^{i}Val)_3(H_2O)_2]_2$ has been detemined by XRD. The unit cell contains two centrosymmetric dimers, formed with two chelate-bridging ^{i}Val-ligands and containing two 9-fold coordinated Gd ions. RE isovalerates have reacted with MEA and DETA forming hydroxogels, except La. Hydroxogels decompose in air at temperatures as low as 600°C forming RE oxides that allows their application as solution precursors for MOCSD. Solid crystalline complex $[La(MEA)(^{i}Val)_3]$ has been obtained and it also seems to have typical dimeric structure which was modeled by DFT calculations.

Deposition of Y_2O_3, $LaAlO_3$, $LaLuO_3$ thin films were performed as follows. RE isovalerates were dissolved in isopropanol with the excess of DETA to achieve the resulting concentration of 0.2-0.3M. Obtained solutions were used for chemical deposition on single crystalline ($SrTiO_3$ (100) and YSZ (111)) and polycrystalline (hastelloy) substrates and heat treated at 150 and 550°C. Deposited films were characterized by XRD and AFM.

The presented metal-organic precursors were successfully applied for deposition of both amorphous/nanocrystalline and crystalline textured films. For example, obtained Y_2O_3/Hastelloy films have average roughness of 0.8 nm which is perfect for smoothing layers. On the other hand, annealing of as-deposited mixed-oxide films at 1000°C results in formation of crystalline oriented films ($LaLuO_3$(100)/STO(100) or $LaLuO_3$(110)/YSZ(111)).

Therefore, developed metal-organic precursors show good results in deposition of RE mixed-oxide films. Furthermore, solutions of RE isovalerate amine complexes are compatible with solution of transition metal ones. This fact allows to use the developed precursors for deposition of RE and transition metal mixed-oxide films (RE ferrites, manganites, nickelates, etc.)

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IRIDIUM(III) COMPLEXES WITH CYCLOMETALATED 4-(4-BROMOPHENYL)-2-METHYL-1,3-THIAZOLE AND ISOCYANIDES: SYNTHETIC AND STRUCTURAL STUDY

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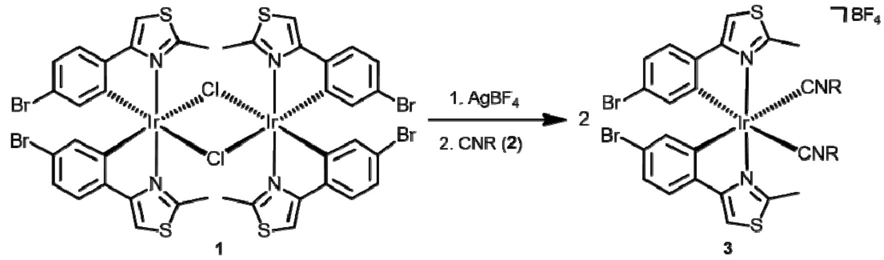
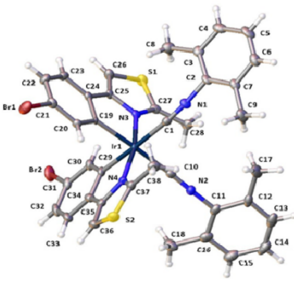
Cyclometallated iridium(III) complexes draw attention because of their superior excited-state lifetimes and phosphorescence quantum yields; they are widely used in organic light-emitting diodes, light-emitting electrochemical cells, in oxygen sensing, catalytic applications, and biological imaging. Heteroleptic cyclometalated iridium complexes such as $[Ir(C^\wedge N)_2(LL')]^{0/+}$, where C^N = cyclometalating ligand and LL′ = ancillary ligand, are of particular interest because the structure of the C^N and LL′ ligands may control the emission energy and affects the excited-state character [1].

In the current work, we describe the preparation of iridium(III) isocyanide complexes with cyclometalated 4-(4-bromophenyl)-2-methyl-1,3-thiazole (bptz) and evaluation of the influence of isocyanide donating properties on the optical, luminescent and electrochemical properties of these compounds. Complexes *cis*-$[Ir(bptz)_2(CNR)_2]BF_4$ (R = *t*-Bu **3a**, Xyl **3b**, BrC_6H_4 **3c**) were prepared from $[Ir_2(bptz)_4(\mu\text{-}Cl)_2]$ (**1**), isocyanide (CNR, **2**) and silver tetrafluoroborate ($AgBF_4$) in 70–86% yields and characterized by HRESI$^+$-MS, FTIR, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy. Structure of complex **3b**•3¼CH_2Cl_2 was elucidated by a single-crystal X-ray diffraction. Presence of donating BrC_6H_4NC, XylNC, and *t*-BuNC ligands leads to a bathochromic shift of metal-to-ligand charge transfer (MLCT) bands and to a decrease in the difference between the one-electron oxidation and reduction potentials of complexes. Quenching of the phosphorescence of complexes in solution is related to the thermally-induced population of excited *d*–*d** states with subsequent nonradiative deactivation.





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LOW-COORDINATED MIXED-LIGAND LANTHANIDE COMPLEXES

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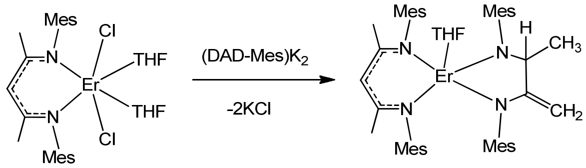
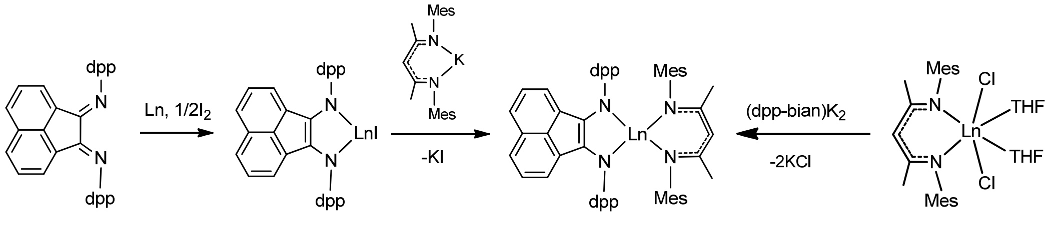
Recently, a convenient method for the preparation of rare earths chlorides [$LLnCl_2(THF)_2$] (Ln = Y, Dy, Er, Sm, Yb) supported by N-mesityl substituted β-diketiminato ligand (L = 2,4,6-$Me_3C_6H_2$-NC(Me)CHC(Me)N-2,4,6-$Me_3C_6H_2$) was established [1] and proposed to use the complexes of such a type as precursors for the synthesis of novel β-diketiminato derivatives via further metathesis of Ln-Cl bonds. The salt metathesis reactions of erbium dichloride [$LErCl_2(THF)_2$] with potassium salt of direduced diazabutadiene (DAD-Mes)K_2 (DAD-Mes = 2,4,6-$Me_3C_6H_2$-NC(Me)-C(Me)N-2,4,6-$Me_3C_6H_2$) prepared in situ, afforded a new mixed-ligand erbium complex [LEr(CH_2-DAD-Mes)(THF)] containing dianionic DAD ligand with an unusual double bond and hydrogen redistribution (CH_2-DAD-Mes = 2,4,6-$Me_3C_6H_2$-NC(H)(Me)-C(=CH_2)N-2,4,6-$Me_3C_6H_2$). Single-crystal X-ray diffraction reveals unsymmetrical structure of DAD ligand with one deprotonated methene group bound to sp^2-hybridized carbon backbone atom and sp^3-hybridized carbon backbone atom bound to hydrogen atom as well as methyl group. Such an unexpected structure is discussed through the instrumentality of quantum-chemical calculations. In all cases (free direduced DAD ligand, solvated and non-solvated potassium salts as well as erbium complex) the energy preference of symmetric “classical” DAD-Mes form with double central C=C bond and two methyl groups was found.



In the case of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) another reaction pathway was established. Corresponding iodides were synthesized by the direct reduction of neutral dpp-bian with rare earth metals excess (Ln = Y, Dy, Er) in the presence of iodine and utilized in situ in the further reaction with potassium β-diketiminate. The unique four-coordinated complexes with the distorted tetrahedral geometry of central atom were isolated. It was shown that this reaction is preferred in comparison with the proposed earlier route starting from rare earths chlorides [$LLnCl_2(THF)_2$].



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REACTIONS OF OXO-GALLIUM COMPLEX WITH ACID OXIDES

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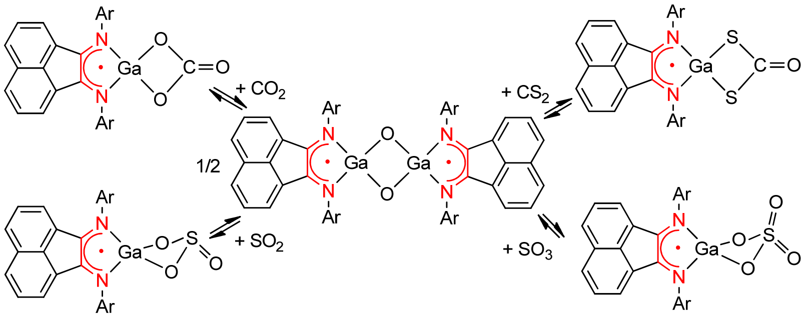
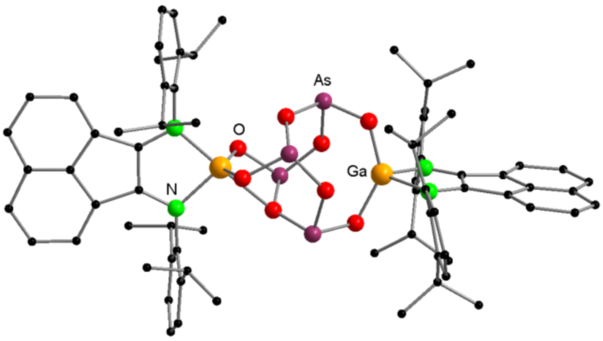
It was shown that binuclear gallium oxo-complex [(dpp-bian)GaO]$_2$ containing the anion-radical ligand 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian) reacts with typical acidic oxides - inorganic anhydrides - and related compounds. The reversible binding of such small molecules as CO_2, CS_2, SO_2, SO_3 was found by the monitoring reaction mixtures with EPR spectroscopy.



The interaction of the gallium oxo-complex [(dpp-bian)GaO]$_2$ with oxides of heavy analogs of elements of the 14-16 Groups of the Periodic system was studied. It was found that SeO2 quantitatively oxidizes [(dpp-bian)GaO]$_2$ to neutral dpp-bian. The oxo-complex [(dpp-bian)GaO]$_2$ does not react with oxides such as GeO_2, SnO_2, Sb_2O_3, Bi_2O_3, TeO_2, possessing a polymeric structure, even with heating (100°C) for a long time. The arsenic and phosphorous oxides (As_4O_6 and P_4O_{10}) react with the gallium oxo-complex [(dpp-bian)GaO]$_2$ at room temperature, partially oxidizing the ligand to neutral dpp-bian and leading to polynuclear heteroelement oxo-complexes containing the radical anion dpp-bian, coordinated to gallium. The radical nature of the organic ligand is unambiguously established by EPR spectra. Molecular structure of arsenic derivative was determined by single crystal X-ray diffraction analysis.



Acknowledgements – This work was supported by RFBR (project 16-33-00465-mol_a).

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EPR STUDY OF DYNAMIC PROCESSES IN COORDINATION SPHERE OF SPIN-LABELLED TRANSITION METAL COMPLEXES

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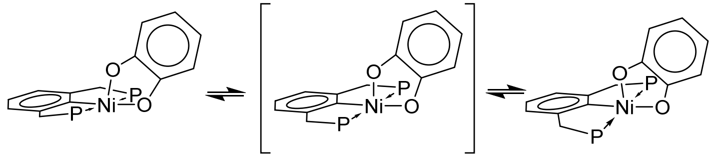
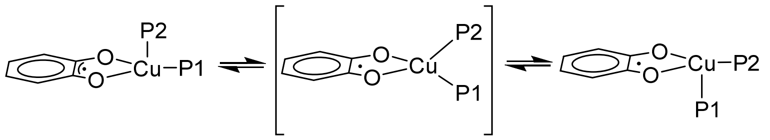
Advanced technique of simulation of dynamic processes in cw EPR spectra allows estimation of spectral parameters and the structure of intermediate states directly unobservable by EPR. Some of the studied dynamic processes in o-semiquinonic transition metal complexes:

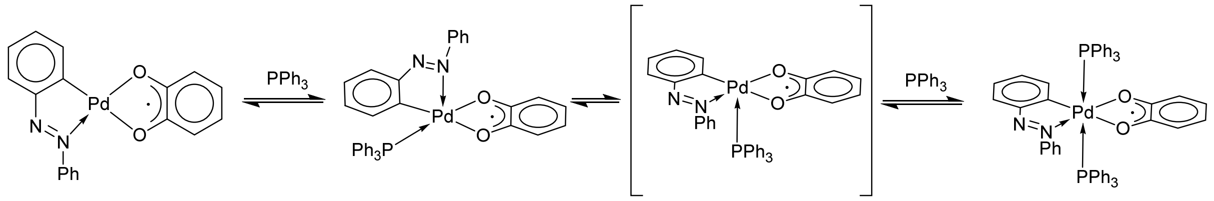
- “Fan” oscillations in PCP nickel complexes via “straight” intermediate state.



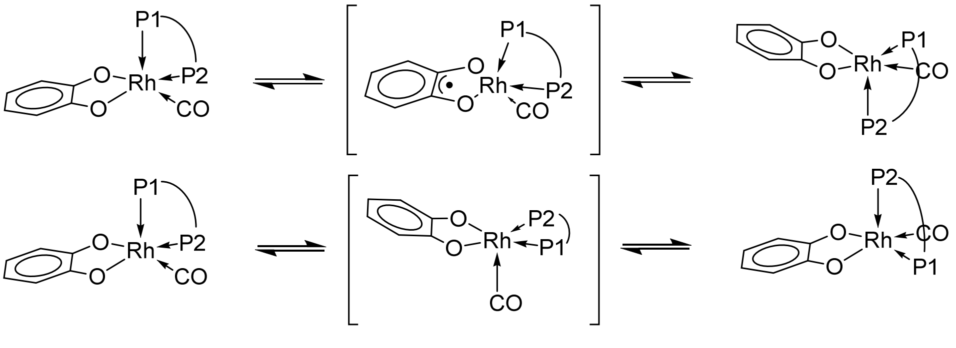
- Exchange of apical and basal phosphoruses in trigonal pyramidal copper complexes via tetrahedral intermediate state.



- Isomerization of square pyramidal palladium complexes with azoaryl and phosphine ligands.



- Exchange of apical and basal phosphoruses in square pyramidal rhodium complexes with chelating diphosphines via trigonal bipyramidal either square pyramidal intermediate state.



Acknowledgements – the work was supported by RFBR (grant 16-03-00844a) and Russian President (grant NSh-7916.2016.3)

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SYNTHESIS, STRUCTURE AND PROPERTIES OF COORDINATION COMPOUNDS OF 3d-METALS 1,5-NAPHTHALENEDISULFONATES AND 2-NAPHTHALENESULFONATES WITH THIOSEMICARBAZIDE

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The anions of naphthalenesulfonic acids in recent decades have attracted the attention of many researchers as compounds on the basis of which the possibility of creating stable systems is realized due to the simultaneous effect of coordination interactions and hydrogen bonds. The interaction of cobalt(II), nickel(II), copper(II) and zinc(II) 1,5-naphthalenedisulfonates and 2-naphthalenesulfonates with thiosemicarbazide (Tsc) has been studied in this paper. Methods for the synthesis of complexes have been developed, the effect of solvent (water, ethanol), reagent ratios, and temperature on the products compositions has been studied. The composition and structure of the compounds formed are determined by chemical analysis, IR and diffuse reflection spectroscopy. For nickel(II), the change of the solvent results the formation of various complexes. In all cases, thiosemicarbazide is bidentate with coordination through sulfur and nitrogen. The thermal stability of the complexes has been studied by thermogravimetry. Thermostability decreases in the series of complexing agents: Cu^{2+}>Zn^{2+}>Ni^{2+}>Co^{3+}, and for 1,5-naphthalenedisulfonates it is higher than for 2-naphthalenesulfonates.

The structure of $[Cu(Tsc)_2](Nds)$ and $[Zn(Tsc)_2](Nds)\cdot H_2O$ (Nds - doubly deprotonated anion of 1,5-naphthalenedisulfonic acid) was established by the X-ray diffraction method. In both cases, the structures consist of complex cations $[M(Tsc)_2]^{2+}$ (M = Cu, fig. 1, M = Zn, fig. 2) and anions Nds^{2-}, thiosemicarbazide is bidentate chelate (S, N). Coordination polyhedra: a square for copper and a distorted tetrahedron for zinc. For zinc, the compound contains crystallization water molecules. The structural units of both crystals are joined together by a branched network of hydrogen bonds.

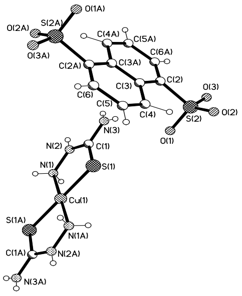

Fig. 1. The structure of compound $[Cu(Tsc)_2](Nds)$

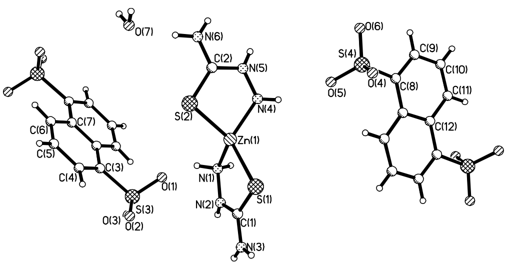

Fig. 2. The structure of compound $[Zn(Tsc)_2](Nds)\cdot H_2O$

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LANTHANIDE COMPLEXES WITH FORMAMIDINATE AND CHALCOGENOLATE LIGANDS: SYNTHESIS, STRUCTURE AND PROPERTIES

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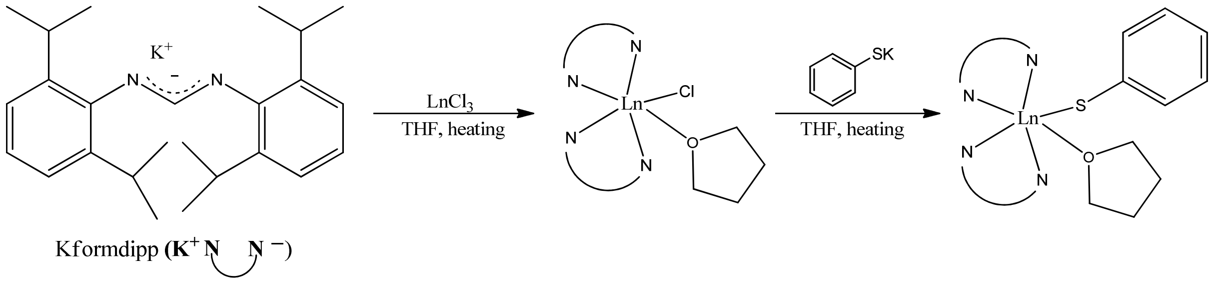
Lanthanide chalcogenolate complexes continue to attract considerable attention due to their fascinating structures and their potential applications in the preparation of new advanced materials, and catalysis [1, 2]. This work is devoted to the synthesis of chloride lanthanide complexes with bulk formamidinate ligands (formdipp$^-$, scheme) and the study of their reactions with aromatic chalcogenolates.



Formamidinate lanthanide complexes were synthesized by reactions of 2 equivalents of K(formdipp) with $LnCl_3$. Two type of products were isolated: $[Ln(formdipp)_2Cl(thf)_x]$ (Ln = Y, Dy, Sm, x = 1, Ln = Tb, x = 2) or $K[Tm(formdipp)_2Cl_2]$. It should be noted that only Tb complex has been known before this work. Reactions of $[Ln(formdipp)_2Cl(thf)_x]$ (Ln = Tb, Dy) with potassium thiophenolate proceed as salt metathesis and result in novel mononuclear complexes $[Ln(formdipp)_2(SPh)(thf)]$. All the new compounds were characterised by single-crystal X-ray analysis. The photoluminescent properties of the terbium complexes obtained were studied.

[1] G.A. Kumar, R.E. Riman and John G. Brennan, *Coord. Chem. Rev.*, **2014**, *273–274*, 111–124.
[2] Hong-Xi Li, Yan-Jun Zhu, Mei-Ling Cheng, Zhi-Gang Ren, Jian-Ping Lang and Qi Shen, *Coord. Chem. Rev.*, **2006**, *250*, 2059–2092.

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COORDINATION CHEMISTRY MATERIALS IN RUSSIAN CHEMICAL BULLETIN

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In 2016 issue 8 composed of the articles on Coordination Chemistry, based on the materials of previous Chugaev Conference, issues 10 and 11 included the articles on Coordination Chemistry.

Russian Chemical Bulletin is International Edition of a prominent Russian Journal *Izvestiya Akademii Nauk. Seriya Khimicheskaya. It was* founded in 1936 and has been published in English since 1952. During these years, the Journal has become one of the leading Russian periodicals in chemistry. Russian-language version is published by the Russian Academy of Sciences, while the English-language version is published by *Springer.* The Editorial Board of the journal includes prominent chemical scientists, in particular, thirteen full members and ten corresponding members of the RAS. The foundation in 1995 of the International Advisory Board with participation of renowned chemical scientists from various countries including three Nobel Prize winners in chemistry also contributed to the high scientific level and international prestige of the journal.

Since 1993, the journal has published papers presenting the results of original studies as full papers, brief communications, and letters to the Editor, but also analytical reviews, in particular, authors' reviews and predictive analytical papers on topical issues of the chemical science. During this period, the volume of the journal increased more than 1.5-fold, which considerably shortened the publication time and made it possible to extend the journal coverage, first of all, by including papers in Coordination Chemistry, Organic Chemistry, Materials Chemistry, Supramolecular Chemistry, Chemistry of Natural Compounds, Bioorganic and Biomolecular Chemistry, Medicinal Chemistry, Polymer Chemistry, Nanochemistry, and interdisciplinary articles. Besides ordinary issues, containing materials on different areas of chemical science, specialised issues are regularly published. In 2016, more than 350 papers from 100 scientific centres of the Russian Federation and 30 scientific centres from the former USSR and other foreign countries were published.

In recent years, the Journal has become widely known in Russia and abroad. The journal is abstracted and indexed in the following base dates: RZhKhimiya, Chemical Abstracts, Chemical Titles, Current Contents/Physical, Chemical and Earth Sciences, Reaction Citation Index, Science Citation Index, Science Citation Index Expanded, The ISI Alerting Services, Chemistry Citation Index, and Energy Research Abstracts. Information about the Journal and the publications is available at the websites of the Journal (www.russchembull.ru) and Springer (www.springerlink.com). The electronic versions of the journal are available online for subscribers. Since 2005, all papers published in English starting with the first journal issue, which appeared in 1952, are available in the electronic library of Springer. In terms of the number of downloads of the full texts of online articles, *Russian Chemical Bulletin* has the highest score among Russian journals, markedly exceeding the average level (more than 1000 downloads per day on average, Information about the journal is available at www.springer.com/11172), which attests to the high need for the Journal. Several hundreds of both individual institutions and large consortia combining many institutions have subscribed for the Journal, which made the access to the Journal global.

We invite researchers to take part in preparing of issues of the Journal. Perfectly prepared articles are published 4 months after submission; for letters to the Editor this period is even shorter (2 months).

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CHALCOGENIDE COMPLEXES OF VANADIUM: SYNTHESIS AND REACTIVITY TOWARDS LANTHANOCENCES

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Chalcogenide complexes of lanthanides, namely compounds containing Ln-Q bonds (Q = S, Se, Te), possess unique chemical and physical properties due to the combination of “highly ionic” metal and “highly covalent” ligand. Unexpected structural motives, unique magnetic, electronic and luminescent properties may appear as a result of this combination. In this regard, heterometallic chalcogenide complexes containing lanthanide and *d*-metal are particularly interesting, and synthetic approaches to such compounds are desired.

Herewith we report about synthesis and structural study of new vanadium chalcogenide complexes with diimine ligand [HC(CMeN(2,6-diisopropylphenyl))$_2$] (nacnac). The complexes containing sulfur and selenium are similar: they have the $\{(V{=}Q)(\mu\text{-}Q_2)(V{=}Q)\}$ central unit, while the tellurium compound contains only the $\{V_2(\mu\text{-}Te)_2\}$ moiety (Fig. 1.).

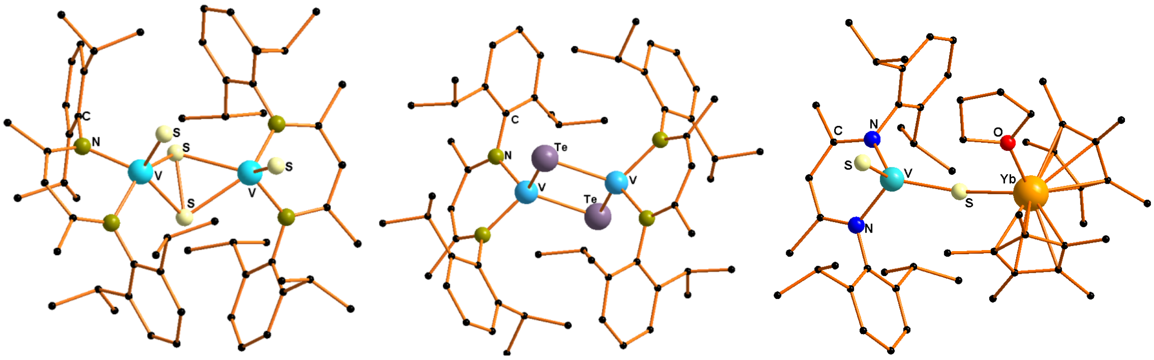

Fig. 1. Molecular structure of $[\{(nacnac)V{=}S\}_2(\mu\text{-}S_2)]$ (left), $[\{(nacnac)V\}_2(\mu\text{-}Te)_2]$ (middle) and $[Cp^*_2(thf)Yb(\mu\text{-}S)V{=}S(nacnac)]$ (hydrogen atoms are omitted for clarity)

It has been found that the $[\{(nacnac)V{=}Q)\}_2(\mu\text{-}Q_2)]$ (Q = S, Se) complexes react with $[Cp^*_2Sm(thf)_2]$ and $[Cp^*_2Yb(thf)_2]$. In the case of Yb the heterometallic compounds $[Cp^*_2(thf)Yb(\mu\text{-}Q)VQ(nacnac)]$ were isolated and characterized.

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27th International Chugaev Conference on Coordination Chemistry
4th Conference-School for Young Researchers "Physicochemical Methods in Coordination Chemistry"
October 2-6, 2017, N. Novgorod, Russia

X-RAY PHOTOELECTRON SPECTRA AND THE ELECTRONIC STRUCTURE OF CARBOXYLATE COMPLEXES OF Nd(III)

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X-ray photoelectron spectroscopy and quantum chemistry methods (DFT) are used to study carboxylate complexes of Nd(tol)$_3$ and Nd(cor)$_3$ and their adducts with 1,10-phenanthroline. New information on the electronic structure of the complexes (the geometric parameters, the nature of chemical bonding) is obtained. The quantum-chemical studies reveal patterns in the variations of the electronic structure, which depend on ligands and adducts (fig.1). Band identification was obtained for the valence bands of carboxylate complexes of Nd(tol)$_3$Phen, Nd(cor)$_3$Phen$_2$ in the X-ray photoelectron (condensed state) spectra (fig2) .

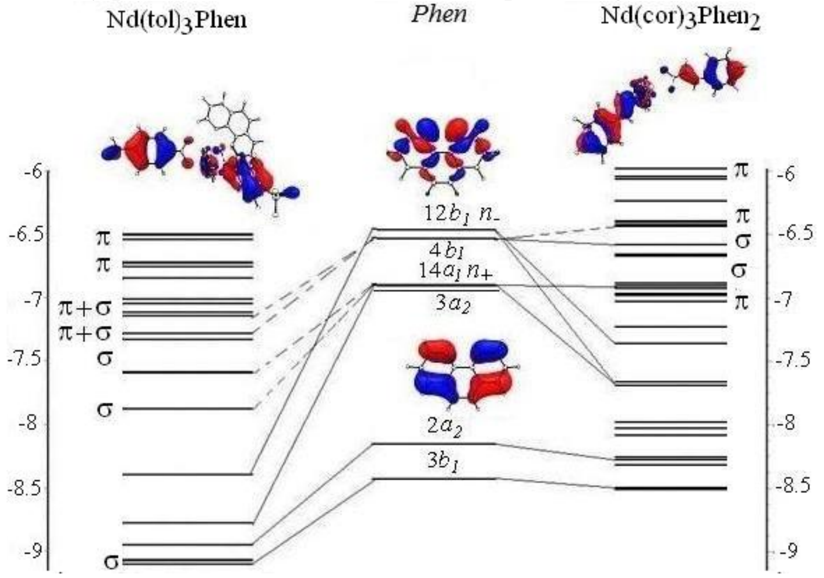

Fig.1 Correlation diagram molecular orbital (MO)(eV).

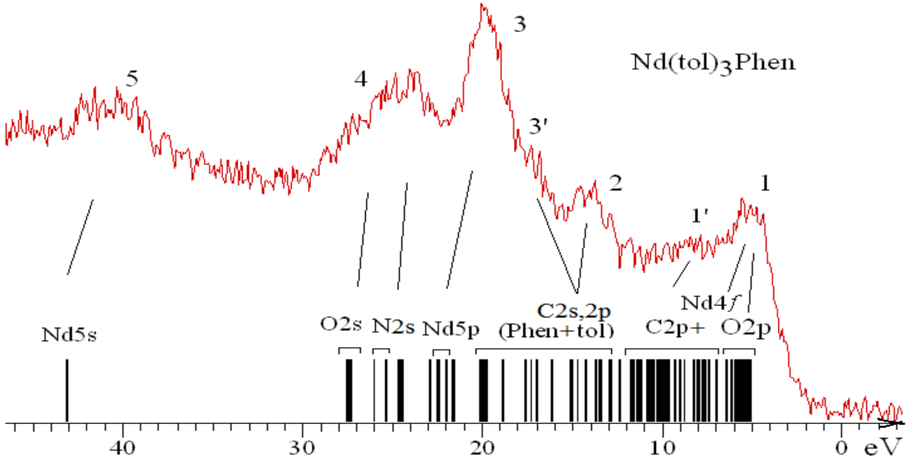

Fig 2. The identification of bands of valence region of X-ray photoelectron spectra.

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OXALATOPALLADATES COBALT AND NICKEL AS PRECURSORS OF NANOALLOYS: FROM THERMAL PROPERTIES TO SUPPORTED CATALYSTS

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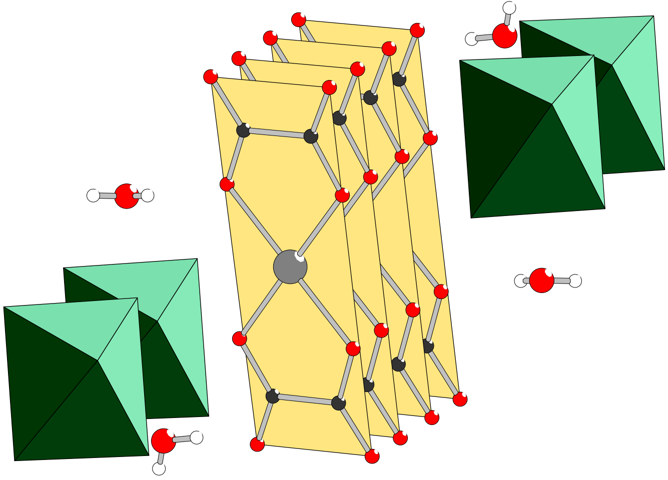
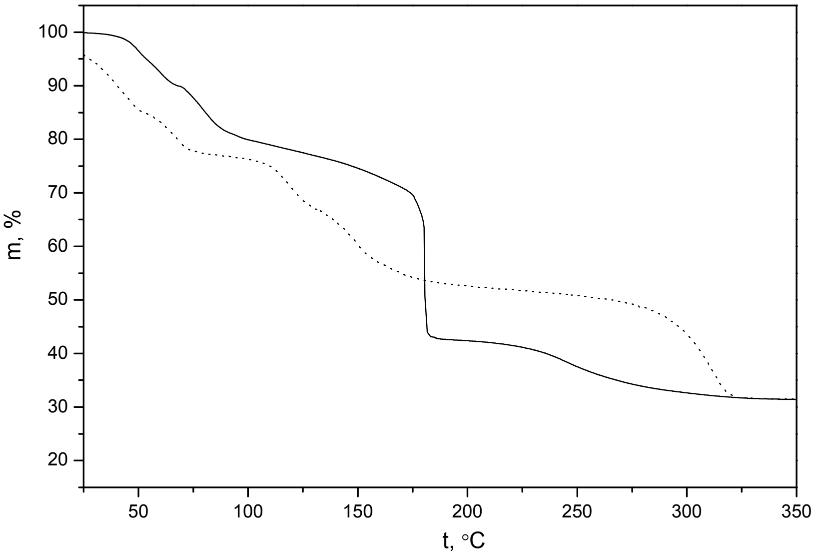
Thermal decomposition of complex salts comprising both cationic and anionic coordination entities is a handy way for preparation of bimetallic nanoalloys.



Hexaaquocobalt and -nickel oxalatopalladates $[M(H_2O)_6][Pd(C_2O_4)_2]\cdot xH_2O$ (M=Co, Ni) were chosen as precursors of high dispersed bimetallic phases $M_{0.5}Pd_{0.5}$. The main advantages of these composition is rather high solubility relatively to other double complex salts and a presence of ligands with remarkably reductive properties. Structurally the salts differ from each other inessentially and thus open up possibility to form solid solutions with partially substituted non-noble metals.

Thermal behavior of complex salts (by example of $[Co(H_2O)_6][Pt(C_2O_4)_2]\cdot 4H_2O$) strongly depends on atmosphere of decomposition experiment. The first stages of thermolysis correspond to full dehydration. This process is divided in some steps and passes through formation of lower hydrates. The further heating in both reductive (hydrogen) and unert (helium) atmosphere leads to full reduction of metals. Reduction in hydrogen takes place at lower temperatures but the last non-metallic byproduct oxalic acid decomposes at temperatures higher than 200°C.



Acknowledgements. The work is supported by the Russian Foundation for Basic Research (grant no 17-03-00693)

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PALLADIUM NITRATO COMPLEXES IN CONCENTRATED NITRIC ACID SOLUTIONS: A ^{15}N NMR STUDY.

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Palladium 108 is long-lived radioactive product of nuclear fusion and its separation are of great importance for recycling of spent nuclear fuel. As current technology of the recycling bases on dissolution of the spent fuel in nitric acid, speciation in nitric acid solutions of palladium (NASPD) appears as a key knowledge for elaboration of palladium extraction from such objects. Also, NASPD and solid palladium(II) nitrate are useful raw materials for preparation of heterogeneous Pd-based catalyst including car exhaust gases converters. Moreover, due to lability of nitrato groups, palladium(II) nitrate being prepared from NASPD is itself valuable starting reagent for the synthesis of palladium compounds. Therefore, studies of palladium speciation in NASPD are of great importance both from technological and academic point of view.

In this work for the first time ^{15}N NMR is used for detailed study of palladium speciation in NASPD with high concentration of nitric acid (6-13M). It was found that cooling of the solutions below -40°C slows down the nitrato ligand exchange and results in ^{15}N NMR patterns clear depicting $[Pd(NO_3)_n(H_2O)_{4-n}]^{2-n}$ species distribution. These ^{15}N NMR data were used for calculation of the cumulative formation constants of palladium nitrato complexes, which were found to decrease with number of NO_3^- ligands.

Acknowledgements - This work was supported by the Russian foundation for basic research grant 16-03-00549 A. D.V. thanks the Ministry for Education and Science of the Russian Federation for the award of a fellowship of the President of the Russian Federation for young scientists.

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STRUCTURAL DIVERSITY OF TRANSITION METAL CYMANTRENECARBOXYLATES.

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Heterometallic carboxylates including one of the metal atoms in an organometallic ligand belong to a poorly studied type of compounds. In recent years we have obtained Mn-rare earth heterometallic complexes containing cymantrenecarboxylate ligand $CymCO_2^-$ (Cym = $(\eta^5$-$C_5H_4)Mn(CO)_3)$; their structures and physicochemical properties were studied [1-4].

It was found that in aqua-organic media, in which the lanthanides tend to form polymeric cymantrenecarboxylates [1,3], the transition metals give rise to the isostructural complexes $[M(H_2O)_6](CymCO_2)_2 \cdot 4H_2O$ (M = Co (**1**), Ni (**2**), Zn (**3**)) built of the isolated ions. In the presence of various organic ligands in appropriate organic media the complexes $[Co(CymCO_2)_2(bpy)_2] \cdot 2PhMe$ (**4**; bpy = 2,2′-bipyridyl), $[Co(CymCO_2)_2(imidazole)_2]$ (**5**), $[Ni(CymCO_2)(bpy)_2(H_2O)][CymCO_2] \cdot 0.5MePh \cdot 2H_2O$ (**6**), $[Cu(CymCO_2)_2(imidazole)_2]$ (**7**), $[Cu(CymCO_2)_2(bpy)(H_2O)]$ (**8**), $[Fe_3(CymCO_2)_6(bpy)_2] \cdot 2PhMe$ (**9**), $[HNEt_3][(VO)_6(SO_4)O(CymCO_2)_3(MeO)_6(MeOH)_2] \cdot 5H_2O$ (**10**), and $[Ni_2Cl((2\text{-}Py)_2C(O\text{-})(OH))_2(CymCO_2)]_2 \cdot 2MeCN$ (**11**) showing notable structural variety were obtained (Fig. 1). Complexes **5** and **6** display the properties of field-induced single molecule magnets. Thermolysis of the complexes **1-8** in air brings about the spinels MMn_2O_4 which are valuable magnetic materials.

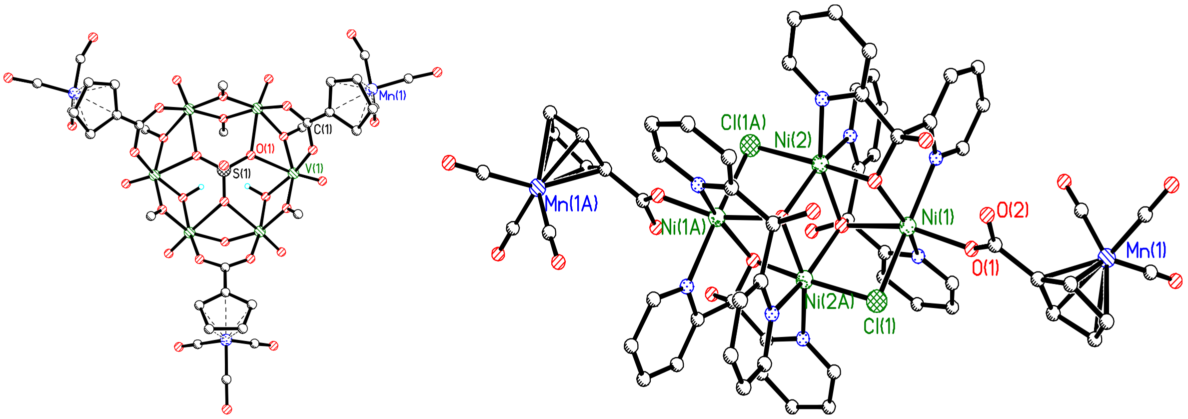

Fig. 1. Structures of complex anion in compound **10** (left) and of complex **11** (right).

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TRIMETALLIC FERROCENECARBOXYLATE AND CYMANTRENECARBOXYLATE 3D-3D'-4F-COMPLEXES WITH DEFECT-DICUBANE STRUCTURE: SYNTHESIS, MAGNETISM, AND THERMOLYSIS

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Heterometallic carboxylates containing one of the metal atoms as a part of organometallic ligand represent relatively poorly studied type of compounds. In recent years we have obtained and studied *3d-4f*-heterometallic complexes containing cymantrenecarboxylate $CymCO_2^-$ (Cym = $(\eta^5\text{-}C_5H_4)Mn(CO)_3$) or ferrocenecarboxylate $FcCO_2^-$ (Fc = $(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe$) ligands [1-3].

It seemed interesting to prepare compounds including three different metals in the molecule. Using $FcCO_2H$ and triethanolamine (H_3tea) as core-forming ligands, we have obtained the isostructural trimetallic complexes $[Ln^{III}_2Cr^{III}_2(OH)_2(FcCO_2)_4(NO_3)_2(Htea)_2]\cdot 2MePh\cdot 2THF$ (Ln = Tb (**1**), Dy (**2**), Ho (**3**), Er (**4**), and Y (**5**); $H_3tea = N((CH_2)_2OH)_3$) having defect-dicubane structure [4]. In all of the complexes, doubly deprotonated triethanolamine chelates the chromium ion, however, for Tb a similar isomeric complex **1a** in which Tb^{3+} is chelated by triethanolamine as a tetradentate ligand, was also isolated. For Dy, an analogue complex on a basis of Fe^{3+} and cymantrenecarboxylic acid, $[Dy^{III}_2Fe^{III}_2(OH)_2(CymCO_2)_4(NO_3)_2(Htea)_2]\cdot 2MeOH\cdot 2MeCN$(**6**), was obtained. DC magnetic studies revealed ferromagnetic interactions in the metal core of Dy and Ho complexes at T ≈ 25 K and in Y complex below 20 K. Complexes **1**, **2**, **3**, **4** and **6** display the properties of single-molecule magnets with magnetization reversal barriers Δ_{eff}/k_B of 56, 80, 48, 14 and 20K, respectively. Thermolysis of the complexes **1-5** was studied by means of TG and DSC; the products obtained under air atmosphere contain mixed oxides $LnCrO_3$ and $Cr_{0.75}Fe_{1.25}O_3$.

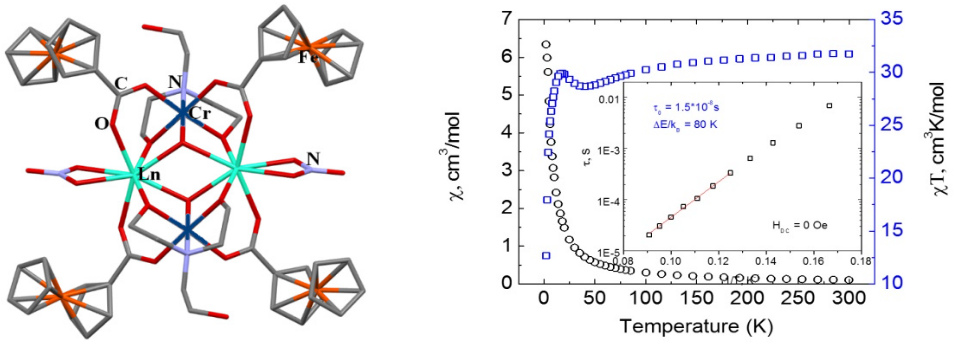

Fig. 1. Structure of complexes **1-5** (left); DC magnetic data (right) and fitting of AC data to Arrhenius law for Dy complex **2** (right, inset).

[1] P.S. Koroteev, Zh.V. Dobrokhotova, A.B. Ilyukhin, N.N. Efimov, A.V. Gavrikov and V.M. Novotortsev, *Russ. J. Coord. Chem*. **2016**, 42, 591-603.
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[3] N.N. Efimov, P.S. Koroteev, A.V. Gavrikov, A.B. Ilyukhin, Zh.V. Dobrokhotova and V.M. Novotortsev, *Magnetochemistry*, **2016**, 2(4), 38.
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SYNTHESIS AND REACTIVITY OF NOVEL ALKYNILATED CARBORANES AND METALLACARBORANES

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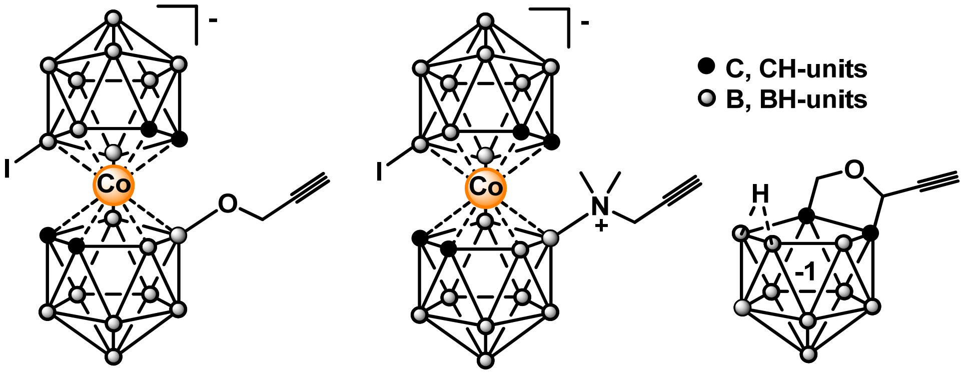
Terminal alkynes play crucial role in modern organic synthesis. Sonogashira and click reactions became powerful instruments for the preparation of many new compounds, including drugs, ligands, nanomaterials etc. Our continuous interest aims towards synthesis of the small biomolecules boron cluster conjugates. Since carboranes modified with terminal alkyne groups were barely studied [1], herein we present synthesis, of novel alkynylated carboranes and metallacarboranes, investigation of their reactivity in Sonogashira and click reaction as well as synthesis of conjugates with small biomolecules.



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Acknowledgements -Authors are grateful to Russian Foundation for Basic Research (Grant 17-03-00476) for the partial financial support.

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ROOM TEMPERATURE POLARIZED LUMINESCENCE OF NEMATIC LANTHANIDMESOGENS

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Lanthanide containing compounds are widely used in various optical electronic devices, organic light emitting diodes of different colors, at panel and flexible displays, optical waveguides, etc. Addition of liquid crystalline properties to those style complexes can create media with polarized luminescence due to uniaxial orientation of molecules. Lanthanidomesogens having nematic mesophase are more interesting due to their viscosity that is the least of all other types of mesophases[1,2].

At this work the features of nematic phase behavior in some lanthanidmesogens are described. The dielectric, magnetic, optical and luminescence properties (fig.1) of a paramagnetic lanthanide containing nematic LC have been studied.

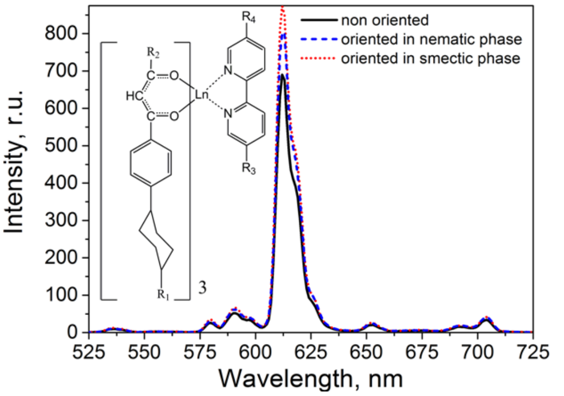

Figure 1. Structure and polarized luminescence spectra of oriented complex Ln (III)

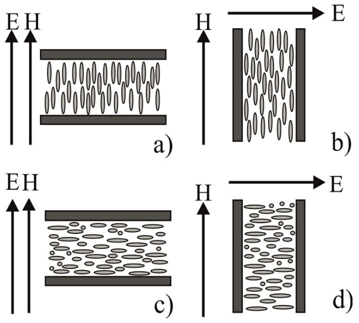

Figure 2. The orientation of nematic LC in the sample cell under the influence of the magnetic (H) and electric (E) field with a positive (a, b) and a negative (c, d) magnetic anisotropy

The orientation of the molecules of a nematic liquid crystal in a sample cell under the action of a magnetic field H relative to the direction of the probe electric field E has been studied. Remarkable property of compounds under investigation is their possibility to save orientation created in mesophase after cooling till ambient temperatures. The optical and dielectric anisotropy of the liquid crystal complexes under discussion is the same in sign and close in magnitude. The luminescence properties of synthesized lanthanide complexes are investigated. However, it can be concluded that the change in the central ion exerts a strong influence on the dielectric and optical properties of lanthanidemesogens with the same ligand environment.

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Acknowledgements -The work was supported by the Russian Foundation for Basic Research (RFBR) grant № 16-03-00443

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COORDINATION COMPOUNDS OF PALLADIUM(II) WITH SULFUR-CONTAINING SUBSTITUTED DERIVATIVES OF *CLOSO*-DECABORATE ANION

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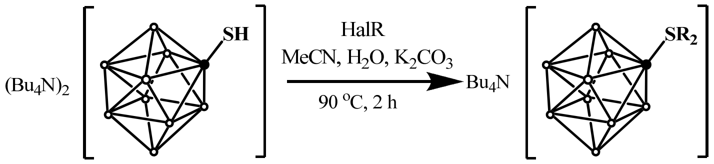
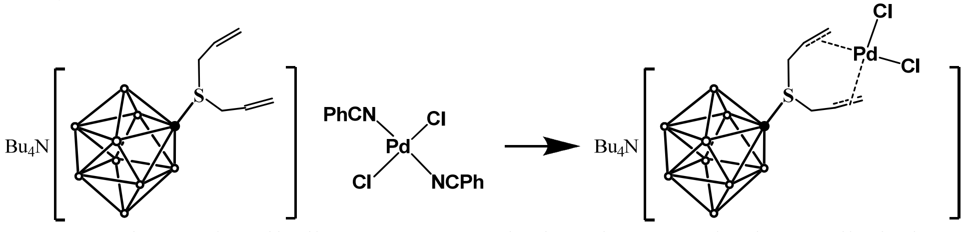
Boron neutron capture therapy (BNCT) is a promising approach in the treatment of cancer. This is due to the possibility of its selective effect directly on the cells of malignant tumors. At the moment, the clinical interest in BNCT in neurooncology is focused on the therapy of gliomas, in particular, glioblast. It can also be used for metastatic brain damage. Firstly, a thermal neutron source corresponding to the requirements of BNCT is needed and, secondly, a ^{10}B-containing preparation that will selectively accumulate in the tumor tissue [1]. In this regard, it is extremely important to obtain boron-containing drugs that can meet all the requirements of therapy.

In this paper, methods have been developed for the synthesis of substituted sulfonium salts of the *closo*-decaborate anion of $[2\text{-}B_{10}H_9SR_2]^-$ by the reactions of the sulfanyl-*closo*-decaborate anion $[2\text{-}B_{10}H_9SH]^{2-}$ with an excess of alkyl halides. This method allows to obtain derivatives with various functional groups, such as phenyl, carboxyl, allyl, amide, hydroxyl, etc.



Hal = Br, Cl
R = $-CH_2COOEt$, $-CH_2CHCH_2$, -Bu, $-CH_2Ph$, $-CH_2CONH_2$

These derivatives represent a promising synthon for obtaining coordination compounds with platinum-group metals. It was shown that the chelate complex $(Bu_4N)B_{10}H_9S(CH_2\text{-}CH{=}CH_2)_2PdCl_2$ formed in the reaction of the derivative $(Bu_4N)B_{10}H_9S(CH_2\text{-}CH{=}CH_2)_2$ with trans- $-(PhCN)_2PdCl_2$.



Recently, a new class of palladium compounds has been actively studied that has high, antitumor activity equal to or superior to cisplatin [2]. The boron-containing palladium complexes obtained by us are certainly of interest as drugs for use in combined therapy of malignant tumors. The structure of the obtained derivatives was established by the methods of multi-nuclear NMR spectroscopy, elemental analysis, IR spectroscopy, and X-ray diffraction analysis of single crystals.

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LANTHANIDE COMPLEXES BASED ON TRIFLUOROALKYLATED LITHIUM 1,3-DIKETONATE BEARING ACETAL FRAGMENT

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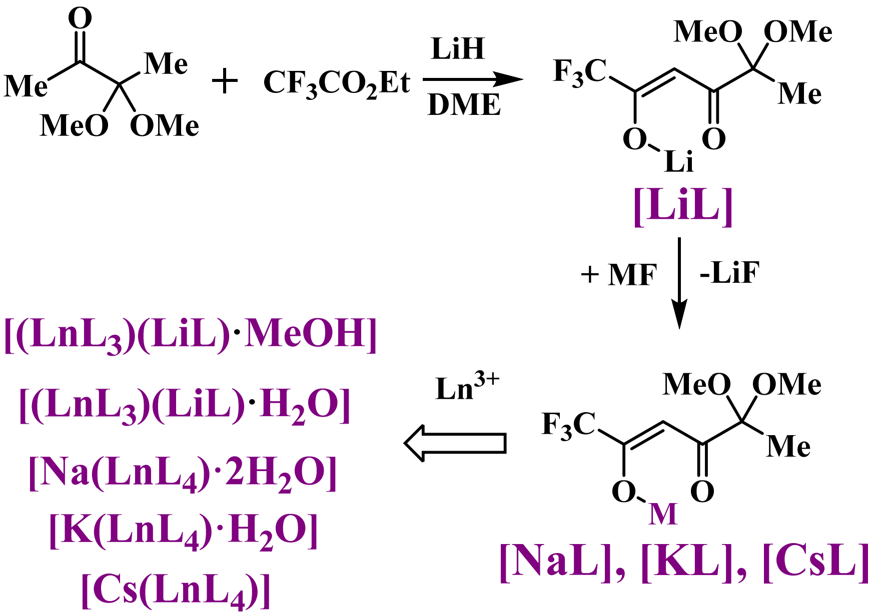
1,3-Dicarbonyl compounds and their derivatives have been extensively studied for more than a century and their ability to give rise to a rich coordination chemistry is well documented. Strong interest to the synthesis of mono- and polynuclear complexes and clusters with 3d and 4f metals is caused by their luminescent and magnetic properties.

Recently we have elaborated a synthetic approach to trifluoroalkylated lithium diketonate (**LiL**) bearing acetal fragment (Scheme 1) [1]. The interaction of alkali fluorides and **LiL** proceeds with *in situ* formation of alkali diketonates (**ML**) that revealed the broad possibilities for novel lanthanides complexes preparation (Scheme 1).



M = Na, K, Cs; Ln = Eu, Tb, Dy

Scheme1

[1] D.N. Bazhin, D.L. Chizhov, G.-V. Roeschenthaler, Yu.S. Kudyakova, Ya.V. Burgart, P.A. Slepukhin, V.I. Saloutin and V.N. Charushin, *Tetrahedron Lett.*, **2014**, *55*, 5714-5717.

Acknowledgements - This work was financially supported by Russian Foundation for Basic Research (grant no. 16-33-60048 mol_a_dk).

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HYDROXO COMPLEX OF SIX-COORDINATED WATER-SOLUBLE ZINC PORPHYRIN

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The ability of the central metal ion to coordinate two axial ligands, on both sides of the macrocycle plane, is a crucial factor for 3D porphyrin metal-organic framework (MOF) construction. Zinc porphyrins bind one axial ligand much more strongly than second one, but they can coordinate two axial ligands on both sides of the porphyrin platform to form a six-coordinated zinc complex. So, zinc porphyrins with two axial ligands can be formed in crystal structures or even in solution, when the whole system is suitably stabilized [1-4].

Here we demonstrate that water-soluble Zn-5,10,15,20-(tetra N-methyl-4-pyridyl)porphyrin can form six-coordinated dihydroxo complex with an excess of axial ligand at high pH values. By means of potenciometric titration technique with synchronous UV-Vis absorbtion and fluorescence spectra registration and also quantum-chemical calculations, step-by-step Zn-porphyrin five-coordinated monohydroxo and six-coordinated dihydroxo complexes formation was investigated. Obviously, organic bases (such as pyridine and imidazole) can change pH values during the experiment in aqueous media, or even in buffer systems when significant addition of organic bases.

Investigation these processes opens the opportunity for new porphyrin MOF construction and as a result, creation the new extremely promising ecological materials for use in biology, medicine and other medical and technical fields.

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THE UNPRECEDENTED BINUCLEAR RUTHENIUM COMPLEX WITH THREE BRIDGING THIOUREA

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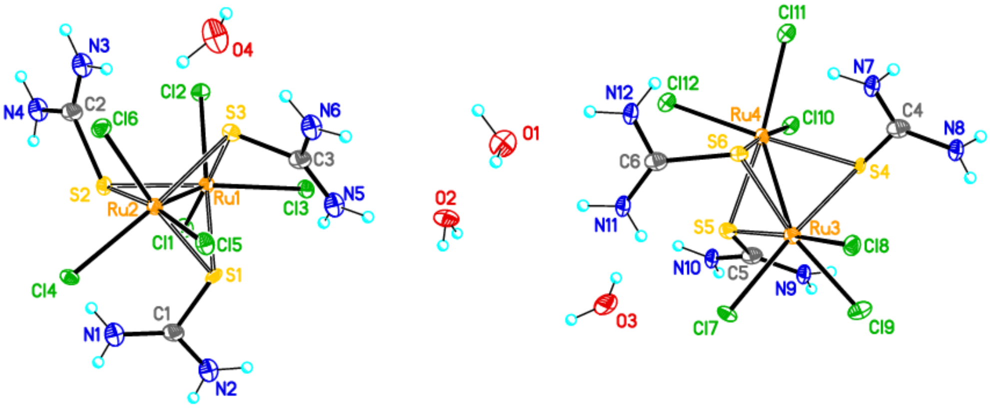
Thiourea (thiocarbamide, Thio) is a classical ligand in coordination chemistry. A variety of transition-metal complexes with thiourea have been reported to date. Thio can coordinate through the S donor atom in a monodentate fashion and can bridge two and even three metal atoms *via* the S atom. Binuclear (Cu, Ag) and trinuclear (Cu, Ag, Pd) compounds are known, where metal atoms are bonded by two bridging Thio [1], but complexes with three bridging Thio have remained elusive so far.

Here we report on the synthesis and structure determination of diruthenium(III) complex $Ru_2(Thio)_3Cl_6\cdot 2H_2O$, which reveals unprecedented three bridging Thio ligands. The complex was prepared as dark red crystals by prolonged storage of $K_4[Ru_2OCl_{10}]$ and bis(α,α′-dithiobisformamidinium) chloride in an HCl solution.

Crystals of $Ru_2(Thio)_3Cl_6\cdot 2H_2O$ are triclinic, space group $P1$, with $Z' = 2$, lattice parameters $a = 8.6654(17)$, $b = 9.1046(18)$, $c = 13.621(3)$ Å; $\alpha = 103.26(3)°$, $\beta = 94.38(3)°$, $\gamma = 111.28(3)°$. According to X-ray crystallographic data, the complex is binuclear with two face-sharing coordination octahedra joined together by three Thio bridges (figure). Thiourea molecules are coordinated *via* the S atoms, the Ru-S distances are in a range 2.295(6)-2.360(6) Å, the terminal Ru-Cl bond lengths lie in a range 2.390(5)-2.423(6) Å. The Ru-Ru distances are 2.676(3); 2.668(3) Å strongly implying the emergence of the direct metal- metal bond.



The thiourea groups remain planar. Water molecules are H-bonded with thiourea NH_2-groups and Cl atoms.

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SYNTHESIS OF NEW ORGANIC RECEPTORS BASED ONUPPER RIM SUBSTITUTEDCALIX[4]AREN DERIVATIVES WITH TRIAZOLYL AND HYDRAZINE FRAGMENTS FOR FORMATION OF NEW POLYFUNCTIONAL MATERIALS IN CRYSTALLINE PHASE

E.I. Latypov [a,b], A.S. Ovsyannikov[a,b], E.V. Popova[a], S.E. Solovieva[a,b], I.S. Antipin[a,b], A.I. Konovalov[a,b]

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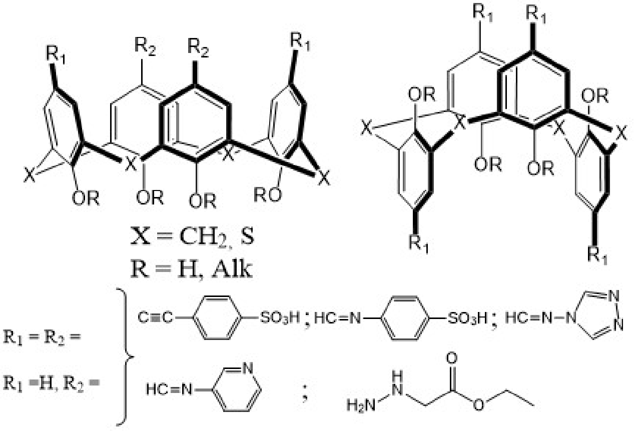
Nowadays design of magnetic complexes of metals expands very widely. They can be used in construction of sensors, molecular switches, also in medicine as contrast agents etc. One of most attractive issues is development of materials and systems for quantum computers and nanoelectronics[1]. It can be achieved by investigation of new single-molecule magnets (SMM) which can be charactarised by a slow nuclear spin magnetic relaxation on the single molecule level. Typically SMMs present coordination compounds containing cluster nodes of paramagnetic metal cations (d/f elements)[2]. From another hand, the organic ligands play the crucial role in formation of SMMs. (Thia)calix[4]arenes possessing of different attractive features such as capacity to be modified on the upper/low rim and adopted in 4 stereoisomer forms is a very suitable molecular platform to design the SMMs[3]. Here we report the synthesis of new molecular building blocks based (thia)calix[4]arene adopting cone and 1.3-alternate conformations and bearing sulfonate, triazole and pyridine coordinating groups. We expect that these compounds are promising to be useful in formation of new magnetic active coordination networks by combining with different paramagnetic metal cations.



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MONO- AND BINUCLEAR COMPLEXES Cu(II) WITH 4,6-DIMETHYLPYRIMIDYL HYDRAZONE DIACETYL MONOXIME

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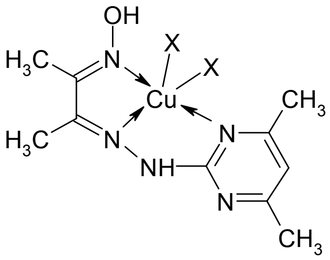
The mono- and binuclear complexes of Cu(II) with 4,6- dimethylpyrimidyl hydrazone diacetyl monoxime (H_2L) have been synthesized for the first time. The composition and structure of complexes have been established with the elemental analysis, IR, ESR spectroscopy, magnetochemistry and single crystal XRD. Mononuclear complexes 1 in which H_2L acts as uncharged NNN-tridentate ligand were obtained by reaction of H_2L with copper(II) chloride and bromide. Presence of crystalline water molecules result in formation of hydrogen-bonded dimers (see fig. 1) ensuring weak intermolecular magnetic exchange interaction of antiferromagnetic and ferromagnetic type between copper(II), which was shown by ESR spectroscopy and cryomagnetic magnetic susceptibility measurements.



X = Cl$^-$, Br$^-$

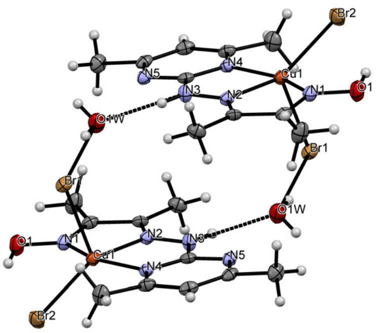
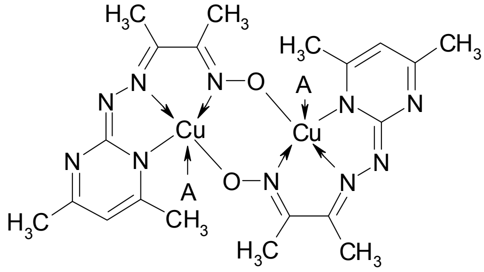
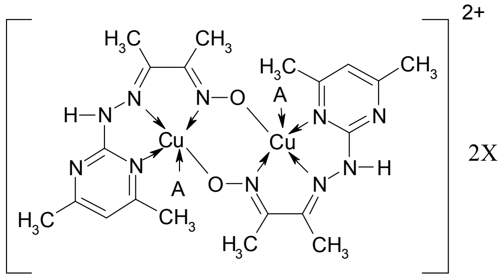


Fig.1. Centrosymmetric hydrogen-bonded dimers.

Cu(II) complexes of types 2a and 2b, synthesized by reaction of H2L with Cu(II) acetate, nitrate and perchlorate are characterized by dimeric structure with bridging N-O groups of deprotonated oxime moiety.



A = CH_3OH



X = ClO_4, NO_3

Magnetochemical measurements demonstrate that in complexes of copper(II) nitrate and acetate strong antiferromagnetic type interaction is present. Metallochelate based on copper(II) perchlorate is diamagnetic at the room temperature.

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POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF *O*-IMINOQUINONES AND O-IMINOSEMIQUINONE COMPLEXES OF TIN(IV) UNDER UV-IRRADIATION

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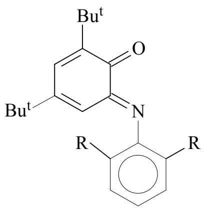
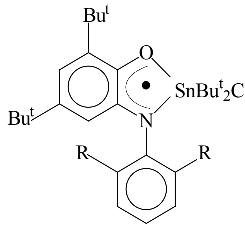
The aim of this work was to compare the polymerization of methyl methacrylate (***MMA***) with azobis(isobutyronitrile) (***AIBN***) and *o*-iminoquinones (***1a-c)*** or *o*-iminosemiquinone complexes of tin(IV) (***2-3***) using heating and UV-irradiation.

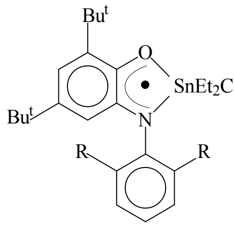
o-Iminoquinones ***1a*** and ***1c*** in equimolecular ratio to the initiator acts as strong inhibitors at 30°C. Under UV-irradiation conversion of MMA reaches ~ 20%. Number average molecular weight (***M_n***) of polyMMA and the indexes of polydispersity (***PDI***) are similar to the values obtained in the absence ***1a-c***.



1a-c



2a-c



3a-b

*R = Me (**a**), Et (**b**), Pr^i(**c**)*

The introduction of ***1a*** has slightly effect on the rate of the polymerization of MMA at 50°C. Molecular weight of polyMMA samples increases with conversion. Molecular weight distribution (***MWD***) increase with conversion too; PDI reaches ~ 4-5 at the high conversion. Synthesis of polyMMA in the presence of ***1a*** passes under UV-irradiation at 50°C without autoacceleration. Molecular weight of polyMMA increases linearly with conversion and PDI is ~ 1.6-1.8.

Maximum conversion of MMA in ratio ***1c*** / AIBN = 1 / 1 at 50°C does not exceed ~ 20% as under UV-irradiation also without it. Molecular weight of polyMMA increases linearly with conversion; samples of polyMMA have PDI ~ 1.2-1.5 on both case.

PolyMMA prepared with participation of ***1c*** under UV-irradiation or without it at 30-50°C may be used as macroinitiators for postpolymerization MMA at 70-90°C.

o-Iminoquinones ***1a-c*** reduces the rate of polymerization of MMA in proportion to its concentration at 70°C. Molecular weight of polyMMA increases linearly with conversion and in case of ***1b-c*** PDI of polyMMA is ~ 1.4-1.8.

It was found that that each of the ***2a-c*** acts as iniferter of MMA polymerization at 70-90°C. In case of influence of UV-irradiation each of complexes ***2a-c*** also initiated polymerization of MMA at 30°C. The curves MWD of polyMMA samples characterized by bimodality.

Molecular weight of polyMMA prepared with ***2-3*** in case of initiating by AIBN increase proportionally with conversion at 70°C. Samples of polymers obtained with complexes ***3a-c*** have PDI ~ 1.4-2.0. Polydispersity of polyMMA samples prepared in the presence of AIBN and complexes ***3a-b*** under UV-irradiation at 30°C increases with conversion.

Thus, the role of *o*-iminoquinones in radical polymerization of MMA initiated by AIBN at 30-70ºC depends on their structure. *o*-Iminosemiquinones of tin(IV) acts an effective chain growth regulators only on condition of thermal initiation.

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THE HETEROMETALLIC COMPLEXES SUPPORTED WITH POLYANIONIC REDOX-ACTIVE DIIMINE LIGAND

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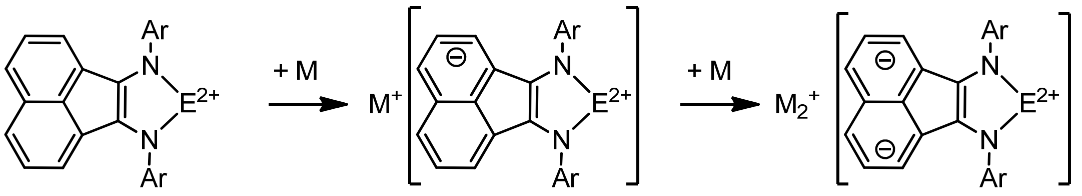
Despite the steady interest of researchers in molecules with a high negative charge, only a few examples of reliably characterized metal complexes based on tri- and tetraanionic organic ligand are known at present. Moreover, the ability of the ligand to accept or to donate negative charge to the metal is paramount to the fine-tuning of the redox potential of the metal, and of its Lewis acidity which, in turn, determines the chemical behaviour of the metal complex.

In 2003 we have synthesised and structurally characterized four anionic forms of dpp-bian (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) as alkali metal salts [1]. Here we report the synthesis and characterization of new heterometallic complexes, containing tri- and tetraanion of dpp-bian.



E = Ca, Yb, TmCl, Ge, LaI, BBr, BONa
M = Li, Na, K

The heterometallic complexes have been obtained by reduction of the calcium, boron, germanium and some lanthanides complexes containing dpp-bian dianion by alkali metals in thf or diethyl ether. The paramagnetic compounds comprising the trianion dpp-bian have been characterized by EPR spectroscopy, diamagnetic with tetraanion dpp-bian – by NMR spectroscopy, some complexes – by single-crystal x-ray diffraction. The reactivity of the obtained complexes towards water and ketones has been investigated.

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Acknowledgements - we thank the Russian Foundation for Basic Research (Grant № 16-03-00946) for financial support.

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COMPLEXATION OF ORGANIC SPECIES BY d^0 ZIRCONOCENE: PHOTOPHYSICAL AND DFT STUDY

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In contrast to phosphorescence of organic molecules, reports on phosphorescence of metal complexes, especially organometallic ones, are limited and the known instances are mostly referred to late-transition metal complexes. Reports on photosensor properties of organometallics are very rare. Recently, we obtained *ansa*-zirconocene(IV) *rac*-$C_6H_{10}(IndH_4)_2ZrCl_2$ that exhibits markedly efficient phosphorescence at room temperature (RT) in various media. [1] Emission quantum yield (Φ) and the excited-state lifetime (τ) of *rac*-$C_6H_{10}(IndH_4)_2ZrCl_2$ in fluids are highly sensitive to the external environment (i.e. to electronic-structural peculiarities of solvents at molecular level) at RT: they span over 2 orders of magnitude. The observed strong solvent effects cannot be explained by electrostatic or van-der-Waals interactions; however, they indicate significant specific interactions between the d^0 complex and surrounding organic species. We suggest that a main factor, determining Φ and τ of the phosphorescent state is the type of coordination (inner- or outer-sphere) with organic molecules in local microenvironment. Specificity of the interaction is manifested as a monotonic decrease in Φ and τ with the enhancement of steric hindrance in the C_6-ring of the solvent molecules (Fig. 1). Such systematically modified hindrances are, for instance, the alkyl substituent size in alkylbenzenes: at virtually identical macroscopic medium properties (ε, n^2, influence on E_{00} and E_{max}, etc.) a strong solvent effect (outer-sphere coordination) on Φ and τ is observed. Presumably, strong outer-sphere solvation restricts conformational freedom and leads to more rigid, “frozen” architecture of the complex (“rigid matrix” effect at microscopic level) reducing vibrational relaxation of the ligand sphere and also depresses dynamic bimolecular quenching of phosphorescence. In opposite, strong inner-sphere coordination leads to decrease of Φ and τ (quite strong donor – acceptor coupling exists, e.g., with ethers: Zr← OR_1R_2 (Fig. 2) [2]). All experimental findings are in line with our DFT data.

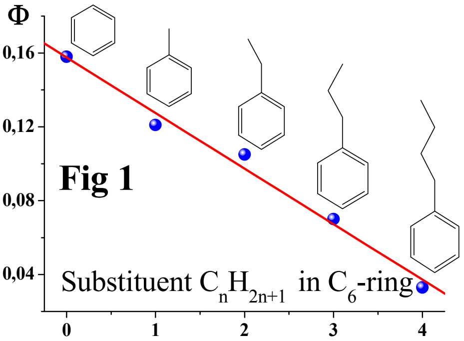

Fig 1

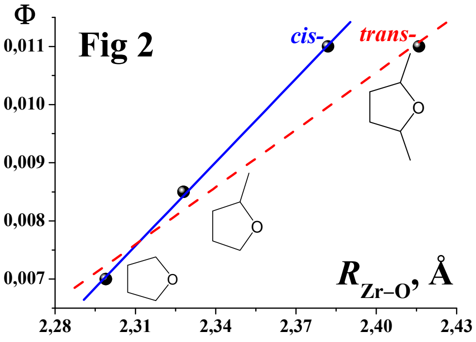

Fig 2

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CRYSTAL STRUCTURE AND PTOPERTIES OF DL-SERINIUM HEPTAFLUORODIANTIMONATE(III)

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New information on the types of metals coordination to amino acids (AA) contributes to the theory of directed synthesis of defined composition and structure complexes, which may be useful for creating new promising materials with predictable properties. In the course of systematic chemistry and structure studies of antimony trifluoride compounds with AA, several molecular adducts, a number of complex tetrafluoroantimonates(III) with cations of protonated amino acids have been synthesized, and their structures are investigated [1-7]. Data on the physicochemical properties of complex compounds of SbF_3 with AA are few [8], but there are no data on biological properties. For the first time, during studying the interaction of antimony trifluoride with *DL*-serine in aqueous solution, heptafluorodiantimonate(III) of *DL*-serine ($C_3H_8NO_3$ Sb_2F_7 (**I**) in form of mono crystals was obtained. (Monoclinic crystal system: a = 6.6367 (1), b = 5.9521 (1), c = 13.5562 (3) Å, Z = 2, space group P21).

The resulting complex compound is stable when stored in air and it is highly soluble in water. In the IR absorption spectrum **I**, there are an intense absorption band at 1732 cm^{-1} and a medium-intensity band with a maximum of 1256 cm^{-1}, indicating the presence of a protonated COOH group in the SerH$^+$ cation entering in **I**. The conclusions of IR spectroscopic research were justified by determining it's crystal structure, which represents a new structural type of SbF_3 with amino acid complex compound, because it is formed from protonated cations *DL*-serine $(C_3H_8NO_3)^+$ and anionic dimeric complexes $[Sb_2F_7]^-$. Complex anions $[Sb_2F_7]^-$ consist of two trigonal bipyramid SbF4E, linked by a common vertex. Via hydrogen bonds N-H···F, O-H···O and O-H···F structural units are combined into a three-dimensional framework (Fig. 1).

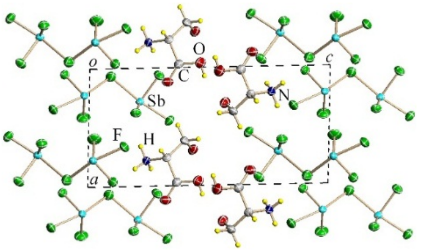

Fig. 1. Crystal structure of $(C_3H_8NO_3)Sb_2F_7$.

Antimicrobial action of **I** was found in the Total Microbial Test. The substance introduced into the experimental environment at a concentration 0.01 M/l completely inhibits the growth of saprophytic microorganisms.

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STRUCTURE FEATURES AND MAGNETIC PROPERTIES OF BIS-O-BENZOSEMIQUINONATO ZINC COMPLEXES WITH DIFFERENT N-LIGANDS

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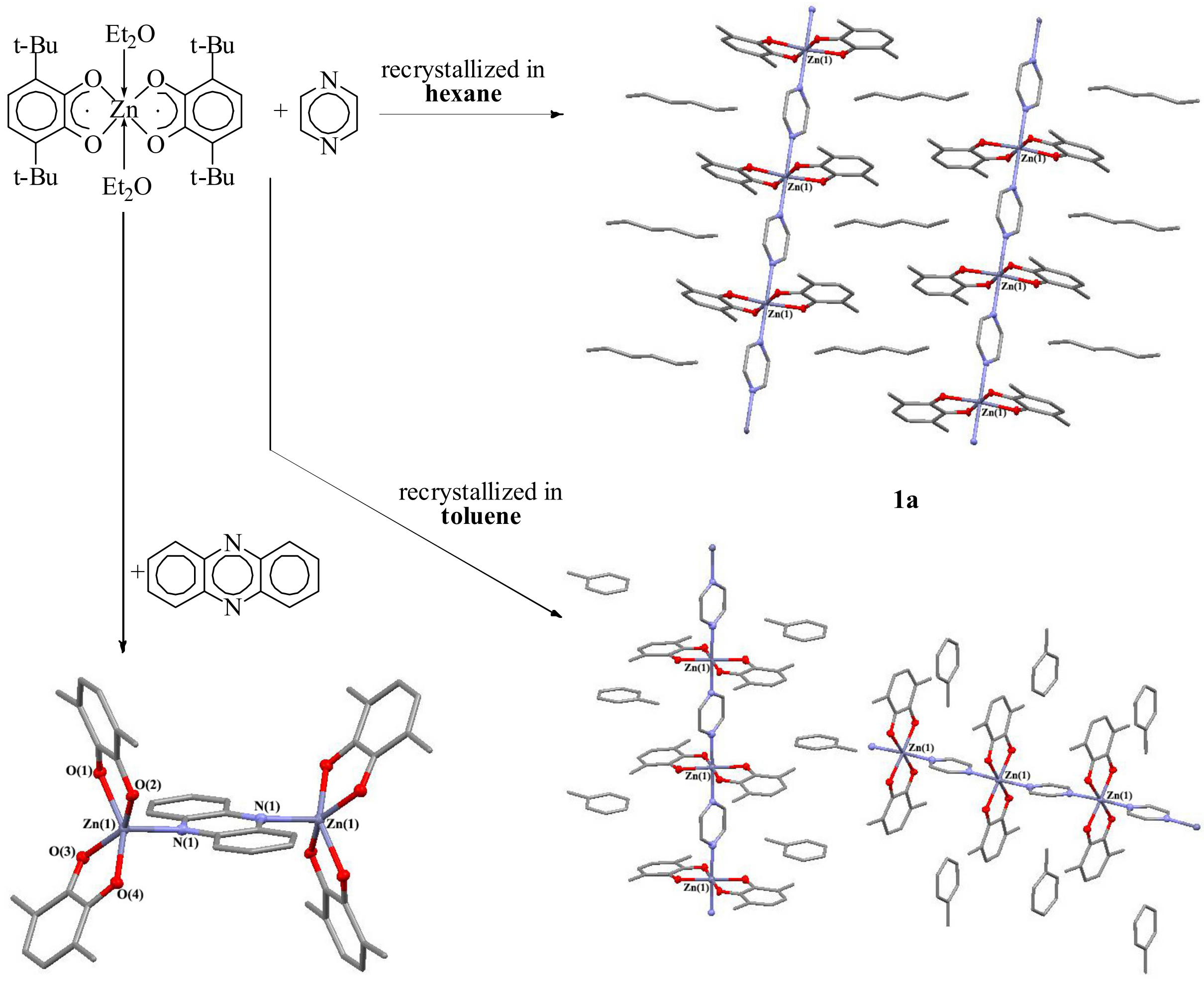
Bis-o-semiquinolate zinc complexes with different N-ligands were synthesized:



1a

2

1b

All complexes were isolated and characterized by IR, EPR, magnetic measurements and X-ray diffraction. The orientation of the polymer chains of complex **1** was influenced by the crystallization method. The dependence of the magnetic moment on temperature demonstrates the presence of antiferromagnetic exchange between paramagnetic centers in all three crystalline complexes.

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SYNTHESIS, STRUCTURE AND PROPERTIES OF COORDINATION COMPOUNDS OF 3d-METALS VALERATES AND BENZOATES WITH PHENYLACETHYDRAZIDE

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3d-Metals complexes with carboxylic acid hydrazides are a fairly well-studied class of coordination compounds. At the same time, complexes of 3d-metals carboxylates with hydrazides have been studied very little. In this paper, the interaction of cobalt(II), nickel(II), copper(II) and zinc valerates and benzoates with phenylacethydrazide (L) was studied. 7 Complexes of the composition $[ML_3](RCOO)_2$ (R = C_4H_9-, M = Co, Ni, Zn, R = C_6H_5-, M = Co, Cu, Zn) and $[NiL_3](RCOO)_2{\cdot}4H_2O$ have been isolated by the interaction of a methanolic solution of the corresponding 3d-metal carboxylate with an aqueous solution of phenylacethydrazide with heating. The composition and structure of the complexes are determined by the methods of chemical analysis, vibrational spectroscopy (IR in pure form and in tablets with KBr, Raman) and diffuse reflection spectroscopy. In all cases, the bidentate ligand is coordinated through oxygen and nitrogen, and the anions are outer-sphere. The thermal stability of the complexes has been studied by thermogravimetry. Thermostability decreases in the series of complexing agents: $Co^{2+}>Ni^{2+}>Zn^{2+}>Cu^{2+}$, and for benzoates is higher than for valerates. The X-ray diffraction method was used to establish the structure of $[NiL_3](RCOO)_2{\cdot}4H_2O$, this is the first structurally characterized complex with phenylacethydrazide. The structural units of the crystal are complex $[NiL_3]^{2+}$ cations, $C_6H_5COO^-$ anions and crystallization water molecules. The Ni atom is coordinated along the apexes of the octahedron by three oxygen atoms and three nitrogen atoms of three bidentate chelating (O, N) ligands of L in cis, a trans-medial (fac) conformation. The structural units of the crystal are joined together by a branched network of hydrogen bonds O-H ... O, N-H ... O.

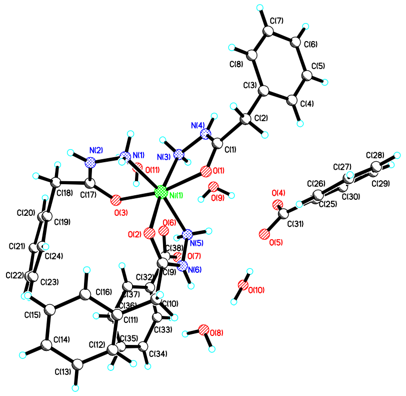

Fig. The structure of compound $[NiL_3](RCOO)_2{\cdot}4H_2O$

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NICKEL COMPLEXES WITH STERICALLY-HINDERED O-QUINONE, ANNELATED WITH DITHIETE

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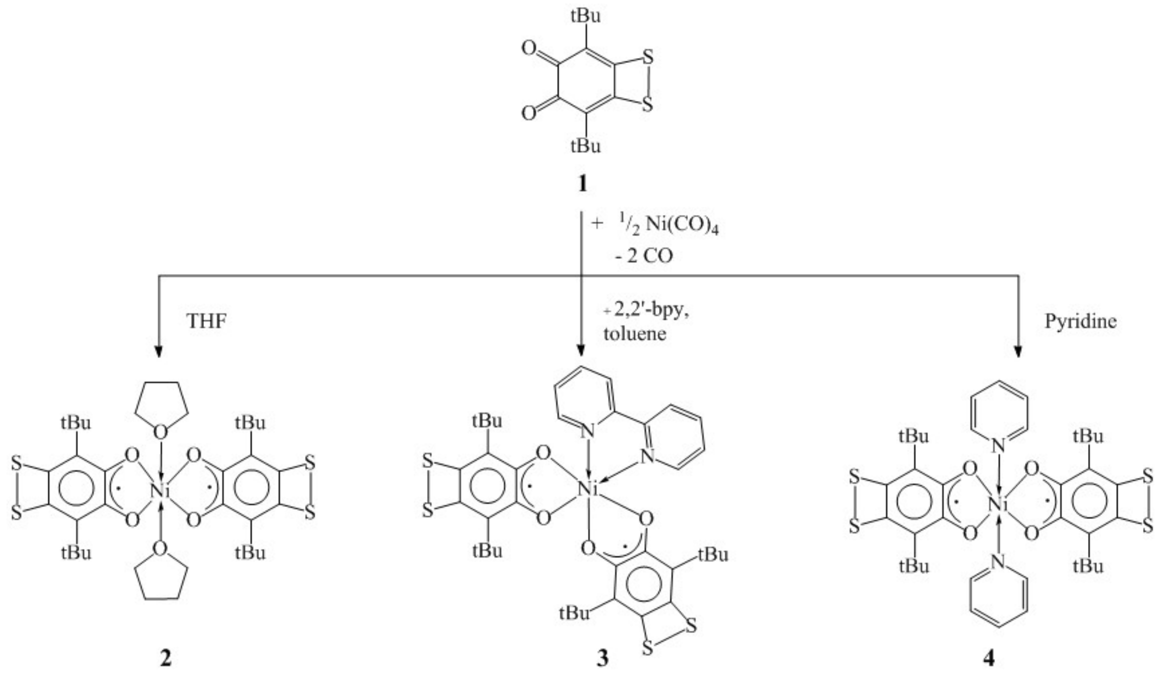
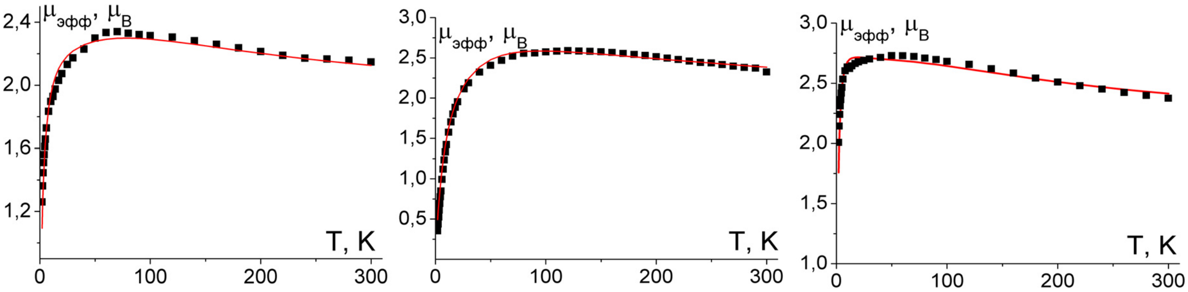
Sterically-hindered o-quinone, annelated with dithiete cycle – is a bifunctional ligand, comprising two redox-active coordination centers: dioxolene and dithiolene. It was shown previously, that soft Lewis acids attack dithiolene site, whereas hard Lewis acids and one-electron oxidants react towards dioxolene site.

Herein, novel complexes of ligand **1** with nickel are presented. These complexes are bis(o-semiquinonate), containing also auxiliary neutral ligands. The structure for **2** is established by X-ray crystallography. Magnetic properties of synthesized complexes **2-4** were studied. According to effective magnetic moment temperature dependence, all compounds demonstrate antiferromagnetic exchange between semiquinonates as well as ferromagnetic exchange between metal center and semiquinonate ligands.





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SYNTHESIS OF COORDINATION POLYMERS WITH BIS(1,2,3-BENZOTRIAZOLE) LIGANDS

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Metal-organic frameworks (MOFs) are extremely perspective structures due to their gas storage and separation abilities, possibility of functionalization and extreme surface areas. MOFs can be applied in industrial and medical branches. These structures consist of ligand and metal ion. To produce unique MOFs different coordination polymers with new ligands should be obtained, combined and modified. Azoles are perspective building blocks for this purpose [1,2].

There are no universal synthesis methods for coordination polymers with 1,2,3-bisbenzotriazole. To produce coordination structures, metal ions, ligands, temperature, time, metal-ligand ratio, solvents and additional other ligands were varied. Structures were studied by X-ray crystal analysis. 1D coordination polymer with 1,3-bis(benzo-1,2,3-triazol-1-yl)propane (prBta2) and $Cd(NO_3)_2$ was obtained (Figure a). The compound of composition $[(prBta2)_2Cd(NO_3)_2]_n$ was synthesized at 1:2 metal-to-ligand ratio by slow methanol evaporation during four days. Elementary cell parameters: a = 15.8620 Å, b = 8.5384 Å, c = 24.0489 Å, α = 90°, β = 94.157°, γ = 90°. The polymer has chain structure.

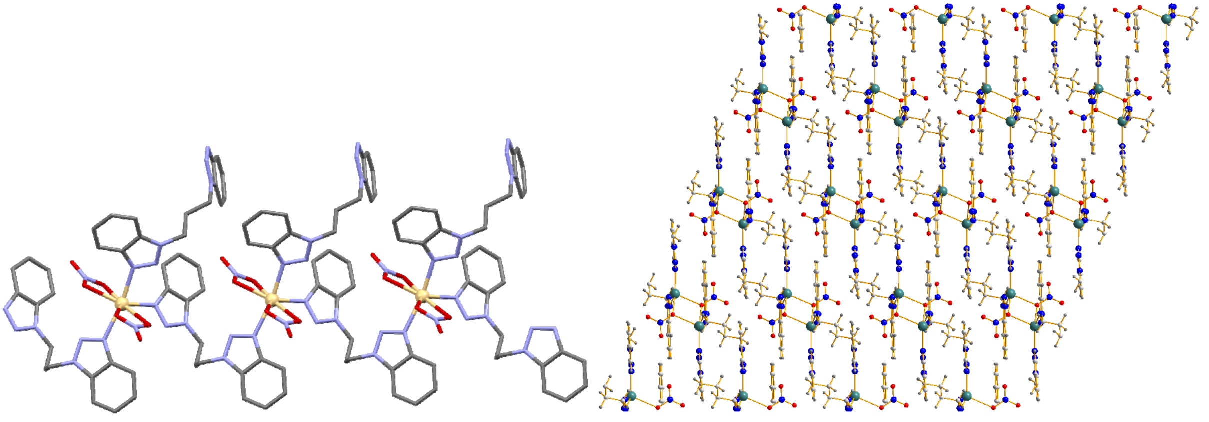
a *b*

Figure – Coordination polymers structures, a – chain, b – layer

2D coordination polymer with 1,4-bis(benzo-1,2,3-triazol-1-yl)butane (buBta2) and $AgNO_3$ was obtained (Figure b). The compound of composition $[(buBta2)_2AgNO_3]_n$ was synthesized at 1:2 metal-to-ligand ratio in methanol during 4 days. Elementary cell parameters: a = 19.2738 Å, b = 10.0159 Å, c = 19.2702 Å, α = 90°, β = 113.107°, γ = 90°. The polymer has layer structure. Both polymers can be used to produce original MOFs.

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SYNTHESIS AND CHARACTERIZATION OF NEW ARENE-RUTHENIUM(II) COMPLXES WITH 11H-INDENO[1,2-b]QUINOXALINE DERIVATIVES

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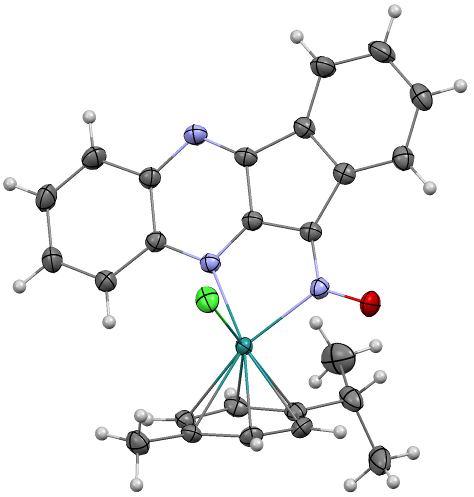
Arene-ruthenium(II) complexes are interesting due to their catalytic activity, photophysical and electrochemical properties, but most importantly – high antitumor activity, exceeding that of platinum coordination compounds [1]. The activity of Ru(II) complexes can be tuned by introduction of different ligands into a coordination sphere. If the ligand itself possesses biological activity, interesting synergetic effects can be observed, as was demonstrated, for example, for curcumin derivatives [2]. Recently, 11H-indeno[1,2-b]quinoxaline derivatives were descrived as specific cJun N-terminal JNK3 kinase inhibitors [3]. JNK kinases are involved in for cell apoptosis, inflammatory processes, reperfusion and insult pathogenesis. It therefore interesting to combine arene-ruthenium(II) and 11H-indeno[1,2-b]quinoxaline ligands in a series of coordination compounds and explore their structural features and biological activity. In this contribution we report the synthesis and crystal structure of the first example of cymene-ruthenium(II)-11H-indeno[1,2-b]quinoxaline-11-one oxime (IQ-1). The complex was prepared by the reaction of IQ-1 ligand with cymene-ruthenium(II) chloride dimer in methanol solution. The molecular structure of the complex in shown in the figure below. The asymmetric unit of the complex consists of one neutral [Ru(cym)(IQ-1)Cl] molecule. The oxime IQ-1 undergoes deprotonation upon the coordination, but it is interesting to note, that only nitrogen atoms of IQ-1 ligand take part in coordination, while a negatively charged oxygen atom remains uncoordinated.



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SYNTHESIS, STRUCTURE AND PHOTOLUMINESCENCE PROPERTIES OF HETEROMETALLIC COORDINATION COMPOUNDS {Zn_2Ln} WITH PIVALATE ANION AND 1,10–PHENANTHROLINE

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The relevance of light-emitting materials in some modern electronic devices promotes the development of technologies in increasing the efficiency, decreasing energy costs and making the technologies of the production of future molecular electronic systems cheaper. In the meantime, one of the most perspective directions in the field of the design of light-emitting materials is the obtainment of luminescence d-4f-heterometallic coordination compounds, photophysical characteristics of which can be finely tuned by selecting functional ligands-antennas, involved in the d-block, by the variation of different rare-earth elements (REE) ions ratio in the crystal of the complex compound, by the packing of molecules in crystal, etc.

In this work we have synthesized two systematic series of cocrystals with common formulae $[Zn_2Gd_xTb_{(1-x)}(OH)(NO_3)_2(Piv)_4(phen)_2]$ and $[Zn_2Tb_xEu_{(1-x)}(OH)(NO_3)_2(Piv)_4(phen)_2]$ in order to determine the influence of doping one REE ions with another ones on lifetimes of excited states and quantum yields of photoluminescence.

According to X-ray diffraction data the initial complexes $[Zn_2Ln(OH)(NO_3)_2(Piv)_4(phen)_2]$ (Ln = Eu, Tb, Gd) are completely isostructural. Both phenanthroline fragments in the molecules of complexes are located almost parallel due to π-stacking interactions.

The isostructural fact of complexes and the presence of π-stacking interactions allow receiving on their base continuous "solid solutions", in which effects of the energy transfer from one molecule to another can be expected. Based on this, two series of cocrystals $[Zn_2Gd_xTb_{(1-x)}(OH)(NO_3)_2(Piv)_4(phen)_2]$ and $[Zn_2Tb_xEu_{(1-x)}(OH)(NO_3)_2(Piv)_4(phen)_2]$ were obtained with the percentage of terbium in the first case of 5, 10, 25 and 50 percent; and 10, 25, 50 percent of europium in the second case respectively. The phase purity of all synthesized compounds was determined by the method of X-ray powder diffraction analysis.

Thus, the detailed examination of photoluminescence properties of all of obtained compounds was conducted and effects of the luminescence enhancement of both Tb^{3+} ions by Gd^{3+} ions and Eu^{3+} ions by Tb^{3+} ions were revealed.

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NEW HYBRID MATERIALS BASED ON REDUCED GRAPHENE OXIDE AND D-BLOCK ELEMENTS OXIDES AND SULFIDES. SYNTHESIS AND APPLICATION FOR SUPERCAPACITORS

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Hydrogen peroxide sol-gel processing is a known way to obtain a hybrid composites for different applications [1-9]. In this research we propose a hydrogen peroxide technique to obtain reduced graphene oxide supported d-block elements oxides and sulfides composite materials On the first stage ammonium peroxoborate is used to coat graphene oxide (GO). Then peroxide containing thin film interacts with d-elements and corresponding oxides or sulphides based films are deposited on the graphene oxide. Obtained materials were studied by different chemical and physical analytic methods such TEM, XRD, XPS. We demonstrate Na- and Li-ion hybrid electrochemical capacitors assembled using graphene oxide supported V_3O_7, VO_2, MnO or MnS insertion electrode and an activated carbon counter electrode in an organic electrolyte. Performance of active material and AC electrodes were evaluated in half-cell configurations with metallic Na. Composites were tested as electrode in hybrid capacitor demonstrating a good capacity retention characteristics, high power capability and energy density.

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APPLICATION OF RARE-EARTH METALS COMPOUNDS IN THE PREPARATION OF LACTIDE

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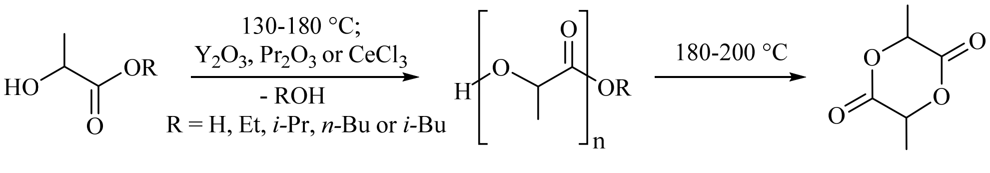
Due to its biocompatibility and biodegradability, polylactic acid (PLA) based materials are perspective for medical applications such as bone implants or tissue regeneration technologies. Herein, the efficient method for high molecular PLA production implies the catalytic polymerisation of a lactic acid cyclic dimer, that is, lactide [1-3]. The common processes for making lactide involve the catalityc oligomerisation of lactic acid (LA) or alkyllactates and further decomposition of obtained polycondensates to the cyclic dimer [4]. Usually, most efficient catalytic systems used in lactide synthesis, based on toxic elements like Sn, Sb or Pb [5-9].

Here, we report on the using of the rare-earth metals compounds as low-toxic catalysts for the lactide preparation by LA oligomerization-depolymerization method. In order to characterize the catalytic activities of praseodymium (III) and yttrium (III) oxides as well as cerium (III) chloride the LA degree of oligomerization and total lactide yield have been compared. It has been shown that Pr_2O_3 and $CeCl_3$ allow obtaining of lactide in 52 and 46% yield, respectively. However, Y_2O_3 does not exhibit catalytic properties [10]. We also produced lactide using these catalysts from some alkyllactates. The effects of a number of variables on the oligomerization-depolymerization of alkyllactates, such as the alkyl group length, reaction conditions (*e.g.* temperature or reaction time) and catalyst type have been investigated (Scheme 1).



Scheme 1.

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SYNTHESIS, STRUCTURAL AND THERMAL PROPERTIES OF RARE-EARTH METAL AND ZIRCONIUM DIPIVALOYLMETHANATES

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In present time beta-diketonates of rare-earth elements and zirconium are used as precursors for obtaining different films and coatings by metal organic chemical vapour deposition (MOCVD). Physico-chemical properties of these materials allow their usage, for example, as high-k dielectric, optic and optoelectronic coatings in microelectronics and in fuel cells. One of the actively developing areas is the production of thermal barrier coatings based on yttria stabilized zirconia (YSZ) doped by rare-earth metals (neodymium and samarium in this case), which is perspective material of new generation gas turbines for the purpose of energy supply. From technological point of view a simple synthetic procedure is necessary for obtaining the precursors. We synthesized yttrium(III), neodymium(III), samarium(III), and zirconium(IV) dipivaloylmethanates (dpm) with purity no less than 98% at ordinary conditions in lab-scale quantities with high yields (at least 70%).
From the point of successful MOCVD process, the information on the structural and thermal properties of the precursors already known in the literature as well as new, perhaps, more appropriate ones is also needed. As a result, new crystal structures of $[Y(en)(dpm)_3]$ (en = ethylenediamine), $[Nd(dpm)_3]_2$, $[Sm(dpm)_3]_2$ were studied; the information on melting temperatures, vapour pressures and condensed phase behaviours was obtained for yttrium(III), neodymium(III), samarium(III) and zirconium(IV) dipivaloylmethanates as well as for yttrium(III) dipivaloylmethanate derivatives with ethylendiamine, tetramethylethylendiamine (tmeda) and bipyridyl (bipy) by using TG/DTA and Knudsen effusion method with mass-spectrometric registration of the gas phase composition and static method.
Since the thermal barrier coatings used in gas turbines consist of zirconium dioxide doped by rare-earth metals it seems to be effective to investigate also the thermal properties of the precursors mixtures. Mixtures of $Zr(dpm)_4$ and $Y(dpm)_3$/$[Nd(dpm)_3]_2$/$[Sm(dpm)_3]_2$with different ratio were prepared in two ways (with solvent and mechanical mixing). The XRD powder studies showed that there are no any solid solutions in the mixture phases. Condensed phase behaviours of mixtures were also carried out by TG/DTA and the tensimetric investigation of them were provided by flow method.

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STRUCTURE AND PROPERTIES OF MIXED-METAL CLUSTERS WITH {$Re_3Mo_3Se_8$} CORE: FROM POLYMERIC SOLID TO SOLUBLE SPECIES

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Chemistry of the octahedral chalcogenide clusters of a {M_6Q_8} (M = Re, Mo; Q = S, Se, Te) type is in a stage of rapid development. An interest to these compounds is caused by a fascinate chemistry and a set of perspective physical properties including structural features, redox transformations of cluster core, magnetism and luminescence [1, 2]. Nonisovalent substitution of metal atoms within the cluster core changes the electronic structure of the resulting compounds greatly in comparison with homometallic species [3, 4].

Here preparation and detailed experimental study of mixed-metal octahedral clusters based on $\{Re_3Mo_3Se_8\}^n$ core (n= –1 ÷ +2) are discussed. Mixed-metal cluster species preparation was carried out by high-temperature synthesis using $ReSe_2$, $MoSe_2$ and KCN as precursors. Long-term reaction resulted in formation of chain-like polymeric compound having the composition of $K_6[Re_3Mo_3Se_8(CN)_5]$ (**1**). The cluster depolymerisation reaction allowed us to obtain the water-soluble molecular complex with the composition of $K_5[Re_3Mo_3Se_8(CN)_6]\cdot 10H_2O$ (**2**) comprising cluster anion $[Re_3Mo_3Se_8(CN)_6]^{5-}$. Metathesis reaction of **2** and Ph_4PBr proceeded with oxidation caused the formation of paramagnetic compound $(Ph_4P)_4[Re_3Mo_3Se_8(CN)_6]\cdot DMF$ (**3**) containing $\{Re_3Mo_3Se_8\}^{2+}$ core with 21 CVE.

Reaction of cluster cyanide anion $[Re_3Mo_3Se_8(CN)_6]^{5-}$ with a number of metal cations in aqueous solution leads to formation of a set of new coordination polymers. The crystallographic study revealed compounds with crystal structures of different dimensionalities, including chain-like, layered and 3D-network assemblies.

In present work, we report on practical aspects of preparation, crystallographic study and spectroscopic characterization of mixed-metal octahedral clusters. Redox properties of the $[Re_3Mo_3Se_8(CN)_6]^{n-}$ cluster anion in solution were investigated using cyclic voltammetry.

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LUMINESCENT NANOMATERIALS BASED ON TERBIUM(III) COMPLEXES AND SILVER NANOPARTICLES

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Today the core-shell composite nanomaterials, where silica spheres are coated by a noble metal (mainly, gold and silver) shell, are attracted great attention in nanoscience due to their potential applications in medicine, biosensing and catalysis. It is known, silver nanoparticles are thermodynamically unstable in aqueous solution. The deposition of silver (Ag(0)) nanoparticles onto larger-sized silica supports is a convenient approach to prevent their incontrollable aggregation. The regularities of silica surface coating by Ag(0) nanoparticles were not enough studied today.

In this work silica spheres with a surface decorated by amino-groups were synthesized by well-known Stöber technique (Fig. 1). Also highly luminescent amino-modified silica nanoparticles doped with Tb(III)-p-sulfonatothiacalix[4]arene complex were obtained by reverse microemulsion method. The novel method of a uniform silver coating of the silica nanoparticles surface was developed through treatment by hydrogen peroxide. The size of obtained Ag(0) nanoparticles onto silica surface is 2-8 nm by transmission electron microscopy method. The absorption spectra of the aqueous dispersions additionally confirm the formation of Ag(0) nanoparticles onto nanoparticles surface. The synthesized nanoparticles can be used as catalysts of different chemical or electrochemical reactions.

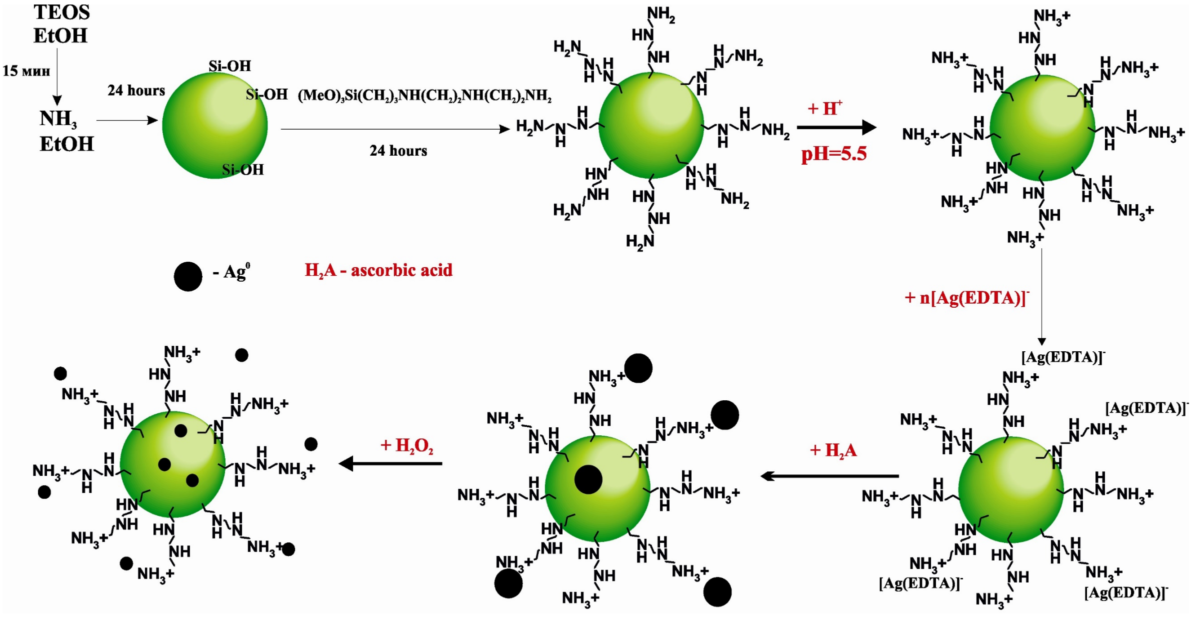

Figure 1. Schematic representation of SNs synthesis and immobilization of Ag(0) on the silica surface.

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SYNTHESIS AND FUNCTIONALIZATION OF RUTHENIUM AND OSMIUM CONTAINING POLYOXOMETALATES

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Polyoxometalates (POM) are polynuclear complexes consisting of transition metals (Mo, W, V, Nb, Ta) in higher oxidation states and linked together by oxo ligands. POMs can be used as polydentate ligands for coordination of different metals, metal clusters or organometallic fragments. Complexes with noble metals in the structure are in particular interest due to combination of "POM-noble metal" can provide a synergistic effect in different catalytic applications such as photocatalytic water splitting, transormation of organic substrates etc.

In that work preparation methods for the ruthenium and osmium containing Keggin and Dawson types ions have been investigated. In the case of ruthenium we found a way to the selective preparation of $[PW_{11}O_{39}\{Ru(NO)\}]^{4-}$ Keggin ion, when ruthenium coordinates NO ligand, which can be removed producing $[PW_{11}O_{39}\{Ru(CH_3CN)\}]^{4-}$ that is very important for the further modification. In the case of osmium we selectively prepared $[PW_{11}O_{39}\{OsN\}]^{4-}$ Keggin type anion, when osmium has an oxidation state +6 and coordinates additional nitrido ligand. Similarly the $\{OsN\}^{3+}$ group was introduced into the Dawson type anion leading to $[P_2W_{17}O_{61}\{OsN\}]^{7-}$ anion.

The second important group of the heterometallic POM is complexes with group 5 elements forming the area for numerous catalytic applications such as oxidation of methane, water splitting etc. In this field of research preparation of niobium and tantalum containing POMs still has a lot of problems due to the absence of good heterometal source, numerous equilibria in solution and formation of different isomers. In this research niobium oxalate has been used for the preparation of niobium containing POMs such as $[(TeW_9O_{33})_2(NbO)_{3-x}]^{n-}$ and $[Bi_2W_{20}O_{70}(NbO(C_2O_4))_{2-x}]^{n-}$ anions.

All complexes were characterized by NMR, ESI-MS, IR and coupled HPLC-ICP-AES technique. Also electrochemical properties of resulting compounds were studied by cyclic voltammetry.

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FORMATION OF MANGANESE(II) COMPLEXES WITH AMINOMETHYLATED CALIX[4]RESORCINOL AND HYDROXYETHYLIDENE DIPHOSPONIC ACID IN PRESENCE OF AMPHIPHILIC COMPOUNDS

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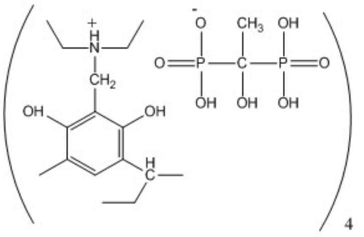

Today magnetic resonance imaging (MRI) is the main non-invasive method for diagnosing various diseases in medicine. In some cases the contrast agents (CA) must be administered to the body during MRI procedure. Development of new non-toxic CA for MRI is the perspective direction for diagnostics of pathologies on early stages. In medical practice generally compositions based on gadolinium(III) complexes are applied for contrasting MRI images[1]. However, these drugs have a number of disadvantages: low contrast ability and nephrotoxicity. Therefore, recently, contrast agents based on manganese(II)[2,3], which ions are involved in biochemical cycles of living organisms, have become increasingly important in medical diagnostics. Earlier we discovered that complexes of manganese with ligands on the calixarene platform have increased relaxation efficiency, which is a measure of the contrasting ability of the composition. But such complexes were not up to the commercial preparation based on manganese in terms of stability[4]. In this regard, for receiving strong and highly relaxivity manganese complexes, the macrocyclic compounds combining complexing and amphiphilic properties in their composition were used as the objects of investigation. Such properties are manifested by a multifunctional ligand based on aminomethylated calix[4]resorcinol (AMC) and hydroxyethylidene diphosphonic acid (HEDP).

For solubilization the manganese complexes with HEDP-AMC in a weakly alkaline medium a nonionic surfactant - polyoxyethylated lauryl alcohol Brij 35 was used. The state of manganese(II) in HEDP, AMC and HEDP-AMC micellar solutions was studied using NMR relaxation. The pH-metric titration data were mathematically processed and the constants of acid-base equilibria for HEDP, AMC, and HEDP-AMC ligands were determined. Thus, according to the magnetic-relaxation characteristics of manganese complexes with multifunctional ligands, one can conclude such systems can be assumed as models of CA for MRI.

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A NEW METHOD OF BIOINORGANIC SYSTEM SYNTHESIS BASED ON NUCLEOPHILIC ADDITION OF AMINOACIDS DERIVATIVES TO [2-$B_{10}H_9NCR]^-$ (R = Me, Et, ^{t}Bu, Ph) ANION.

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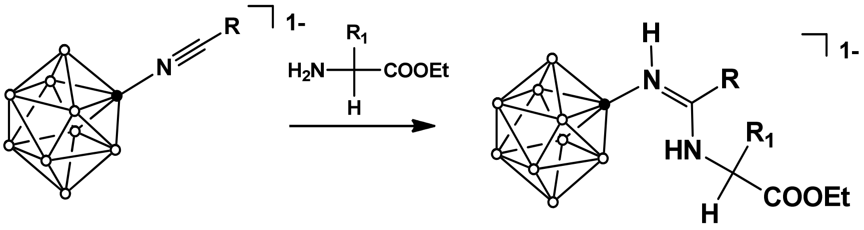
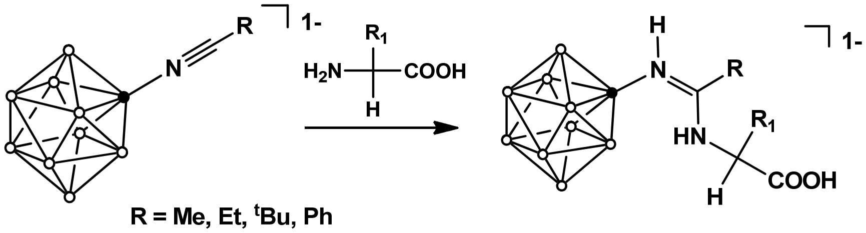
An important aspect of boron compounds application, in particular, of higher boronhydrogen anions is ^{10}B-NCT of malignant tumors. Thus such boron drugs should be capable to accumulate selectively in tumor cells; so biologically active compounds and fragments of biomolecules etc. are most selected transport groups.

In this work, the method for preparation of substituted derivatives of closo-decaborate anion containing in the structure amino acid fragments was proposed. Thus, the process of nucleophilic addition of amino acids esters to the nitrilium derivatives [2-$B_{10}H_9NCR]^-$ was investigated (R = Me, Et, ^{t}Bu, Ph).



R = Me, Et, ^{t}Bu, Ph
R_1 = H, Bn

Reaction occurs under mild conditions (MeCN, 80°C, 1 h) and in quantitative yields (on the boron). Furthermore, we proposed and optimized a method of functionalization of free amino acids in water-alcohol solution. N-iminoacylation reaction of certain aliphatic and aromatic amino acids proceeds in the presence of acetate buffer (pH = 6.0), and at the ratio of anion [2-$B_{10}H_9NCR]^-$ / amino acid = 1/2:



R = Me, Et, ^{t}Bu, Ph
R_1 = H, Me, Bn

A significant advantage of this process is the simplicity of the apparatus, high yields and ease of product isolation. The received data allow us to consider the proposed approach as a perspective for the creation of products for ^{10}B-NCT.

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THE NEW NICKEL(II) CARBOXYLATE COMPLEXES AS POTENTIAL CATALYSTS IN SYNTHESIS OF BIOCOMPATIBLE POLYESTERS

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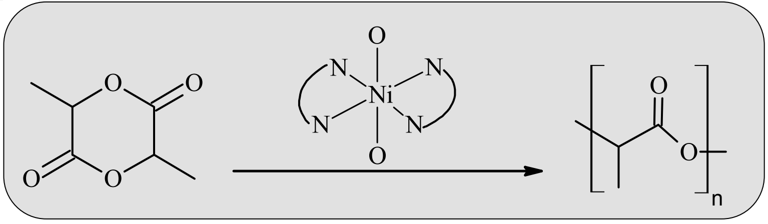
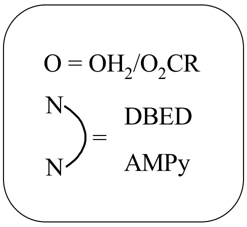
Poly(lactic acid) (PLA) is a biocompatible and biodegradable polyester, which is actively used as biomedical material for the manufacture of surgical sutures, pins for fixing damaged bones and joints, bioabsorbable stents and the basis of scaffolds in reparative therapy. The significant amount of PLA is currently synthesized by a ring-opening polymerization (ROP) of lactide catalyzed by tin(II) octoate (2-ethylhexanoate). Its major disadvantages are high toxicity and difficulty of removing from the polymer, which adversely affects the use of the received biomedical polymers. Replacement of tin(II) complexes with the catalytically active compounds of biogenic or less toxic metals can significantly reduce the toxicity of the obtained polymeric materials.




O = OH_2/O_2CR

DBED
AMPy

In the presented work, the reaction of the nickel(II) carboxylates with corresponding amines results to series of mononuclear carboxylate complexes of nickel(II) – potential catalysts for the ROP of D,L-lactide: *trans*-$[Ni(DBEN)_2(CF_3COO)_2]\cdot C_6H_6$ (**I**), *trans*-$[Ni(DBEN)_2(Me_3CCOO)_2]\cdot Me_3CCOOH$ (**II**) and the previously described *trans*-$[Ni(AMPy)_2(OH_2)_2](HCO_2)_2\cdot 6H_2O)$ (**III**) [1], where DBED – N,N`-dibenzylethylenediamine, AMPy – 2-(aminomethyl)pyridin were obtained. All obtained complexes have been described using X-ray diffraction (XRD) and elemental analysis, IR spectroscopy and mass spectrometry, and also their catalytic activity in the process of ROP of D,L-lactide was explored. According to XRD data, the complex (**I**) crystallized in the triclinic crystal system (a = 8.9998(2) Å, b = 9.3083(2) Å, c = 13.4098(3) Å; α = 95.568(2)°, β = 90.678(2)°, γ = 113.699(2)°, V = 1022.20(4) Å^3, Z = 1, R = 3.34%), (**II**) – in monoclinic (a = 14.1992(6) Å, b = 11.4582(3) Å, c = 17.4222(7) Å; β = 106.633(4)°, V = 2715.94(18) Å^3, Z = 2, R = 5.85%).

Molecular mass distributions of the samples of polymers, which were synthesized by using the described compounds, were measured with chromatography method. It has been shown that when carrying out the polymerization in bulk the formation of polymer fractions with average weighted molar mass M_w = 11511, 8702 and 5963 Da, with yield 83.0%, 66.7%, 76.0%, and polydispersity index 1.89, 1.84, 1.61 for complexes **I**, **II** and **III** respectively is occured.

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INFLUENCE OF AMINO ACIDS ON THE COMPOSITION OF COMPLEX COMPOUNDS OF CHROME(III) USED IN THE SKIN OINTMENT PRESSURE

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In the report at the XXVI International Chugayev Conference we proposed one of the variants of the structure of the tanning complex compound of chromium [1]. With further study of the structure of the tanning complex chromium compound, it was established that in the presence of amino acids in the inner sphere of the chromium environment, water, sulfo groups, hydroxo groups and amino acids are present.

For the sulfate of chromium (III) when dissolved in water, the formation of both neutral complexes $[Cr_2(SO_4)_3(H_2O)_8]$ and cationic complex ions as a result of dissociation of the salt $[Cr_2(SO_4)_2(H_2O)_8]SO_4$ is characteristic. In concentrated solutions, it is possible to form chains consisting of several molecules linked together by axial sulfo groups.

The yield of equatorial sulfo groups from the inner sphere of complex ions with the entry of hydroxyl groups into it with the formation of a polar covalent bond, for example, with the addition of a solution of sodium hydroxide, is possible. The sulfo group in the presence of sodium hydroxide is in solution as a neutral sodium sulfate salt. A polar covalent bond with the complexing agent is also formed when the equatorial sulfo group is replaced by a carboxyl group of the amino acid. It can be assumed that this process is accompanied by a change in the pH towards acid values because of the increase in the concentration of sulfuric acid in the solution.

It is possible to replace the water molecules of the inner sphere of the complex ion with compounds with a free electron pair, for example, the amino group of the amino acid. In this case, a covalent bond with the complexing agent-chromium (III) is formed by the donor-acceptor mechanism.

The change in the pH and activity of chromium (III) solutions indicates that solutions of both chromium (III) sulfates and the basic chromium (III) salt react with amino acids [2]. The interaction schemes depend on the composition of the salt and on the structure of the amino acid. Amino acids are part of complex ions either by displacing water molecules from the inner sphere of the ion, or by displacing the sulfo group. The presence of the OH group in the complex chromium (III) ion leads to the fact that the interaction of such a compound with the amino acid leaves the sulfone group, which leads to the formation of a strong bond between the chelating agent (III) and the carboxyl group of the acid. The results obtained in the studies show the stability of complex compounds in solutions of chromium sulphate of any concentration with the obligatory finding of a sulfonic group in the complex ion. In the presence of sodium hydroxide, stronger chromium complex compounds are formed, which include hydroxyl groups in addition to the sulphonic group and water.

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DESTRUCTION OF ENVIRONMENTALLY SAFE COMPLEXES, DERIVATIVES OF DISUCCINIC ACID, UNDER THE ACTION OF UV RADIATION

V.M. Nikolskiy, T.I. Smirnova, N.I.Lukyanova and L.N.Tolkacheva

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The process of degradation of complexones, succinic acid derivatives (IDS, EDDS, DCGDS), and complexones, derivatives of acetic acid (EDTA and IDA), with the determination of the qualitative composition of the degradation products was studied.

Solutions of EDDS, IDS, DCGDS, EDTA and IDA with a concentration of about 10^{-2} mol/l were irradiated for 1 hour with the light of a mercury lamp LUV 15W ECO (EU) installed at a distance of 2 cm from the surface of the solution. Analysis of samples for ammonium ions in samples of solutions after UV irradiation was carried out with the help of the Nessler reagent. A residual concentration of ligands was determined by a titrimetric method using a standard 0.01 m solution of $Cu(NO_3)_2$, an ammonium buffer solution, and a metal chromic indicator of murexide.

Samples of complexones and photodestruction products prepared in the form of tablets with potassium bromide were studied by IR Fourier spectroscopy using the Bruker spectrometer Equinox 55 in the range 400-4000cm^{-1}, the resolution was 4cm^{-1}, the number of scans was 32. Identification of the absorption bands were carried out on the basis of the literature data [1].

A one-dimensional upward chromatography on paper using a solvent of a mixture of butanol-1, acetic acid and water in a ratio of 4:1:1 in the presence of "witnesses" was used to determine the amino acid composition of the EDDS, IDS and DCGDS photodestruction products.

The presence of succinic acid in the degradation products was determined according to a standard procedure by one-dimensional ascending chromatography on paper using a mixed solvent (butanol-1, formic acid, water in a ratio of 18: 2: 9) and succinic acid as a "witness". Chromatograms after drying were shown by spraying with a 0.05% ethanolic solution of bromophenol blue.

The samples of solutions of all five complexones after exposure to UV radiation gave a positive result with the Nessler reagent for the presence of ammonium ions. This fact is evidence of the deamination reaction of the ligands under investigation. Complexion of the monoamine type IDS, as well as the derivative of trans-1,2-diaminocyclohexane- DCGDS, is subjected to the greatest degree of destruction, which can be explained by the structural features of these ligands. The results of the IR spectroscopic study confirm the destruction of the chelating agents, succinic acid derivatives.

The identification of the main degradation products was carried out by the method of one-dimensional paper chromatography. In the composition of the products of the decomposition of IDS, EDDS and DCGDS, succinic acid was detected by paper chromatography.

The discovered products of the decay of IDS, EDDS and partially DCGDS (amino acids, carboxylic acids, ammonium ions) are not only nontoxic for microorganisms, plants, animals, but they are natural metabolites and can be successfully absorbed by green plants and microorganisms from soil and aquatic environments.

[1] T.I. Smirnova, S.D. Khizhnyak, V.M. Nikolskiy and others // *Journal of Applied Chemistry*, **2017**, Vol. 90, *4*, 406-411.

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COMPLEX OF CEFOPERAZONE WITH Bi(III)

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Cephalosporin antibiotics are the most used antimicrobial drugs in the treatment of bacterial infections caused by sensitive microorganisms. A cefoperazone is the III generation of β-lactam cephalosporin antibiotics. The antibiotic has antibacterial activity against gram positive and gram negative bacteria. Many metal complexes of this antibiotic have toxicological and pharmacological properties but the problem is that some of them lose their antibacterial properties *in vivo*. The metalloantibiotic complexes, for example bismuth compounds, can be used in medicine. In addition, bismuth compounds are used against bacteria *Helicobacter pylori*. The purpose of the paper is to study the synthesis of complexes of cefozaline with Bi(III) and discuss its physicochemical and antibacterial properties.

The compound was synthesized in the molar ratio of metal to ligand 1:1 in water medium, pH=2. A milk-white precipitate was formed in 3 hour. The product yield was 80-90%. The complex was determined by physicochemical, elemental and thermal analysis, IR, Raman and NMR spectroscopy, X-ray.

The compounds have the chemical composition of $[Bi(CFPZ)(OH)_2]\cdot XH_2O$ (X=1, 2). The complex is soluble in DMSO and DMFA but it is insoluble in water and EtOH. The complex $Bi(CFPZ)(OH)_2]\cdot XH_2O$ (X=1, 2) is obtained in crystalline form. Cell parameters determined for the complex: a =17,677 Å, b = 15,860 Å, c =10,258 Å, α =90,0°, β = 93,562°, γ=90,0°, V = 2870,31 $Å^3$, space group symbol: P1 2/m 1, system group: centrosymmetric, space group number: 4.

To establish the type of coordination of cefoperazone to bismuth ions, the FT-IR, Raman and NMR spectra of sodium cefoperazone and $Bi(CFPZ)(OH)_2]\cdot XH_2O$ (X=1, 2) were analyzed. Cefoperazone has several donor atoms: oxygen atoms of carboxylate, lactam group and phenolic hydroxy group. In the IR spectrum of the complex, ν(C=O)-lactam vibration and symmetric and asymmetric stretching vibrations of COO^- group are shifted relative to the spectrum of sodium cefoperazone. This shows that the oxygen atoms of the lactam and carboxylate group are coordinated to the metal ion. The ν(M-S) are not observed in the Raman spectrum of the complex. NMR spectra of sodium cefoperazone and $Bi(CFPZ)(OH)_2]\cdot XH_2O$ (X=1, 2) shows that phenolic hydroxy group does not bind with metal ion. This analysis is in agreement with previous studies where cefoperazone is described as a bidentate ligand. In addition, a bismuth ion is bound with two hydroxy groups.

Complex $Bi(CFPZ)(OH)_2]\cdot XH_2O$ (X=1, 2) has antibacterial activity against bacteria *Staphylococcus aureus, Pseudomonas aeruginosa, Escherichia coli*.

Acknowledgements Authors express their thanks to the Centre for Equipment Joint User of Siberian Federal University, Institute of Chemistry and Chemical Technology SB RAS for technical support.

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DEVELOPMENT OF THIRD GENERATION PHOTOSENSITIZERS BASED ON CHLORIN-E$_6$ METALLOCOMPLEXES AND SELECTIVE DELIVERY AGENTS FOR ANTITUMOR PHOTODYNAMIC THERAPY

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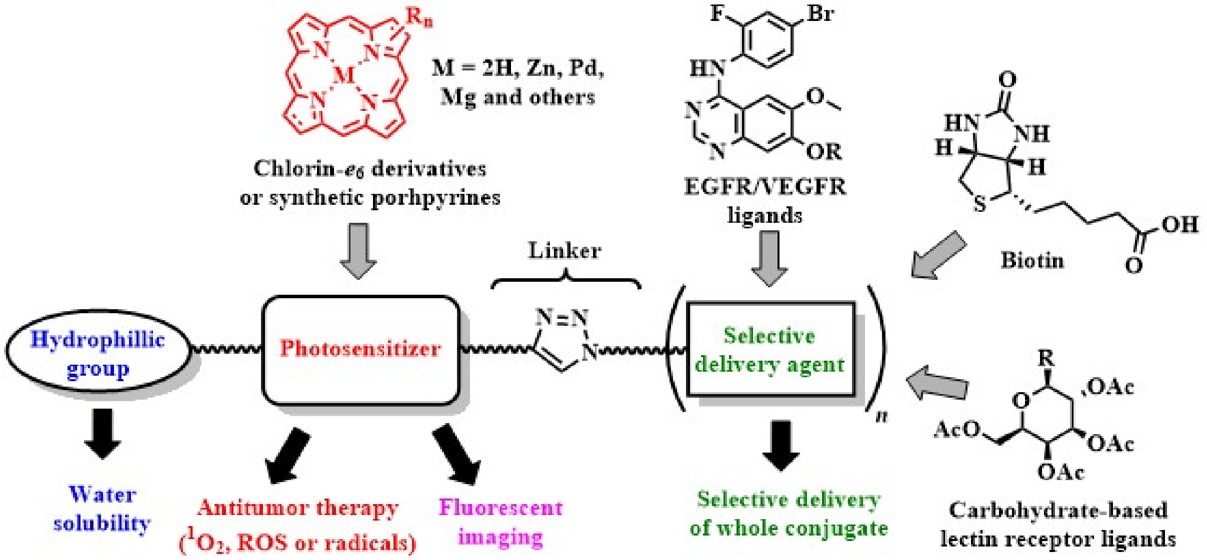
Photodynamic therapy is promising method for treatment oncological diseases due to minimal toxicity of using photosensitizers [1].

In this work new photosensitizers belonged to third generation were synthesised with using our previous synthetic strategy [2]. This molecules contain: *i)* photosensitizer responsible for PDT based on synthetic or naturally-occurred porphyrin-type compound; *ii)* target delivery/therapy ligand – a molecular fragment with affinity to specific receptors expressed by tumor cells (EGFR/VEGFR ligands, biotin, several carbohydrate-based lectin receptor ligands); and *iii)* the parts responsible for water solubility – quaternary ammonium groups or carbohydrates.



For all metallocomplexes biological activity were investigated through *in vitro* and *in vivo* experiments.

[1] M.R. Hamblin, *Nat. Rev. Cancer*, **2006**, *6*, 535.
[2] A.Yu. Fedorov, Synthesis, **2015**, *47*, 3717.

Acknowledgements – We are expressing our gratitude to Russian Foundation of Basic Research for financial support (grant number 16-03-00464).

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DIAZADIPHOSPHAPENTALENE WITH FORMALLY DIVALENT PHOSPHORUS BASED ON TETRALONE AZINE

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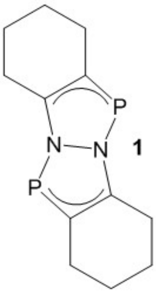
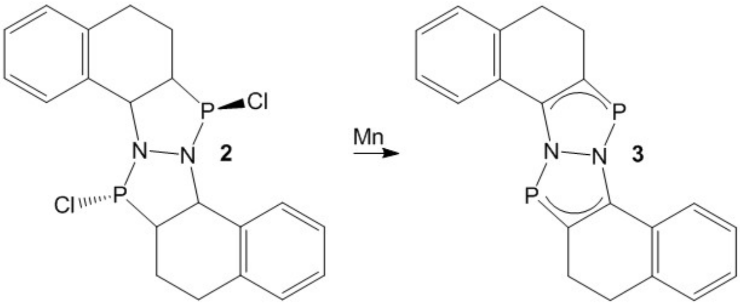
Diazadiphosphapentalene (DDP) [1] based on c-hexanone azine (**1**) till up today was a single representative of a novel type of 10π-electron heteroaromatic system with two-coordinate and formally divalent phosphorus atom. At the same time, the existence of DDP analogues was questioned.

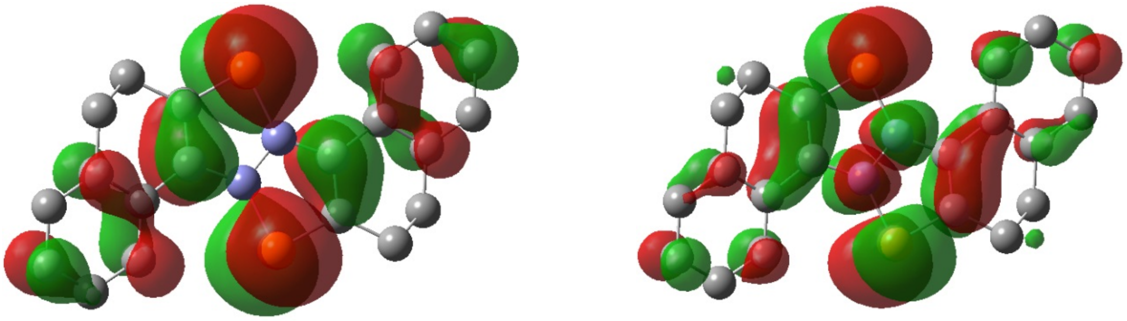


We succeeded in the synthesis of another example of 10π-electron diazadiphosphapentalene system (**3**) based on tetralone azine.



The reduction of dichloride **2** with manganese gives quantitative yield of the desirable product. Interestingly, **2** disproportionates in pyridine to form **3** without use of metals.

According to the X-ray data **3** demonstrates planar geometry of the diazaphosphole rings. Planar nitrogen atoms contribute two π-electrons to the aromatic system. Phosphorus atoms are two-coordinate and formally divalent. P-N bond distances in **3** are slightly longer (1.741 Å) than the corresponding P-N bond lengths (1.733(5) Å) in **1**.



HOMO LUMO

(B3LYP)/6-31+G(d) optimized structure of **3**.

DFT calculations reveal that HOMO is localized mainly on the $\pi_{(C=C)}$ bonds and phosphorus p-orbitals whereas LUMO has almost the same localization $\pi^*_{(C=C)}$ together with $\pi^*_{(N-N)}$ orbital. Based on the structural data and calculations unusual coordination properties of **3** are expected.

[1] A. Kornev et al., *Inorg. Chem.*, **2014**, *53*, 3243-3252.

This work was supported by Russian Science Foundation (grant no. 14-13-01015-P).

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THE STRUCTURE AND MAGNETIC PROPERTIES OF HEXACOORDINATED TIN(IV) BIS-*o*-IMINOBENZOSEMIQUINONATO COMPLEXES

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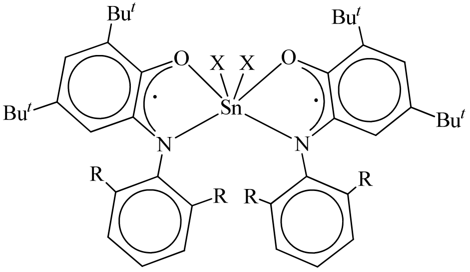
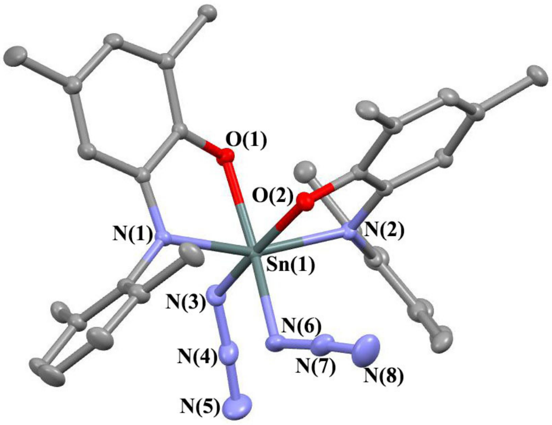
This report presents the investigation of magnetochemical properties of hexacoordinated tin(IV) bis-*o*-iminobenzosemiquinonato complexes. These compounds contain two radical-anion ligands and the character of magnetic interaction between them is influenced by the molecular geometry of complex and the nature of diamagnetic anionic ligands.

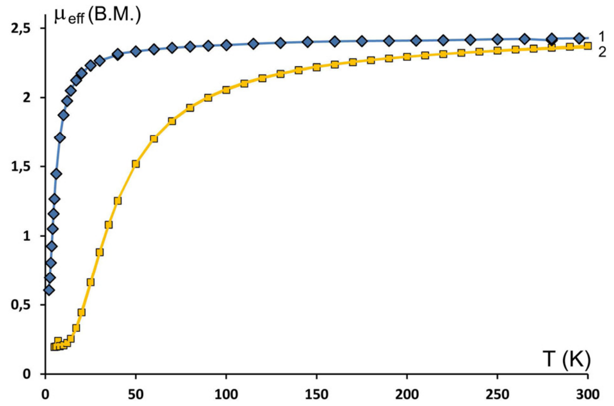


X = Cl, Br, I, N_3, NCS, NCO, Me, Ph

R = Me, Pr^i

The structure of all the tin(IV) complexes synthesized was determined by the X-Ray diffraction analysis. It was found that described compounds have the similar geometry with the distorted octahedral ligand environment of the metal center independently from the nature of the substituents.





Magnetochemical investigations performed show that bis-*o*-iminobenzosemiquinonato tin complexes in which X = Cl, Br, I, N_3, NCO, NCS have the similar temperature dependence of the effective magnetic moment (μ_{eff}) (curve 1 on the picture). At the temperature range 30-300 K the value of μ_{eff} is about 2.45 B.M. typical for system with two non-reacting S = 1/2 centers. Only below 30 K the decrease of the μ_{eff} value occur. This indicates the weak antiferromagnetic exchange interaction between unpaired electrons of two *o*-iminobenzosemiquinone ligands. The tin compounds containing hydrocarbon substituents on metal centre (methyl and phenyl) are characterized by quite stronger antiferromagnetic exchange interaction (curve 2 on the picture).

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SYNTHESIS AND LUMINESCENT PROPERTIES OF POLYNORBORNENES WITH OLIGOETHER AND AMINO ACID GROUPS AND CYCLOMETALLATED IRIDIUM COMPLEXES IN SIDE CHAINS

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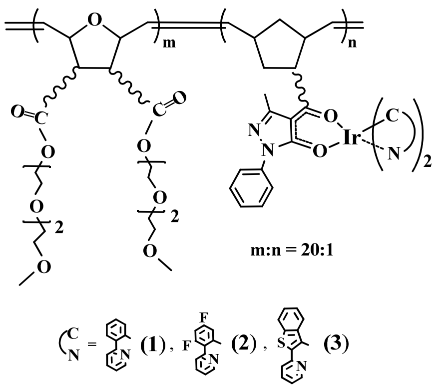
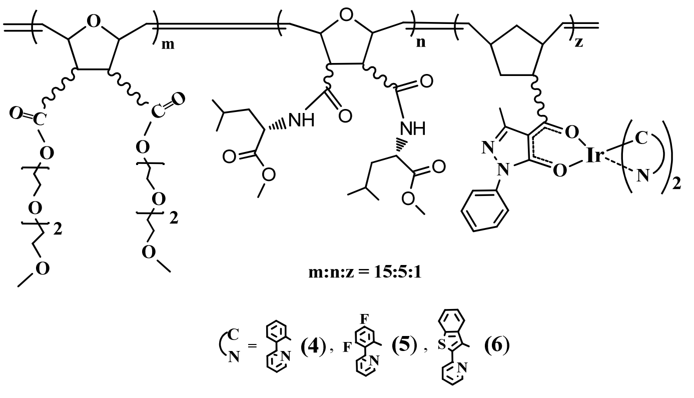
Copolymers containing oligoether and amino acid groups and luminescent iridium complexes in side chains were synthesized by ring-opening metathesis polymerization (ROMP) method.





Polymeric products **1**-**6** were isolated as air-stable viscous liquids soluble in $CHCl_3$, CH_2Cl_2, THF, EtOH, MeOH and in water. The synthesized copolymers revealed an intense photoluminescence (PL) of green (**1**, **4**), bluish-green (**2**, **5**) and red (**3**, **6**) colors. The PL spectra of the copolymers (Figs. 1, 2) contain emission bands attributed to metal-to-ligand charge transfer (MLCT) transitions mixed with ligand-centered (LC) transitions in the cyclometallated iridium complexes bonded to polymer chain.

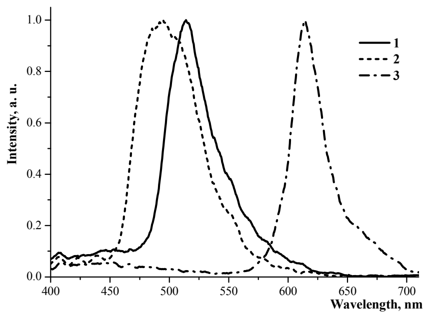


Fig. 1

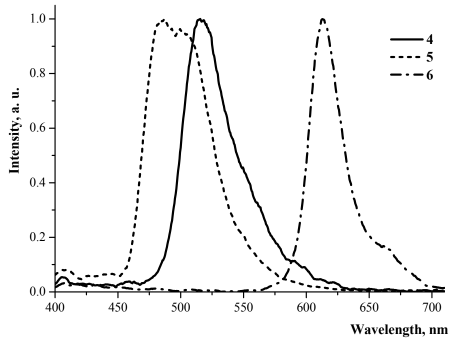


Fig. 2

The prepared polymeric materials can be considered as potential luminescent markers of biological objects.

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NEW ANTIMONY(V) COMPLEXES BASED ON 2,5-DIHYDROXY-3,6-DI-TERT-BUTYL-p-BENZOQUINONE

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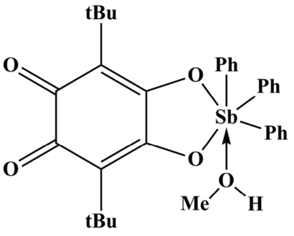
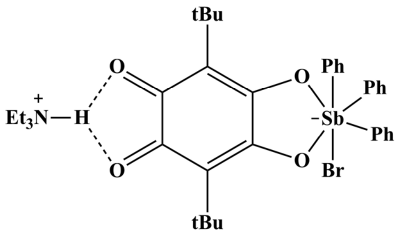
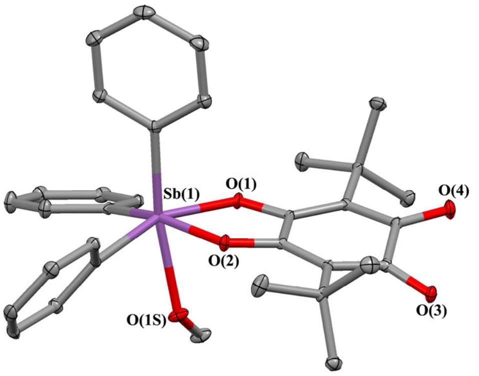
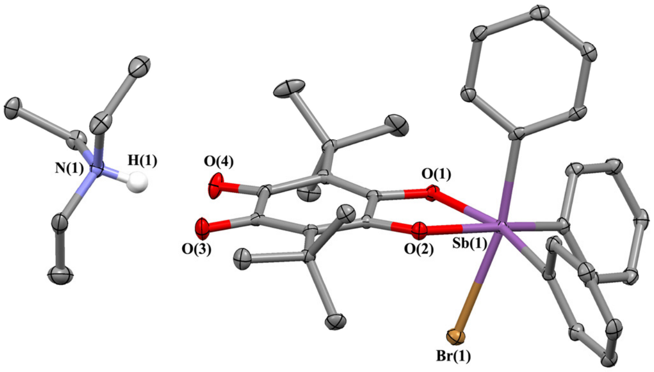
The interaction of 2,5-dihydroxy-3,6-di-tert-butyl-p-benzoquinone with triphenylantimony dibromide in the presence of base in acetonitrile solution leads to the formation of ionic catecholato complex of bromotriphenylantimony(V) with triethylammonium. The recrystallization of this complex from methanol allows to synthesize triphenylantimony(V) diolato complex containing free carbonyl groups.









Here we report on the synthesis, investigation of structural features, electrochemical properties of new functionalized complexes of triarylantimony(V) containing carbonyl groups in redox-active catecholato ligand.

Acknowledgements - Authors are grateful to Russian Foundation for Basic Research (grant N 16-33-60157 mol_a_dk). I.V.S. is grateful to Council of President of Russian Federation (grant MK-5285.2016.3) for support of electrochemical investigations.

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ANTIMONY(V) BIS-CATECHOLATO COMPLEXES BEARING NITROGEN DONOR LINKERS

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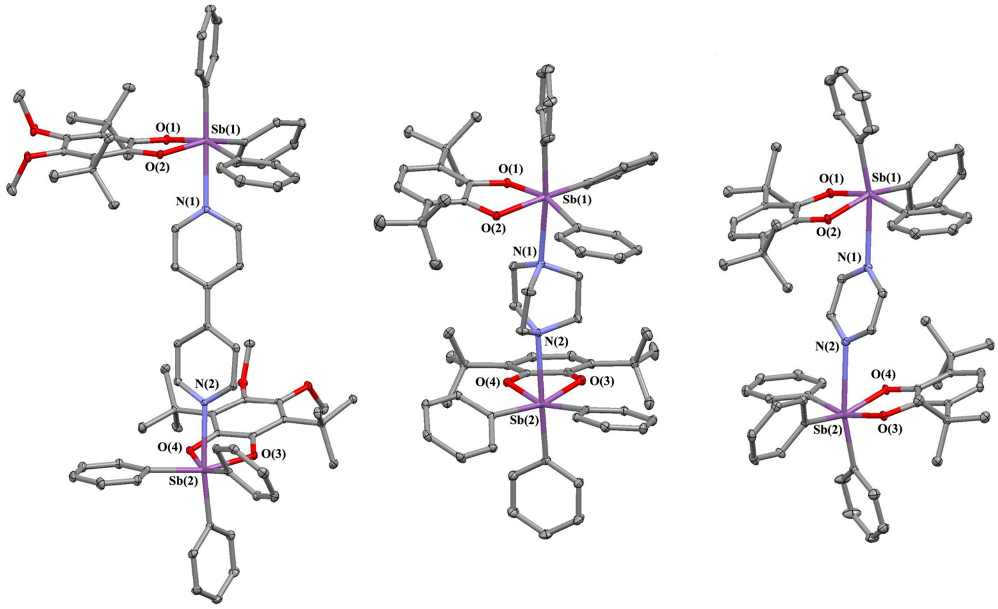
A series of binuclear triarylantimony(V) catecholates based on different substituted o-benzoquinones and 4,4’-bipyridile, diazabicyclo[2,2,2]octane, pyrazine have been synthesized in order to investigate the reciprocal influence of redox-active parts and N-donor ligand.



Here we discuss the results of investigations of molecular and electronic structures and electrochemical properties of new binuclear triphenylantimony(V) bis-catecholates containing neutral donor nitrogen-containing ligands as linkers.

Acknowledgements - Authors are grateful to Russian Foundation for Basic Research (grant N 16-33-60157 mol_a_dk) and Council of President of Russian Federation (grants NSh-7916.2016.3).

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КРИСТАЛЛИЧЕСКАЯ И МОЛЕКУЛЯРНАЯ СТРУКТУРА КОМПЛЕКСНОГО СОЕДИНЕНИЯ НИКЕЛЯ(II) С 10-(2-БЕНЗОТИАЗОЛИЛАЗО)-9-ФЕНАНТРОЛОМ

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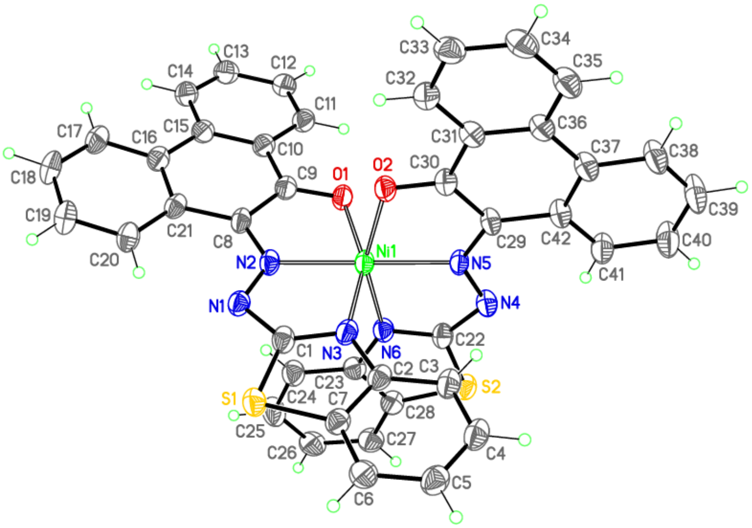
Взаимодействием 10-(2-бензотиазолилазо)-9-фенантрола (HL) с ацетатом никеля (II) получено координационное соединение $[NiL_2]\cdot$ДМФА (I) [1]. Методом РСА определена кристаллическая и молекулярная структура I. Координационный полиэдр атома Ni в комплексе I – октаэдр. Установлено, что в процессе комплексообразованияс атомом Ni молекулы HL переходят в анионную форму с изменением изомерной формы. Потеря протона вмолекулелиганда приводит к разрыву внутримолекулярной водородной связи (N1−H···O), азогруппа меняет свою ориентацию относительно связи N1−C1 из *транс-* в *цис-*, а относительно N2−C8 из *цис-* в *транс*-позицию. В такой форме лиганд может координировать атом Ni в виде аниона с образованием двух пятичленных металлоциклов, выполняя функцию N,N,O –тридентатно-хелатного лиганда:



Кристалл соединения Iсодержит разупорядоченный сольват – ДМФА, который удален из уточнения. Наличие в ИК-спектрах полосыν(C=O) 1677 см$^{-1}$ также подтверждает присутствие сольватной молекулы ДМФА.

[1] Линко Р.В., Сокол В.И., Полянская Н.А., Рябов М.А., Давыдов В.В., Сергиенко В.С. // ЖНХ. 2013. Т. 58. № 2. С. 178-186.

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HETERO-LIGAND COMPLEXATION OF CHROMIUM(III) WITH NITRILOTRIACETIC AND MALONIC ACIDS IN AQUEOUS SOLUTIONS

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The processes of formation of homo- and hetero-ligand complex compounds of chromium(III) in polycomponent solutions are of interest for the expanding the information base and chemical modeling of multicomponent systems, as well as the development of new perspective materials. At present, one of the research areas of chromium(III) coordination compounds is the synthesis and analysis of hetero-ligand chromium(III) compounds, including those based on the nitrilotriacetates of this metal. The spectrophotometric study of the formation of hetero-ligand complex compounds of chromium(III) with nitrilotriacetic (H_3Nta) and malonic (H_2Mal) acids was carried out. It has been established that both the homo- and hetero-ligand chromium(III) chelates retain the doublet nature of the electronic absorption spectra with a hypsochromic shift enhanced by chelation of the metal and the hyperchromic effect of the relative hexaquacoordinated chromium(III) (λ_{max} = 415 and 575 nm) in the transition from malonate (λ_{max} = 410 and 565 nm) to nitrilotriacetate (λ_{max} = 415 and 555 nm) complexes. By varying the acidity of the medium, optimal pH intervals for complexation and the stable existence of homo-ligand complexes of chromium(III) with H_2Mal and H_3Nta, as well as the composition of coordination particles, were determined. The values of lgβ for the chromium(III) chelates $[CrMal]^+$, $[CrMal_2]^-$, $[CrMal_3]^{3-}$, $[CrHNta]^+$, $[CrNta]^0$, $[CrOHNta]^-$ were 7.52, 12.34, 15.73, 9.67, 11.78, 6.81 respectively. The characteristic maxima of the light absorption bands of the doublet spectrum of the chromium(III) solution in the simultaneous presence of H_2Mal and H_3Nta in the solution are located at wavelengths of 405 and 555 nm. Optimal conditions for the existence of hetero-ligand complex particles of chromium(III) with H_2Mal and H_3Nta practically do not differ from those for homo-ligand systems (ΔpH=1.1–5.4). The molar ratio for the hetero-ligand chelate of chromium(III) Cr(III):Nta:Mal = 1:1:1 was established by the saturation method, the value of lgβ was 20.91 [1]. The presence of malonic anions in the coordination sphere of the chromium(III) nitrilotriacetate complex provides the closure of an additional six-membered ring, which increases the thermodynamic stability of the hetero-ligand chelate in comparison with the homo-ligand Nta and Mal complexes. An investigation of the kinetics of the chromium(III) chelation processes in the systems Cr(III)-Nta, Cr(III)-Mal, and Cr(III)-Nta-Mal allowed us to establish that the limiting stages of the complexation reactions had the first order and the range of the rate constants was $5.27\cdot10^{-7}$–$1.25\cdot10^{-6}$ s^{-1}.

[1] D. D. Utkina and N. V. Scheglova, *Modern problems of medicine and natural sciences*, **2017**, *6*, 46–50.

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SPECTROPHOTOMETRIC STUDY OF RESONANCE AND INDUCTIVE EFFECTS ON THE ACIDITY AND COORDINATION PROPERTIES OF PORPHYRINS

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Development of new macroheterocyclic compounds with definite optical properties and/or chemical reactivity to use in the design of new advanced materials is the interdisciplinary problem of high priority. Molecular structure of tetrapyrrolic macrocycles allows suggesting the diversity of new compounds by means of fine tuning of their properties with modifying of the peripheral substitution pattern, formation of chelated complexes with metal ions and axial ligation of the latters. In the most of cases electronic effects arising upon peripheral substitution on the π-conjugated system of macrocycle interfere with concomitant sterical effects. Therefore the discrimination between these two contributions needs the detailed consideration in the each particular case to establish the proper structure-property relationship. To separate the electronic and steric contributions to the rate of the deprotonation and metal ion chelating, the special series of compounds need to be used

In the given study we make the comparison between three porphyrins (2,3,7,8,12,13,17,18-octabrom-5,10,15,20-tetrakis-(trifluoromethyl)porphine, 2,3,7,8,12,13,17,18-octabrom-5,10,15,20-tetraphenyl-porphine, 5,10,15,20-tetrakis-(trifluoromethyl)porphine) which differ in both the electronic communication between the macrocycle and substituents and the steric interactions. The substitution with groups possessing both the inductive and mesomeric (resonance) effects of different sign has been applied. Relative importance of the electronic communication of peripheral substituents via the π-conjugated system of macrocycle or the macrocycle σ-bonds polarization will be analyzed. Moreover, substitution at the pyrroles (2,3,7,8,12,13,17,18 positions) and 5,10,15,20-*meso*-positions may bring nonequivalent contributions due to the different electronic density of corresponding molecular orbitals on the macrocycle atoms. Beside this, the dodeca-substitution pattern enable us to modulate the steric interactions due to the close proximity of the neighboring substituents with moderate bulkiness.

The interaction both of the molecular and the double-deprotonated forms of the dodecasubstituted porphyrins with zinc diacetate is investigated. It is shown that the reaction rate increases by 3 - 4 orders of magnitude for ionic forms of the porphyrins. That could be due to no energy losses upon deformation and cleavage of the N−H bonds of the reactive site as well as higher polarization of the molecule leading to more solvated state of the anionic form in the transition state.

The results obtained for increase in the rate of complexation reactions dianionic forms of porphyrins are the theoretical basis for the creation of highly efficient liquid-phase sensor materials to cations of metals

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STUDY OF THE PROCESSES OF COMPLEX FORMATION IN THE SYSTEM IRON(0) - IRON(II) - GLYCIN – WATER

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Many coordination compounds of transition metals are structural models of active centers of metal-enzymes, based on donor atoms of nitrogen-, sulfur- and oxygen-containing organic legends and their derivatives. Such complexes show high biological activity, on their basis, effective medicinal preparations used in pharmacology and medicine have been developed. Particular mention should be made of the promising use of bioactive iron complexes for the production of micro fertilizers, which in recent years have been used in agriculture as micro additives to animal and bird feed.

The purpose of this study was to investigate the complexation processes in iron (0) -iron (II) – glycine - water systems in a wide range of ionic strengths of the solution (0.1÷1.0 mol / l) at a temperature of 298.16 K using the Clark-Nikolsky oxidation potential method, which is Highly sensitive and reliable. The electromotive force of the system was determined with the help of the ionomer EV-74, using Yusupov's oxidative function, computer programs "EXCEL" and "SIGMAPLOT-10", thermodynamic calculations and statistical processing of all the experimental data were carried out. As a metal electrode, we used stainless steel grade 10-low-carbon, resistant to corrosion in various environments.

Preliminary, by the method of potentiometric titration the ionization constants of glycine at 298.16 K, concentrations 0.001; 0.002; 0.003 M, five values of the ionic strength of the solution in the range 0.10÷1.00 mol / l. The method of oksredmetry used in the work provides for the removal of the experimental dependences of the electromotive force of EMF (E, mV) on the following concentration variables: pH (-lgh), $pC_{Fe(II)}$ ($-lgC_{Fe(II)}$) и pC_L ($-lgC_{HL}$), where h- Activity of hydrogen ions, and $C_{Fe\ (II)}$ and C_{HL}-concentrations of Fe (II) and glycine, respectively. The joint consideration of the results of analysis of experimental curves and inclinations of the partial derivatives of E from pCox, PC_L and the pH allowed to establish the formation of complex compounds of Fe (II) of the following composition: $[FeHL(H_2O)_5]^{2+}$, $[Fe(HL)_2(H_2O)_4]^{2+}$, $[Fe(HL)(OH)(H_2O)_4]^{+}$, $[Fe(OH)_2(H_2O)_4]^{0}$, $[Fe(HL)(L)(H_2O)_4]^{+}$, $[Fe_2(HL)_2(OH)_2(H_2O)_8]^{2+}$.

To calculate the constants of the formation of coordination compounds, Yusupov's oxidative function was used. The true values of the formation constants of the complexes were calculated by the iteration of the experimental and theoretical oxidative functions.

It should be noted that when increasing the concentration ($C_{Fe(II)}$) to $1 \bullet 10^{-3}$ mol / l instead dimeric complex formed coordination compound composition $[Fe(HL)(L)(H_2O)_4]^{+}$ ($lg\beta_{1120}=8.32\pm0.08$ for I = 1.0), and for ionic strength (I) 1.0 mol/l under all experimental conditions $C_{Fe(II)}=1\cdot10^{-3}$ and $1\cdot10^{-4}$, $C_{Gly}=1\cdot10^{-3}\div3\cdot10^{-3}$ mol/l), along with the other listed ones, a complex $[Fe(HL)_2(H_2O)_4]^{2+}$ ($lg\beta_{1220}=3.58\pm0.04$) is formed which is not formed at lower ionic forces (0.1 ÷ 0.75 mol/l). Apparently, this is due to the fact that as the ionic strength increases, the numerical value of the dissociation constant of glycine (Ka_1) in the first stage and, consequently, the concentration of the zwitterion ions decreases, which makes it possible to form a more coordinatively saturated compound.

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DFT-MODELLING OF NEW TYPES OF HARD-AND-SOFT N,O-LIGANDS: THE INFLUENCE OF THE HETEROCYCLE GEOMETRIES ON F-METALS BINDING

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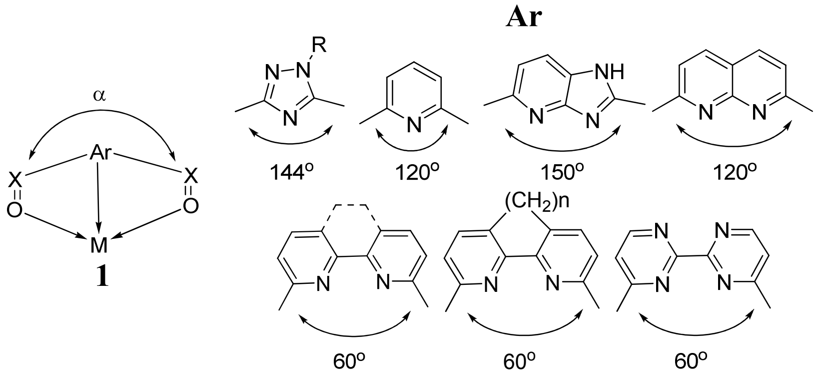
The separation of minor actinides (MA) from reprocessing spent nuclear fuel wastes is one of the most important fundamental tasks in creating a closed nuclear fuel cycle. The selective extraction of MA is complicated by the simultaneous high content of trivalent lanthanides with similar chemical properties. In this work, we proposed a new type of hybrid hard-soft N, O-ligands for the separation of MA and lanthanides in waste fuels with high degrees of burnup. One of the working concept for creation of the MA extragents consist in combination of "hard" oxygen atoms with "soft" nitrogen ones in one molecule in a proper positions. We choose several geometries of central "soft" nitrogen-containing heterocycles (**Ar**) in combination with several different types of "hard" oxygen groups (**X=O**), and we test the energies of complexes formation with Eu(III) and Am(III) ions by DFT modelling (BPE, B3LYP, cc-pVDZ, cc-pVTZ).



X=O

R2C=O
NR2C=O
R2P=O
R2N→O

It is shown that a number of factors need to be taken into account during the quantum-chemical modeling of PES of complexes, such as the relative arrangement of counterions and the arrangement of side **X=O** fragments. A consequence of this is the need either to have independently obtained data on the structure in a crystal or in a solution of the expected complexes, or to search for possible local minima and scan the PES of complexes in order to search for a global minimum. In the lanthanide series, the complexation energy linearly correlates with the ionic radius of the lanthanide ions, as well as the extraction efficiency in conditions identical for all ions. For most reagents, the qualitative characteristics of the selectivity of Am over Eu recovery or relative selectivity in the lanthanide series for one reagent are reproduced well, but the selectivity in dependence on the nature of the substituent in the amide fragment is poorly reproduced. With caution, it is possible to evaluate the selectivity of Am/Eu extraction: the influence of substituent's nature is found which qualitatively reproduces the experimental data. The dependence of the metal ion extraction efficiency on the nature of the substituent **X=O** fragment is reproduced at a high qualitatively level, but the data on the extraction efficiency dependence on the chain length in **X=O** moiety are not reproduced at all.

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SYNTHESIS OF POLYSTYRENE AND POLYMETHYLMETHACRYLATE IN THE PRESENCE OF DIETHYLCATHECHOLATE OF TIN(IV) AND HALOGENATED COMPOUNDS

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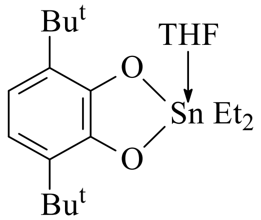

36CatSnEt$_2$·THF

Mono-catecholate complexes of tin(IV) can be used as a chain growth regulator in polymerization of styrene (**St**) initiated by azobis(isobutyronitrile) [1]. Some of them also can be used of methyl methacrylate (**MMA**) polymerization too [2].

The aim of our work was to investigate the influence of combinations diethyl-catecholate complex of tin(IV) (**36CatSnEt$_2$**) and halogenated compounds on polymerization of MMA and St at 70-110°C. Binary combinations of 36CatSnEt$_2$ with **CBr$_4$**, *tert*-butyl bromine (**tBuBr**), ethyl α-bromoisobutyrate (**EBiB**) and (1-bromoethyl)benzene (**PEBr**) were studied in these processes.

It was shown that the introduction of 36CatSnEt$_2$ or each of used organobromine compounds leads to a decrease of the St auto-polymerization rate at 70-110°C. Number average molecular weight (***M$_n$***) of polySt does not change with conversion.

The combinations of 36CatSnEt$_2$ with CBr$_4$ slightly increased the rate of auto-polymerization of St at 90-110°C. In case of other organobromine compounds the rate of auto-polymerization of St decreased. The influence of these systems on the molecular weight of polySt depends on composition of organobromine compounds. In case of CBr$_4$, tBuBr and PEBr molecular weight of polySt proportionally increased with conversion. The index of polydispersity of polySt is ~ 2.0. In case of EBiB ***M$_n$*** of polySt does not change with conversion.

Polymerization of MMA in the presence of 36CatSnEt$_2$ and organobromine compound is somewhat different from the polymerization of St. It was shown that the introduction of 36CatSnEt$_2$ *increased* the rate of MMA auto-polymerization. The combinations of 36CatSnEt$_2$ with organobromine compounds also increase the rate of MMA auto-polymerization. The yields of polyMMA in the presence of 36CatSnEt$_2$ / tBuBr or 36CatSnEt$_2$ / EBiB are less than 30% under the same conditions. Molecular weight of polyMMA which was synthesis in such conditions is very large. Conversion of monomer in case of 36CatSnEt$_2$ / CBr$_4$ is more 90% at 70-90°C. The molecular weight of polyMMA with the conversion does not change.

Thus, complexes of tin(IV) with organobromine compounds can act as regulators of chain growth in polymerization of St. The regulating capacity of using systems depends on the composition of halogenated compounds. In case of MMA polymerization 36CatSnEt$_2$ and its combinations with organobromine compounds acts as a Lewis acid.

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INTERACTION OF H_2OsBr_6 WITH THIOUREA

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Thiourea (thiocarbamide) is a common ligand widely used in chemistry, analysis and technology of noble metals, including osmium determination and extraction. Here we report on the interaction of hexabromidoosmic acid H_2OsBr_6 with thiourea (Thio) in concentrated HBr.

Composition and yield of the solid reaction products depend on the following processes in the system:

1. Ligand substitution reactions in osmium inner coordination sphere involving Thio. In concentrated HBr solution of hexabromidoosmic acid, osmium occurs as kinetically inert complex $[OsBr_6]^{2-}$.The high Br^- concentration (due to the excess of HBr) shifts the equilibrium towards starting reagent $[OsBr_6]^{2-}$ and suppresses the ligand-exchange processes.
2. Thiourea acts as a base accepting a proton in strong acidic media giving rise to a $ThioH^+$ cation.
3. Thiourea can act as a reductant, and in acidic media can be oxidized to bis(α,α′-dithiobisformamidinium)-ion $[S_2C_2(NH_2)_4]^{2+}$. Osmium(IV) acts as an oxidant being reduced to osmium(III).

In reaction media, a set of intact $[OsBr_6]^{2-}$ and probable reaction products, e.g., $ThioH^+$, $[S_2C_2(NH_2)_4]^{2+}$, thiourea complexes of Os^{IV} and Os^{III} can co-exist, whereas the final product is $[Os(Thio)_6]^{3+}$).

Since ionic reactions proceed very fast, $(ThioH)_2[OsBr_6]$ (**1**) is first to precipitate in concentrated osmium solutions [1]. The yield of **1** increases with an increase in C_{Os}, it also depends on the Os:Thio ratio (**1** doesn't form in a case of a large excess of Thio). The precipitation of **1** is soon followed by the formation of redox reaction solid products $[OsBr(Thio)_5]Br_2$ (**2**) and $[S_2C_2(NH_2)_4][OsBr_6]Br_2{\cdot}3H_2O$ (**3**), and further by $(ThioH)[Os(Thio)_6][OsBr_6]Br_2{\cdot}0{,}25H_2O$ (**4**). Finally, $[Os(Thio)_6]Br_3{\cdot}H_2O$ (**5**) and $[S_2C_2(NH_2)_4]Br_2{\cdot}H_2O$ (**6**) can be isolated from the reaction medium upon storage for a few weeks.

The structures of all these compounds have been determined by single-crystal X-ray crystallography, the structures of complexes **1**, **2**, **4** – for the first time.

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THE NATURE AND ENERGY OF INTERMOLECULAR F...F INTERACTIONS IN CRYSTALS OF $(C_6F_5)_4Ge$ AND $(C_6F_5)_3GeCH_2CH_2C_5H_4N$ COMPLEXES

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Fluorination of organometallic complexes is often used to change the physicochemical properties of compounds [1-3]. However, there are a limited number of papers devoted to the study of the nature and energy of intermolecular F ... F interactions. In order to study the energy aspects of the intermolecular F ... F interactions the precision X-ray investigations of compounds $(C_6H_5)_4Ge$ (**1**), $(C_6F_5)_4Ge$ (**2**) and $(C_6F_5)_3GeCH_2CH_2C_5H_4N$ (**3**) were carried out and then study of the topology of electron density (ED) in the framework of Bader's atoms in molecules (AIM) theory.

The investigations of the topology of ED have revealed the presence of 32 $F^{\delta-}\ldots F^{\delta-}$ and 24 $F^{\delta-}\ldots H^{\delta+}$ interactions in a crystal packing of **2** and 25 $F^{\delta-}\ldots F^{\delta-}$, 23 $F^{\delta-}\ldots H^{\delta+}$, 17 $F^{\delta-}\ldots C^{\delta-/\delta+}$ interactions in a crystal packing of **3**. The same fluorine atom can realize several intermolecular interactions at once. The distances F ... F lie in the range from 2.759 to 3.857 Å, and the energy of these interactions is -0.05 ÷ -1.57 kcal/mole, according to the Espinosa-Molins-Lecomte correlation [4]. However, there are examples of the absence of F ... F interaction in crystalline packages **2** and **3** between fluorine atoms located relative to each other at a distance less than 3.8 Å. The investigation of the deformation ED has shown that the realization of $F^{\delta-}\ldots F^{\delta-}$ interactions is possible due to the presence of the regions of higher electron concentration and the regions lowest electron concentration and their mutual arrangement relatively to each other. When the region of higher ED concentration of one fluorine atom corresponds to the region of higher ED concentration of the other fluorine atom, the attractive interaction between them is not observed.

It is important to note that the total attractive contributions of F ... F interactions in compound **2** (-28.85 kcal/mole) and in **3** (-21.74 kcal/mole) are 33% and 51% of the lattice energy, respectively. Comparison of the lattice energy of **1** (-44.87 kcal/mole), **2** (-56.32 kcal/mole) and **3** (-65.45 kcal/mole) shows that in a number of these compounds fluorination leads to a decrease in volatility.

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CHEMICAL DEPOSITION OF FLUORIDE THIN FILMS FROM MIXED-LIGAND COMPLEX SOLUTIONS

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Low refractive indices, high transparency in range from UV to IR and low phonon energy make inorganic fluorides to be important optical materials. Nowadays there is increasing interest to complex fluorides as functionalized materials. Hexagonal β-$NaYF_4$ for example is considered to be one of the most promising host materials for up-conversion phosphors.

Development of easy and cost effective approaches to fluoride thin films deposition is a problem of strategic importance nowadays. One of the most perspective ways to obtain high-quality thin films is metal organic chemical solution deposition (MOCSD) where the solutions of metal carboxylates are used as precursors.

In our work rare earth, alkaline earth and alkaline elements trifluoroacetates and pentafluoropropionates were applied as starting materials for preparation of fluoride films by MOCSD. Pyrolysis of precursors at low temperatures, typically 300 – 600°C, lead to the removal of the organic parts and formation of fluorides.

Because of their polymeric or oligomeric crystal structure, the rare earth carboxylates are poorly soluble in organic solvents. This problem can be solved by preparation of precursor solutions in alcohols, with addition of ancillary ligands, such as polyglymes and polyamines, — diglyme, monoethanolamine (mea), diethylenetriamine (deta), etc. — to increase the solubility of the carboxylates by formation of mixed-ligand complexes with lower nuclearity, as the donor ligand saturates the metal ion coordination sphere.

Mixed-ligand heavy rare earth complexes of trifluoroacetates with diethylenetriamine (deta) of general formula $Ln(tfa)_3(deta)_2$ (Ln = Y, Dy-Lu) were synthesized and characterized by elemental analysis, NMR, FT-IR spectroscopy, TG-DTA analysis and single crystal and powder X-ray diffraction.

Effectiveness of the trifluoroacetate complexes $[Y(tfa)_2(deta)_2](tfa)$ and [Na(tfa)(Htfa)] as fluoride precursors was demonstrated by the example of $NaYF_4$ powder syntheses and thin film depositions. The as deposited films were amorphous/nanocrystalline and required high-temperature annealing in Ar+HF atmosphere to suppress the pyrohydrolysis.
Both α- and β-$NaYF_4$ in various quantitative ratios depending on annealing temperature and composition of precursor solution were obtained (Fig. 1). Surface morphology of thin films was studied by SEM and AFM. Carbon and oxygen impurities (presence and quantitative estimation) were characterized by FT-IR spectroscopy (diffuse reflectance measurements), Raman spectroscopy and EDX analysis. $NaYF_4$ thin films codoped with Yb^{3+} and Tm^{3+} were characterized as up-conversion phosphors.

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TRANSFORMATIONS OF HETEROCYCLIC AMINES AND HALOCARBONS WITHIN COORDINATION SPHERE OF CLUSTER COMPLEX $[(\mu\text{-H})_2Os_3(CO)_{10}]$

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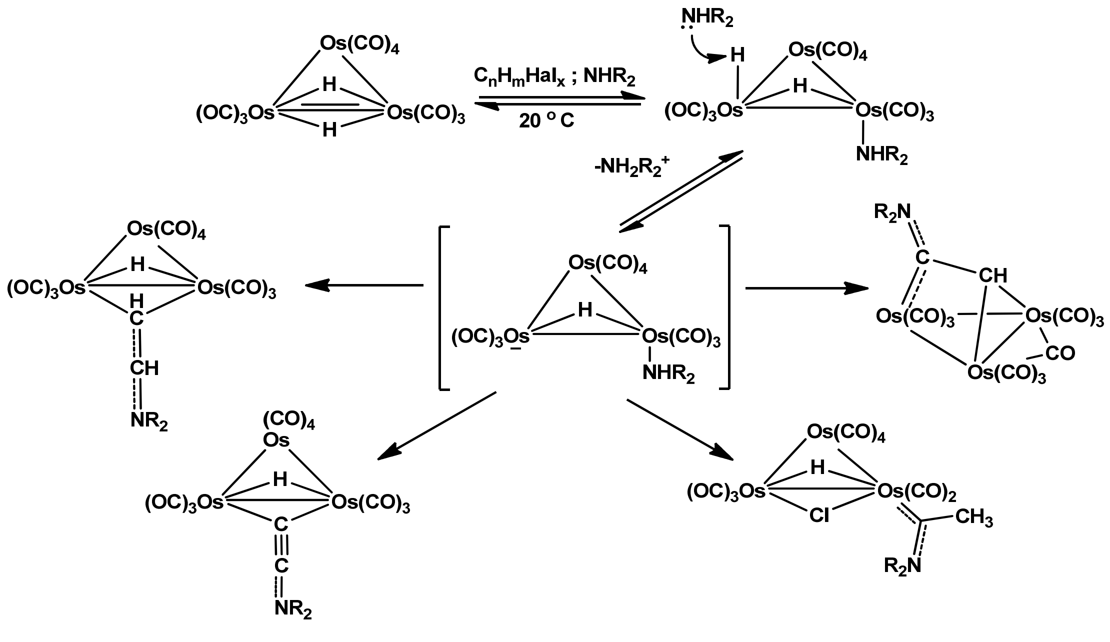
Chemical reactions characterized by C–C and C–H bond formation and breakage play an important role in the majority of technologies for the production of organic, elemento-organic and organometallic compounds. However, the high energy and low polarizability of the C–C and C–H bonds in saturated hydrocarbons greatly complicates their usage use for practical purposes. Therefore, functionalized hydrocarbons, including halocarbons, are mainly used in organic synthesis. For R–X (R = alkyl, alkenyl, aryl; X = Cl, Br, I, F) activation oxidative addition reactions with low-valence transition metal complexes have been especially well studied. These reactions proceed by a variety of mechanisms, but mostly there is a break in an R–X bond and an M–R and an M–X bond are formed. Nucleophilic substitution reactions of metallate anions with R–X (R = alkyl, aryl; X = Cl, Br, I, F) are known but are less studied. A few examples exist of reactions in which chlorohydrocarbon coordination in the metal complexes leads to the formation of new organic compounds, and they proceed as a rule at high temperature. Cluster complexes with several interconnected metal centers are very promising in such reactions, as they allow for simultaneous coordination and activation of more than one organic compound on the neighboring metal atoms with the possibility of their subsequent interaction.

In this report we discuss the reactions of the cluster carbonyl anion generated *in situ* with various halocarbons and heterocyclic amines. Activation of the organic molecules results in formation of C-C, C-N, C-Os, Os-Hal bonds at room temperature. New cluster complexes which are formed in these reactions contain coordinated enamine, ynamine and carbene ligands.



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IODIDES AND POLYIODIDES OF SCANDIUM COMPLEXES WITH AMIDES

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Iodides and polyiodides of scandium complexes containing urea (Ur) and acetamide (AA) have been synthesized. All complexes were characterized by elemental analysis, IR spectroscopy and X-ray diffraction. To assign bands in the FTIR spectra of the complexes, computer simulation was used. The crystal structures of the complexes were determined by X-ray single-crystal diffraction. The trigonal crystals of $[Sc(Ur)_6]I_3$ and $[Sc(AA)]I_3$ are isomorphous to the earlier reported $[M(Ur)_6]I_3$ (M = Ti, V, Cr and Fe). The crystals of polyiodides of scandium complexes with urea and acetamide are monoclinic and orthorhombic, respectively. Complex cations in all complexes have similar structures. Metal ions are located at the centers of distorted octahedral arrangement of oxygen atoms of urea or acetamide. Iodine atoms are not coordinated. Crystal structures of scandium polyiodides differ significantly from the earlier reported $[M(Ur)_6][I_3]_3$ (M = V [1], Cr [2] and Fe [3]). Although polyiodide of scandium complex with urea also contains thiiodide ions, their arrangement is another. The formula of polyiodide of scandium complex with acetamide can be presented as $[Sc(AA)_6][I_5][I_3]I$, since its crystal structure contains V-shaped pentaiodide, linear triiodide and isolated iodide anions. Therefore, scandium complexes continue the tendency of formation polyiodides with different structures from isomorphous iodides, which was found for other metal(III) urea complexes.

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NEW METHODS FOR THE FUNCTIONALIZATION OF THE OCTAHYDROTRIBORATE ANION $[B_3H_8]^-$.

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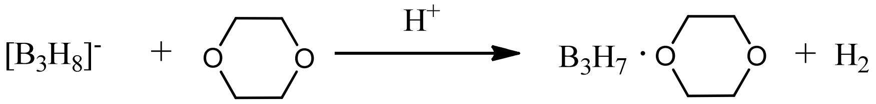
The octahydrotriborate anion $[B_3H_8]^-$, occupying an intermediate position in the chemistry of boron-hydrogen compounds between lower boron hydrides and polyhedral boron hydrides $[B_nH_n]^{2-}$, remains a relevant object for research for several decades. Previously, the sphere of interest of scientific groups dealing with the study of borohydride included new methods for the synthesis of this anion, the preparation of octahydrotriborate complexes with transition metals, and the synthesis of high-molecular polyhedral clusters. Recently, more and more interest has been shown in the processes of the functionalization of the octahydrotriborate anion $[B_3H_8]^-$ with the formation of the B_3H_7L derivatives.

So, under the action of Lewis acid, the octahydrotriborate anion is able to "split" the hydride anion, forming B_3H_7. B_3H_7 is an electron-deficient compound and forms a complex of the type B_3H_7L in the presence of the Lewis base. In our case, the Lewis acid is a proton, and the base is dioxane, which is also a solvent:



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Such products can be obtained in a different way. Thus, in the presence of another reagent ($AlCl_3$) and a suitable solvent (in our case, glyme), the process of addition of a solvent molecule to octahydrotriborate anion is observed:

$$[B_3H_8]^- + AlCl_3 \xrightarrow[-70\ ^{o}C]{glyme} [B_3H_7\cdot(glyme)] + H_2$$

Stronger nucleophiles, for example acetonitrile, are able to displace glyme from the complex:

$$B_3H_7(glyme) + CH_3CN \xrightarrow[-70\ ^{o}C]{glyme} \underset{\mathbf{2}}{CH_3CN\cdot B_3H_7} + glyme$$

All obtained derivatives were characterized by physicochemical methods of analysis (multinuclear NMR-, IR-spectroscopy, elemental analysis).

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REDOX TRANSFORMATIONS AND ANTIOXIDANT ACTIVITY OF TRIARYLANTIMONY(V) CATECHOLATES WITH ELECTRON-ACCEPTOR GROUPS

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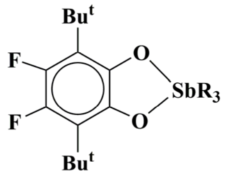
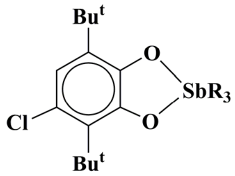
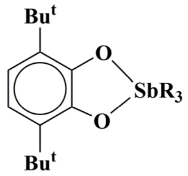
The electrochemical transformations and the antioxidant activity of recently synthesized antimony(V) complexes of $CatSbR_3$ type (**1-8**) (R = phenyl, p-fluorophenyl, p-chlorophenyl) with redox-active catecholato ligands have been studied [1,2].







$(4,5\text{-}F_2\text{-}3,6\text{-Cat})Sb(p\text{-}F\text{-}Ph)_3$	**1**	$(4\text{-Cl-}3,6\text{-Cat})Sb(p\text{-}F\text{-}Ph)_3$	**4**	$(3,6\text{-Cat})Sb(p\text{-}F\text{-}Ph)_3$	**7**
$(4,5\text{-}F_2\text{-}3,6\text{-Cat})Sb(p\text{-Cl-}Ph)_3$	**2**	$(4\text{-Cl-}3,6\text{-Cat})Sb(p\text{-Cl-}Ph)_3$	**5**	$(3,6\text{-Cat})SbPh_3$	**8**
$(4,5\text{-}F_2\text{-}3,6\text{-Cat})SbPh_3$	**3**	$(4\text{-Cl-}3,6\text{-Cat})SbPh_3$	**6**		

The electrochemical oxidation of complexes proceeds as two successive one-electron steps leading to monocations of $[(SQ)SbR_3]^+$ type and dications $[(Q)SbR_3]^{2+}$. The insertion of electron withdrawing fluorine atoms to the 4th and 5th positions of catecholato ligand increases the stability of the *o*-semiquinonato form ($4,5\text{-}F_2\text{-}3,6\text{-SQ}$) of redox-active ligand formed during the oxidation as compared with antimony(V) 4-chloro-3,6-di-tert-butylcatecholates **4-6**. The comparison of electrochemical behavior of compounds **1**,**4** and **7** allows to conclude that the potential of transition "catecholate/*o*-semiquinonate" is more pronouncedly shifted to the anode region by the presence of chlorine atom in catecholato ligand (complex **4**) rather than the presence of two fluorine atoms (complex **1**).

The antioxidant activities of the compounds were evaluated using 2,2'-diphenyl-1-picrylhydrazyl radical (DPPH) assay, in the reaction of oleic acid autooxidation, in the process of lipid peroxidation of rat liver (Wistar) homogenates *in vitro*. In DPPH test the presence of a fluorine atom in the 4th-position of the phenyl ring at an antimony atom reduces the reaction time while the replacement of fluorine by chlorine produces the opposite effect. In the case of complexes **1-3** the effect of substituents in the SbR_3 fragment on the value of TEC_{50} is noted. The antiradical activity for compounds **5** and **6** are practically not affected by the presence of a chlorine atom in the organometallic fragment, the predominant is the electron-acceptor action of the chlorine atom in the ligand. Compounds **1-3** reveal the antioxidant effect in the reaction of oleic acid autooxidation, in the process of lipid peroxidation *in vitro*.

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ELECTROCHEMICAL FEATURES OF NEW MULTIREDOX-ACTIVE Sb(V), Sn(IV) COMPLEXES

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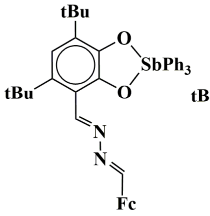
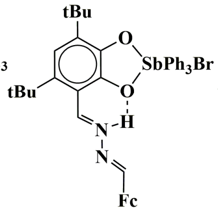
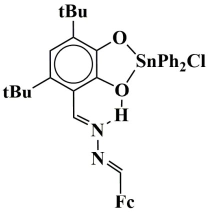
Electrochemical properties a series of multiredox-active Sb(V), Sn(IV) complexes **1-7** containing different redox-active groups (ferrocenyl (Fc), catecholate (Cat)) are discussed.



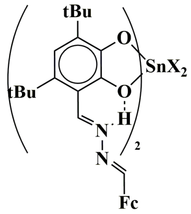
(Fc-L-Cat)SbPh$_3$ **1**



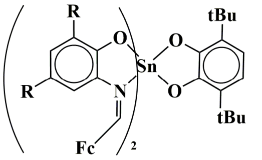
(Fc-LH-Cat)SbPh$_3$Br **4**



(Fc-LH-Cat)SnPh$_2$Cl **3**



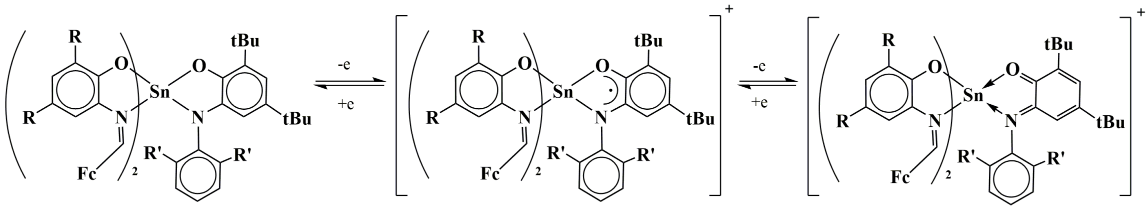
(Fc-LH-Cat)$_2$SnCl$_2$ **4**
(Fc-LH-Cat)$_2$SnPh$_2$ **5**



(Fc-LH-PhOH)$_2$Sn(3,6-Cat) **6**
(Fc-LH-t-Bu-PhOH)$_2$Sn(3,6-Cat) **7**

Compounds **1-5** undergo a series of successive one- (monocatecholates) or two-electron (bis-catecholates) electrochemical oxidation involving redox-active catecholato as well as ferrocenyl moieties, and reductions on the azine linker. The presence of nitrogen-containing linker fragment in the 6th position of catecholato ligand results in the formation of stable complex with a metal-catecholato anionic moiety, it allows the electronic interaction between two redox-active parts of molecule (catecholate and ferrocene). In a case of complexes **6** and **7** catecholato ligand and ferrocenyl group can participate in four anode stages. A combination of CV and EPR spectroscopy allowed us to detect the formation of monocation complexes **7**$^+$ and to reveal that the redox transformation Cat/SQ is the primary in comparison with redox couple Fc/Fc$^+$.

Electrochemical transformations of mixed ligand complexes of Sn(IV) with *o*-amidophenolate (AP) and ferrocenylaldimine phenolate **8,9** were studied by cyclic and square wave voltammetry.



(Fc-LH-PhOH)$_2$Sn(AP) **8**
(Fc-LH-t-Bu-PhOH)$_2$Sn(AP) **9**

In the anode area four one-electron electrochemical stages are observed for the compounds **8** and **9**. The values of the first redox potentials point out the primary oxidation of *o*-amidophenolate ligand to *o*-iminosemiquinonate form. Electron transfer processes at more anode potentials reveal ferrocenyl group oxidation.

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EXTRACTION OF AMERICIUM AND CESIUM FROM ALKALINE MEDIA BY ALKYLATED ON THE UPPER RIM CALIX[8]ARENES: THE IMPACT OF AGGREGATION

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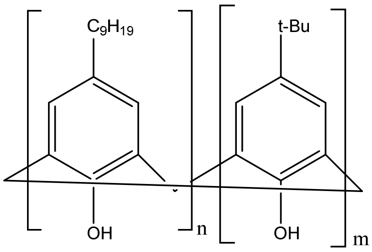
The recovery of long-lived radionuclides from liquid alkaline radioactive wastes with subsequent immobilization and disposal significantly reduces radiological risks in the nuclear industry. Low solubility in organic solvents used in solvent extraction is one of the main problems in using of *tert*-butylcalix[n]arene in the extraction processes. In this regard, the important problem is to enhance the solubility of this class of macrocyclic compounds. The most obvious way to achieve this goal is to increase the lipophilicity of the molecule through the introduction of large alkyl substituents in the structure of calixarene.



Calix[8]arene	n	m	Symbol
tert-butylcalix[8]arene	0	8	TB8
iso-nonyl-*tert*-butylcalix[8]arene	2	6	BN 6/2
	4	4	BN 4/4
	6	2	BN 2/6
iso-nonyl-calix[8]arene	8	0	IN8

In the report synthesis of *iso*-nonyl-calix[8]arene (IN8) and mixed *iso*-nonyl-*tert*-butyl-calix[8]arenes (BN m/n) on the basis of commercially available *iso*-nonylphenol and p-*tert*-butylphenol, as well as their properties, such as solubility, extraction and aggregation ability in comparison with the properties of the *tert*-butyl-calix[8]arene (TB8) will be discussed.

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COMPLEX FORMATION OF IRON(III) WITH HYDROXYBENZOIC ACIDS IN THE SOLUTIONS OF CATIONIC POLYELECTROLYTES

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Iron plays an important role in the functioning of biological systems. Its compounds are also used as medicinal or diagnostic agents. A lack of iron can lead to deficiency anemia. However, its excess, which results from various diseases (hemochromatosis) or technogenic processes, is also harmful, since it can lead to irreversible damage of various organs. Iron is one of the most important metals in the industry, so the development of reagents for rapid and accurate analytical determination of iron in various samples is an urgent task. The most effective mechanism of binding of iron(III) ions was developed by microorganisms. *Escherichia coli* and *Salmonella typhimurium* bind metal ions using an enterobactin molecule. The binding of iron occurs with catecholate fragments of the siderophore. Such fragments show the strongest and most specific binding of iron(III) ions. However, such fragments have a number of drawbacks. The process of binding of iron(III) occurs in a rather narrow region (pH 4-8). In the highly acidic region the complexation process is limited due to the oxidation the pyrocatechol fragment to semiquinones and quinones by iron(III). In the alkaline region the oxidation is caused by the oxygen of an air. In this regard, the use of this ligands in abiotic systems is limited. Another coordinating iron fragment is a salicylate-type capable to bind iron(III) ions quite efficiently and specifically. Coupled with resistance to oxidation and low toxicity, salicylic acid and its derivatives are the most attractive ligands for binding iron(III) ions in biological and abiotic systems.

Another important aspect in the chemistry of solutions of coordination compounds is the role of the medium. In a number of works it was shown that organized media based on solutions of surfactants and macrocycles can significantly change the areas of formation and characteristics of many complexes.

The behavior of iron complexes with a number of hydroxyaromatic ligands (2,4-DHB, 3,4-DHB, 2,6-DHB, SA, Cat, Dopamine) in water and aqueous-polymer solution was studied. The process of complexation for these ligands is similar. Three complexes of metal-to-ligand 1: 1, 1: 2, 1: 3 composition are consistently formed. For the catecholate type ligands stronger binding is characteristic, and the complexes are formed even at the stoichiometric ratios. For the salicylic acids the formation of higher complexes is possible only with a large excess of the ligand. To reveal the role of the polymer, cationic polyelectrolyte polyethyleneimine (PEI) was chosen. The addition of a small amount of PEI resulted in the accumulation of the tris-complexes in a more acidic region and an increase in the apparent stability constants. At the same time, the stepwise complexation disappeared: after formation of the monoligand complex, a tris-ligand complex accumulated missing formation of the bis-complex. A similar phenomenon occurred for both salicylate and catecholate complexes.

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COORDINATION COMPOUNDS – PRECURSORS OF FUNCTIONAL MATERIALS

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The growing interest to functional materials based on the rare-earth elements is connected with the great variety of their properties and widening of their practical use in medicine, atomic and semiconductor, laser and luminophore technics. Rare-earth coordination compounds with polydentate ligands are perspective precursors for obtaining such materials.

Development and improvement of efficient specific techniques for synthesis of functional materials and definition of general regularities of formation of certain nanostructures are one of the important direction of the modern investigations. Technological process of obtaining materials for various purposes in which a rare-earth element is a main bearer of useful properties or a doping agent as thin films on various supports or volume ceramic samples as well as the composition, structure, and sizes of the particles are conditioned by the choice of their synthesis. In this respect, so-call methods of “soft chemistry” or solution methods, e.g. extraction-pyrolytic one, are perspective as compared to the solid-phase high-temperature synthesis. In the case of low- temperature pyrolysis of extracts,one of the main problem consists in the choice of efficient extraction system for synthesis of one or another composite while variety of the extragent compositions determines both a great amount of possible individual products of pyrolysis and chemical and morphologic design of functional composites.

The extraction-pyrolytic method was shown to be perspective for obtaining of coatings and thin films of potential functional materials. Amorphous silicon oxide, titanium and aluminium oxides, quarz were used as supports for applying of thin films of rare-earth oxides and multiferroics on their basis as well as rare-earth oxides and noble metal nanocomposites displaying catalytic properties. Functional properties of the nanocomposites obtained were studied. Obtaining of various functional materials as monocrystal, powder or voluminous samples and, in particular, thin films including nanostructurized ones, from extraction systems may often have preferences as compared to the wide-spread “sol-gel”, gas-phase deposition methods, and support immersion into the melt.

Perspective of use of extractable rare-earth mixed-ligand coordination compounds as precursors of nano-sized materials in the extraction-pyrolytic method was shown at the first time; the dependence of the composition of the extracts pyrolysis products on the ratio of the components in the organic phase, ligands nature, and conditions of the process of pyrolysis was also established.

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COMPLEXATION PECULIARITIES OF MONO- AND DISUBSTITUTED THIAMETHYL DERIVATIVES OF *NIDO*-CARBORANE

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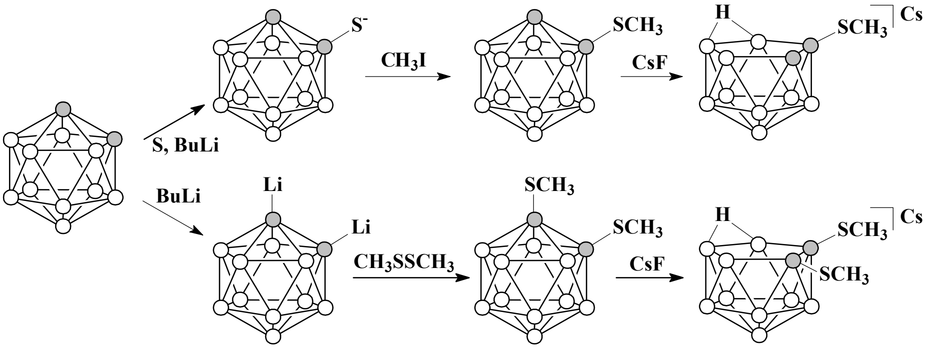
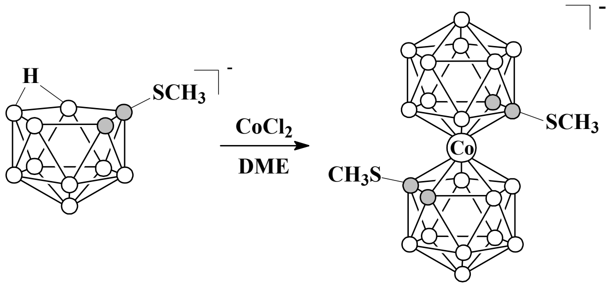
It is well known that *nido*-carborane and its derivatives are good ligands for synthesis of ferrocene-like complexes with various transitional metals. In this work we investigate the complexation of mono- and disubstituted methylsulfide derivatives of *nido*-carborane.

Methylsulfide derivative of *nido*-carborane was obtained via the alkylation of mercapto-*closo*-carborane with the next conversation to its *nido*-form [1]. The disubstituted derivative of *nido*-carborane was synthesized using the reaction of the lithium derivative of *closo*-carborane with dimethyl disulfide [2] followed by its deboronation.



The complexation of methylsulfide derivative of *nido*-carborane with cobalt chloride led to the corresponding derivative of cobalt bis(dicarbollide) as a mixture of *rac*- and *meso*-diastereomers.



At the same time in the case of di(methylsulfide)-*nido*-carborane unexpectedly no traces of cobalt bis(dicarbollide) were observed. We assume that this is due to the formation of chelate cobalt complex with methylsulfide groups of *nido*-carborane. This study now is in progress.

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SYNTHESIS AND STRUCTURE OF IODOPHENYL SUBSTITUTED 1,5-DIAZA-3,7-DIPHOSPHACYCLOOCTANES AND ITS PALLADIUM(II) COMPLEXES

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1,5-Diaza-3,7-diphosphacyclooctanes are eligible ligands for luminescent and catalytic complexes design [1-3]: 1) Ni(II) and Pd(II) complexes have already demonstrated ability to catalyse the hydrogen production or C-C cross-coupling reactions 2) the rigidity of the cycle allows to construct complexes with desired structures 3) it is possible to insert desired functions varying substituents (including cromophoric groups) at nitrogen or phosphorus atoms. The main protocol of those ligands functionalization is basing on the utilizing of various phosphines and amines in condensation reaction. In the aim of the develop novel approach for the functionalization by the C-C or C-N cross-coupling reactions we synthesized p-iodophenyl substituted 1,5-diaza-3,7-diphosphacyclooctanes and Pd(II) complexes based on these ligands.

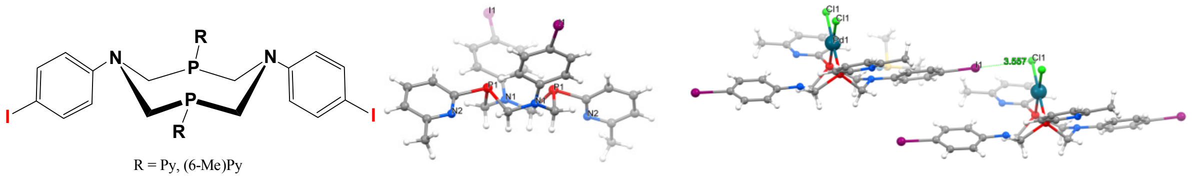

Figure 1. The 1,5-diaza-3,6-diphosphacyclooctanes with p-iodophenyl substituents at nitrogen atoms and Pd(II) complexes.

All compounds were obtained in good yields and their structures were confirmed by NMR-spectroscopy, mass-spectrometry, elemental and X-ray analysis. According to X-ray data ligands display a "chair-chair" conformation of the heterocycle, which is common for the diazadiphosphacyclooctanes. Unexpectedly, the Pd(II) complex also demonstrate "chair-chair" conformation with unusual equatorial orientation of all substituents on the phosphorus and nitrogen atoms. It was found that the distance between iodine atom of p-iodophenyl substituent of one molecule and chloride anion of the $PdCl_2$ core of the proximate molecule is 3.5 Å, angle I-Cl-Pd is close to 90^o. These parameters indicate the halogen Cl-I bonding between two molecules of complex. Possibly, this unusual conformation of Pd(II) complex is induced by the formation of halogen bonding between chloride and iodide atoms.

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AMINATE COPPER(II) COMPLEXES OF AS A NEW POTENTIAL ANTINEOPLASTIC DRUGS

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Cisplatin as an antineoplastic drug is known since the end of 1970s and widely applied for treatment of some tumoral diseases. However, its use restricts with very high nefro-, oto- and neurotoxicity, etc., and also with low bioavailability. Additional problem is the internal (constant) or acquired resistance to platinum drugs. Attempts of the solution to this problems lead to the search of new coordination compounds not only for platinum, but also for other d-elements. Among them, copper complexes, as biometal, can act as potential antineoplastic drugs with the reduced toxicity for healthy body tissues.

Mechanism of action of copper containing drug are rather well investigated and they are quite various, e.g. intercalation and covalent binding with DNA, inhibition of topoisomerases and proteosomal activity. Nowadays, many anticancer complexes of copper, some of them ($[Cu(phen)(Gly)](NO_3)$ and $[Cu(phen)(Acac)](NO_3)$ (phen=1,10-phenanthroline, Gly – glycine, Acac - acetylacetone) are on clinical trials today [1]. Nevertheless, literature with aminate copper complexes with carboxylate ligands is relatively a little.

In this paper, a number of aminate copper(II) complexes with carboxylate ligands was synthesized: $[Cu(phen)Cl_2]$, $[Cu(phen)(O_2CR)_2]\cdot H_2O$, $[Cu(phen)_2(O_2CR)](O_2CR)\cdot HO_2CR$ (phen=1,10-phenantroline, R=CF_3, C_3F_7, C_4F_9). All the compounds were described by structural and elemental analysis and IR-spectroscopy. Using MTT-test and calculations of coloured apoptotic cells the relative cytotoxicity of complexes was discovered, in comparison with cisplatin on human lung carcinoma A549 and artificially produced A549cisDDPR, cell line with the acquired resistance to cisplatin. All the data were shown in Table 1.

Table 1 IC_{50} of complexes, μM

	A549	A549cisDDPR	HCT-116
cis-$[Pt(NH_3)_2Cl_2]$	7,2	25,2	8,33
$[Cu(phen)(O_2CCF_3)_2]\cdot H_2O$	5,3	6,1	10,91
$[Cu(phen)_2(O_2CCF_3)](O_2CCF_3)\cdot HO_2CCF_3$	3,1	3,4	2,82
$[Cu(phen)(O_2CC_3F_7)_2]\cdot H_2O$	4,0	5,1	8,95
$[Cu(phen)_2(O_2CC_3F_7)](O_2CC_3F_7)\cdot HO_2CC_3F_7$	2,5	2,9	2,88
$[Cu(phen)(O_2CC_4F_9)_2]\cdot H_2O$	1,6	2,8	6,19
$[Cu(phen)_2(O_2CC_4F_9)](O_2CC_4F_9)\cdot HO_2CC_4F_9$	0,9	1,2	2,38

Obviously, that the table above shows that addition of carboxylate ligands leads to the increase of the toxicity of obtained compounds; they actively suppress proliferation of A549 cells just as without, so too with stability to cisplatin, showing the high percent of apoptosis cells.

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SYNTHESIS AND INVESTIGATION OF COMPLEXES OF LANTHANIDE NITRATES WITH DIAMIDES OF 2,2'-BIPYRIDYL-6,6'-DICARBOXYLIC ACID BASED ON N'-ETHYLAMINOPYRIDINE.

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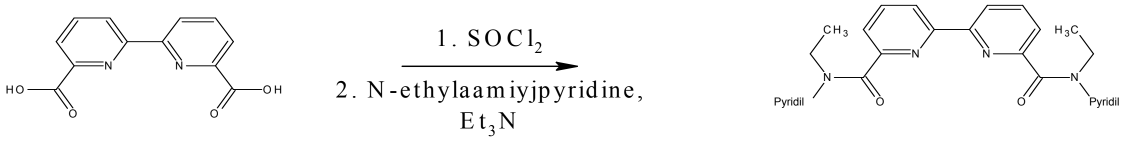
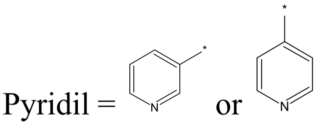
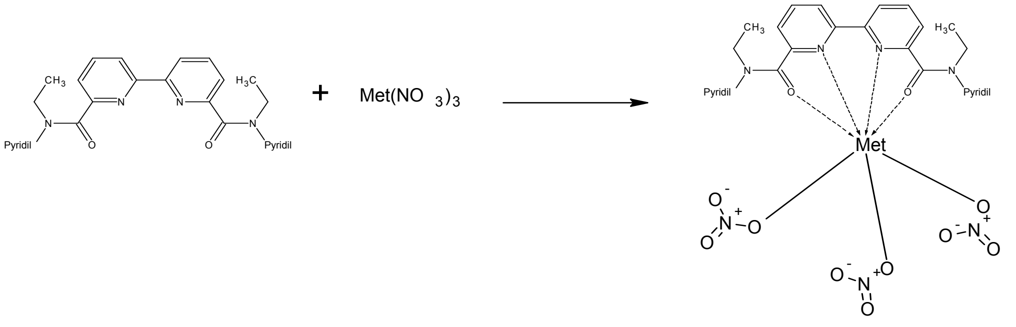
Recently diamides of 2,2'-bipyridyl-6,6'-dicarboxylic acid based on 2-ethylaminopyridine and 6-methyl-2-ethylaminopyridine have been synthesized. Investigation of the luminescence of their complexes with europium and samarium [1], [2] has shown, in particular, that the complex of N, N'-diethyl-N, N'-di (6-methyl-2-ethylamino) diamide 2,2'-bipyridyl-6,6'-dicarboxylic acid with samarium trinitrate has a maximum quantum yield of luminescence in comparison with bipyridyl complexes. Therefore, it is interesting to study the complexes of lanthanides and ligands based on other aminopyridines.

Based on 3- and 4-N-ethylaminopyridines, we synthesized two new diamides of 2,2'-bipyridyl-6,6'-dicarboxylic acid:





The resulting ligands react with rare-earth nitrates in acetonitrile with the formation corresponding complexes:



Met= Sm, Eu, Gd, Tb, Dy

The composition of the complexes was confirmed by mass spectrometry methods, also by UV-visible spectrophotometry.

The luminescence of the complexes in solution and in solid phase is studied.

TGA methods have shown that the complexes are stable for heating up to temperatures of 100-120 ° C, then their decomposition proceeds due to the decomposition of nitrate anions.

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HETEROMETALLIC COMPLEXES OF *p*-CYMENERUTHENIUM

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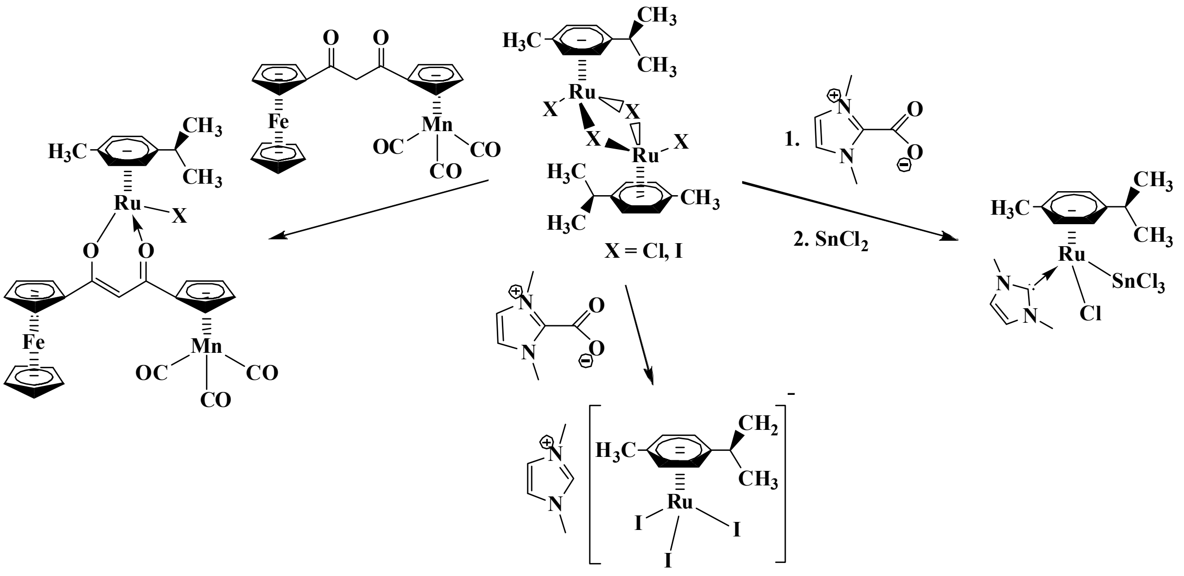
Arene complexes of ruthenium are used as catalysts for olefin metathesis [1] and anticancer drugs [2, 3]. The ruthenium complexes with stable bidentate chelating ligands, a hydrophobic arene ligand and one ligand exchange center, exhibit the greatest anticancer activity [4]. The main purpose of this research is synthesis of new ruthenium complexes based on *p*-cymenerutheniumdihalides (chloride and iodode), which can be used as precursors of anti-cancer drugs.

One of halogen atom of *p*-cymeneruthenium complexes can be substituted by heterometallic β-diketone with for formation of three-legged piano-stool geometry. In the reaction with 1,3-dimethylimidazolium-2-carboxylate (Me$_2$ImCO$_2$) p-cymeneruthenium diiodide gives anionic complex [Me$_2$ImH][(*p*-cymene)RuI$_3$]. Interaction of Me$_2$ImCO$_2$ with *p*-cymeneruthenium dichloride results in neutral compound (*p*-cymene)Ru(Me$_2$Im)Cl$_2$, which can substitute one of chlorine atom by SnCl$_3$ groups.



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SINGLE ION MAGNETS ON THE BASE OF Dy^{III} WITH SHIFF BASE LIGAND

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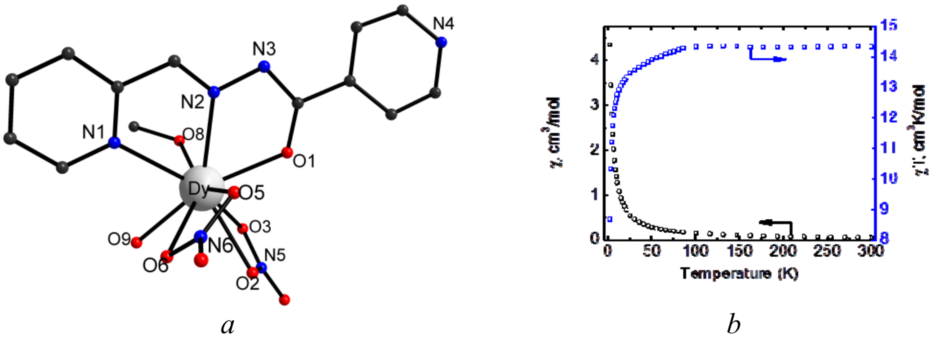
Over the past two decades, the study of single molecule magnets (SMMs), which can exhibit slow magnetic relaxation at the level of one molecule, is an actual research topic in the field of chemistry, physics, and materials science. Such magnetic molecules can potentially be used to create magnetic storage devices with high-density information, quantum computer, spintronics and magnetocaloric materials [1].Considerable attention is paid to the synthesis of molecules containing ions of lantanids [2], especially Dy^{III} ions, mainly because of the presence of large magnetic moments and significant magnetic anisotropy.

We synthesized three new mononuclear complexes of Dy^{III} with Schiff base obtained by the condensation of 2-pyridinecarbaldehyde and 4-pyridinecarboxylic acid (HL). HL is an N,N,O-tridentate chelating ligand. It was found that varying of initial metal salts of Dy^{III} ratio Dy^{III}: HL and presence/absence of triethylamine result in formation of three complexes with different structure - $[Dy(H_2O)(MeOH)(NO_3)_2(L)]$ (**1**), $[Dy(MeOH)(NO_3)(L)_2]\cdot CH_3CN$ (**2**) and $[Dy(L)_3]\cdot 2H_2O$ (**3**) (Fig.1).



a *b*

Fig. 1. $[Dy(H_2O)(MeOH)(NO_3)_2(L)]$ (hydrogen atoms are omitted for clarity) (a);
χ and χ_T versus *T* dependencies for compound **1**(H = 5 кЭ) (b).

Synthesis, structures of new compounds as well as magnetic properties showing that they belong to the family of SIMs will be discussed in detail.

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Acknowledgements –This study was supported by the Russian Science Foundation (16-13-10537).

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STRUCTURE AND THERMAL PROPERTIES OF THE MIXED COMPLEXES OF METALS WITH β-DIKETONATE DERIVATIVES AS LIGANDS: [TM(acacen)Pb(hfa)$_2$], TM=Cu, Ni, Pd

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Many heterometallic compounds combining neutral complex of the transition metal (TM) with Schiff bases (SB) and other metal β-diketonates in one molecule [TM(SB)*M(dik)$_n$] are well known. The possibility of a variation of structure and composition makes these complexes convenient objects for studying composition-structure-property relationship to design compounds with useful functional properties for optical, magnetic, sensor and catalytic applications. The volatility of such complexes presumes a study of them as single source precursors to produce multicomponent inorganic coatings and films by gas-phase methods.

In our report we compare structure and properties of several complexes of [TM(acacen)Pb(hfa)$_2$] type depending on the TM=Cu(II), Ni(II), Pd(II) (acacen=*N,N'*-ethylenebis(acetylacetoniminate), hfa=hexafluoroacetylacetonate). All heterometallics under discussion are prepared by cocrystallization of the monometallic complexes from organic solvents. It is shown that the structure and features of chemical interaction between monometallic subunits differ for the TM used. Such a distinction influences the thermal properties of the obtained heterometallic complexes, namely volatility and thermal stability. All prepared complexes have discrete crystal structure formed by tetranuclear species. Molecular structure of [Cu(acacen)Pb(hfa)$_2$]$_2$ supported by mutual coordination of available oxygen atoms by metal atoms resulting in CN(Cu)=5. In [Pd(acacen)Pb(hfa)$_2$]$_2$ complex the metal–metal interaction is observed to stabilize the tetranuclear structure (Fig.1). For nickel, two heterometallic complexes are separated. [Ni(acacen)Pb(hfa)$_2$]$_2$ has the same crystal structure as palladium-containing analogue and can be prepared by cocrystallization when metal ratio is 1:1. Trinuclear complex [(Ni(acacen))$_2$Pb(hfa)$_2$] is available when metal ratio is 2:1 under the cocrystallization. The1:1 complex transforms to the 2:1 one during heating under vacuum. TG-DTA data and vacuum sublimation test revealed that Cu-containing complex is most thermally stable and volatile while Pd-containing product is less thermally stable, trinuclear Ni-containing complex exhibits intermediate characteristics.

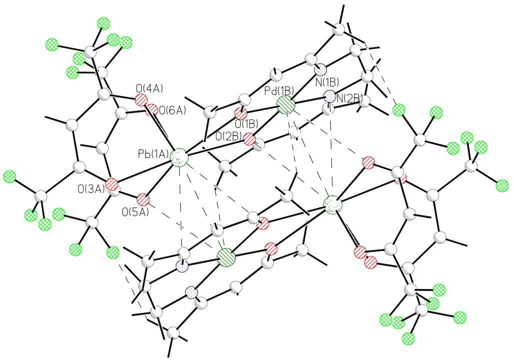

Fig. 1. Molecular structure of [Pd(acacen)Pb(hfa)$_2$]$_2$ complex

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BISMUTH (III) IODIDE COMPLEXES: SYNTHESIS AND PHYSICAL PROPERTIES

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Iodobismuthates built of BiI_6 octahedral units and organic cations form the basis for a wide range of structures of various dimensionality. The structural diversity of iodoplumbate and iodobismuthate hybrid compounds has been recently reviewed [1]. These complexes have become of increasing technological importance since the discovery of high efficiency photovoltaic cells based on the three-dimensional hybrid perovskite methylammonium lead iodide [2]. Commonly, halometalates may be synthesized and deposited into thin film via self-assembly from solution. A wide range of important physical properties including photoluminescence, non-linear optical activity and conductivity from wide band-gap semiconductivity to metallic can be induced as a result of the structure-directing and functional effects of different organic moieties.

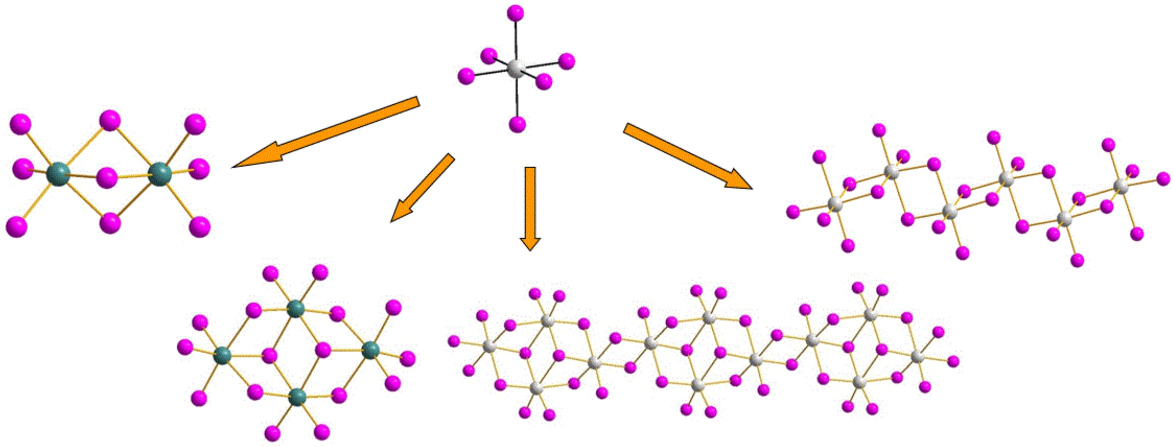

Fig. Scheme for obtaining bismuth iodides of a discrete and polymeric structure.

In this work, we report synthesis and characterization of the series of complexes of general formula $Cat_x[Bi_nI_m]$ (Cat = pyridine derivatives). We discuss the relationships between the structures of resulting iodometalates and the synthetic conditions, including the nature and geometry of organic cations. Some characteristic optical features of reported compounds are also given.

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METAL COMPLEXES BASED ON POLYDENTATE LIGANDS: SYNTHESIS, STRUCTURE AND APPLICATION IN LACTONES POLYMERIZATION

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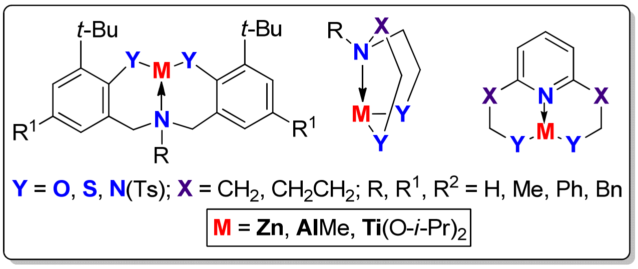
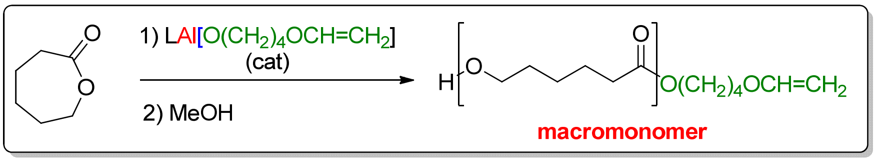
Investigation of synthesis and structure of metal complexes is one of the main questions of modern chemistry, where establishment of "structure – property" relationship is a main task. The design of the polydentate ligands (LH_2) is crucial to regulate the structure and properties of the metal complexes.

In present report the recent results, obtained in our laboratory, on investigation of complexes of Al, Zn, Ti based on polydentate *O*,*N*,*O*-, *N*,*N*,*N*-, *O*,*N*,*N*-, *O*,*N*,*S*- and *S*,*N*,*S*-ligands (synthesis, structure, properties) are presented [1,2]. Furthermore, the macromonomer approach, developed in our laboratory, to the modified polymer materials is also presented [3,4].





It is established that the ligand structure (the size of the chelate ring, nature of the donor atoms, substituents) determines the structure of the complexes formed. All complexes obtained are characterized as very active initiators of ring-opening polymerization (ROP) of lactones, where process of polymerization is highly controllable.

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FORMATION OF Pt-Mo FINE-DISPERSED POWDERS IN AUTOCLAVE CONDITIONS AND SOLID PHASE

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Fine powders have a unique set of mechanical, electrical and other properties that are different from similar compact materials and find an increasingly expanding practical application [1].

The purpose of this work was to identify the regularities of autoclave (at 190 ° C) and solid-phase thermolysis of tetraammine platinum (II) and ammonium paramolybdate (PMA)mixture.

Autoclave thermolysis products are solid precipitates, which are a gray powder (spherical particles, the average size is about 690 nm). According to X-ray diffraction and chemical analysis, they contain metallic phases of Pt and Mo. By the method of acid-base titration, it was established that the amount of experimentally-found free ammonia after the reaction is in satisfactory agreement with the theoretical value corresponding to the reduced reaction equation (1) below:

$12[Pt(NH_3)_4]Cl_2 + (NH_4)_6Mo_7O_{24} + 24KOH \rightarrow 12Pt^0 + 7Mo^0 + 11N_2\uparrow + 32NH_3\uparrow + 24KCl + 48H_2O$ (1)

The interaction reaction of tetraammine platinum (II) with ammonium paramolybdate (PMA) in a solid phase under an inert atmosphere (Ar) and in air up to 500 ° C was studied by thermal analysis and mass spectroscopy. The compositions of products in argon - Pt, Mo and MoO3 and in air - Pt and MoO_3, are established by methods of XRD and chemical analysis, respectively. The solid-phase reaction between $12[Pt(NH_3)_4]Cl_2$ - $(NH_4)_6Mo_7O_{24}$ in an argon atmosphere can be described by the equation (2):

$12[Pt(NH_3)_4]Cl_2 + (NH_4)_6Mo_7O_{24} \rightarrow 12Pt + Mo + 6MoO_3 + 5N_2\uparrow + 44NH_3\uparrow + 6H_2O\uparrow + 24HCl\uparrow$ (2)

A model for the interaction of platinum (II) and molybdenum salts in the solid phase is proposed. An analogy of the processes in solution and in the solid phase is found; since in both cases metallic phases (Pt and Mo) and the same gaseous products are formed.

The obtained materials can be used as catalysts in various chemical processes.

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LAYERED CONDUCTORS WITH COORDINATION IN IONIC LAYERS

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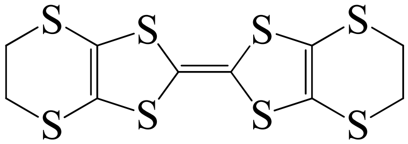
Organic conductors based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) are known to involve the BEDT-TTF$^{+\cdot}$ radical cations providing conductivity and counterions compensating charge of conducting BEDT-TTF layers [1]. We synthesized new BEDT-TTF radical cation salts that contain complex ions of different types, $[Ni(aq)_5Br]^+$, $[CoCl_3(urea)]^-$, $(PbBr_3^-)_n$ and $(Cd_{1.38}I_3)_n$, determined their crystal structures and investigated conducting properties.



BEDT-TTF

Organic conductor of a new unusual composition β''-$[(BEDT\text{-}TTF)_3]^{2+}([Ni(aq)_5Br]^+)_2(Br^-)_4$ includes cations of two types: organic cations containing π conduction electrons and inorganic cations carrying 3d localized magnetic moments. Single-crystal study reveals that the octahedral $[Ni(aq)_5Br]^+$ cations form a network by hydrogen bonds, and the organic cations form conductive layers of a β''-type donor arrangement; the networks and the layers are separated by bromine anions. Resistivity measurements show metallic behavior with metal-insulator transition at T_{MI} =172 K. In the crystal structure below T_{MI}, charge disproportionation between BEDT-TTF molecules was found from the BEDT-TTF intramolecular bond length distribution [2].

New organic metal $(BEDT\text{-}TTF)_5([CoCl_4CoCl_3(urea)](urea)$ includes organic cations containing π conduction electrons and inorganic anions carrying 3d localized magnetic moments. The organic cations form conductive layers, the tetrahedral $[CoCl_4]$ and $[CoCl_3(urea)]$ anions and the urea molecules form insulating layers. Resistivity measurements show metallic behavior with metal-insulator transition at T_{MI} =70 K.

In organic semiconductors $(BEDT\text{-}TTF)_6Pb_3Br_{10}(C_6H_5Br)$ (i) and $(BEDT\text{-}TTF)Cd_{1.38}I_3$ (ii) the BEDT-TTF layers alternate with insulating layers. In (i) anion layers are composed of infinite chains of face-shared $PbBr_6$ octahedrons [3], and in (ii) these layers are formed by CdI_6 octahedra and CdI_4 tetrahedra bound together into a two-dimensional anionic network.

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OPERATION OF THE COMPOSITION AND STRUCTURE OF THE CRYSTALS OF THE PRODUCTS OF EXCHANGE REACTION BETWEEN RARE EARTH ACETATES AND PIVALIC ACID

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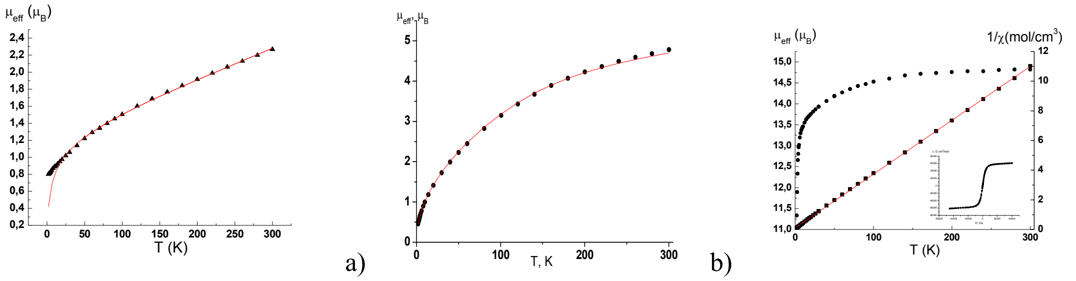
The work presents results on synthesis and structural investigation of single crystals of the complexes of REE(III) $M_2(piv)_6(Hpiv)_6$ (Monoclinic, $P2_1/c$, **1**), $M_2(piv)_6(Hpiv)_6 \cdot Hpiv$ (Monoclinic, $C2/c$, **2**), $\{M(piv)_3\}_n$ (Trigonal, $P6_3/m$, **3**) and $Sm_2(piv)_6(Hpiv)_2(^{i}PrOH)_2 \cdot 2Hpiv$ (Triclinic, P-1, 4), where piv = $(CH_3)_3CCO_2^-$. It was shown, that the variation of the nature salting-out agent - not a coordinating organic solvent in the system «$M(OAc)_3 \cdot 4H_2O$ - Hpiv» leads to the controlled formation of crystals of dimers of **1** or **2** for M = Pr, Nd, Sm, Eu and Gd, in case of using hexane, dimer **1** or 1D polymer **3**, for M = Y, Er and Yb, in case of using EtOH, and dimers of **1** or **4** for M = Sm, in the case of using iPrOH, in the form of bulk single-phase samples. It was shown that the crystals of **1** (*Pn*) undergo the reversible phase transition to the commensurate modulated modification ($P2_1/c$). For complexes **1** (M = Pr, Nd, Eu, Dy, Ho, Er) and **4** the magnetic properties was studied. In the temperature range of 70-300 K, the dependences $1/\chi(T)$ for pivalates **1** (M = Pr, Nd, Dy, Ho, Er) are linear and follow the Curie-Weiss law. The magnetic properties of complexes **1** (M = Eu, Dy) and **4** are displayed in Fig. 1. For **4** and for **1** (M = Eu), the $\chi_M T(T)$ dependences are well described by the expressions for the magnetic susceptibility of the free ion Sm^{3+} и Eu^{3+}, respectively. The calculated parameters of the spin–orbit interaction λ are 232 and 329 cm^{-1} for complexes Sm and Eu, respectively. The transition to magnetically ordered state took place for **1** (M = Dy) at 2 K, the spontaneous magnetization is 54660 G·cm^3/mol.



a) b) c)

Fig. 1. Plots $\mu_{eff}(T)$ (●) and $1/\chi(T)$ (■) for **4** (a), for **1** (M = Eu) (b) and for **1** (M = Dy) (c) (insert: plot $\sigma(H)$) (b), calculated data are represented by the red line.

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SYNTHESIS OF (SUB)MICROCRYSTALS BINUCLEAR $(HPIV)_6Tb_2(PIV)_6$ AND POLYMERIC $Tb(PIV)_3\}_n$ TERBIUM(III) PIVALATES IN THE SUPERCRITICAL CARBON DIOXIDE, PHOTOLUMINESCENT AND MAGNETIC PROPERTIES

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[b]*Federal Scientific Research Centre "Crystallography and Photonics", Russian Academy of Sciences, Moscow, RUSSIAN FEDERATION*
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It is shown, that the using of the supercritical fluid micronization method RESS (Rapid Expansion of Supercritical Solution) and supercritical carbon dioxide ($SC-CO_2$) as the fluid and binuclear complex $(Hpiv)_6Tb_2(piv)_6$ (**1**) [1] as the initial compound, depending on the process parameters allows to obtain single-phase $(Hpiv)_6Tb_2(piv)_6$ (**1a**) or coordination polymer $\{Tb(piv)_3\}_n$ [1] (**2a**, **2b**, **2c**) in the form of (sub)microcrystals of controlled size. For $\{Tb(piv)_3\}_n$ (**2**) demonstrated the fundamental possibility of obtaining polycrystalline particles of different morphology in the conditions of $SC-CO_2$ process (Fig. 1.).

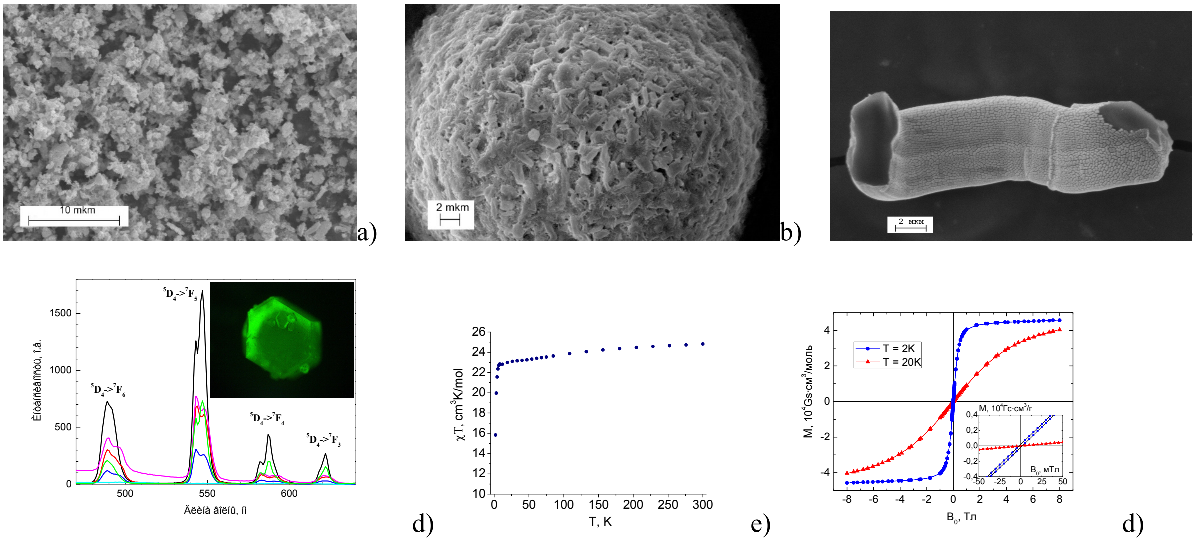

Fig. 1. SEM images of morphology **2**: irregularly shaped polycrystals (a), spheres (b), hollow tubes (c). Photoluminescence (PL) spectra **1** (__, 125 mkm), **1a** (__, 1.1 mkm), **2** (__, 8.7 mkm), **2a** (__, 3.2 mkm), **2b** (__, 2.4 mkm), **2c** (__, 7.6 mkm), insert: PL of **1** in fluorescence microscope; a decrease in the Feret’s diameter [2] of the (sub)microcrystals leads to a decrease in the intensity of their PL, $\lambda_{ex.}$ = 380 nm (d); magnetic properties of **1** [1] and **1a** (the dependence $\chi T(T)$ at 5000 Oe (e), the field dependence of the magnetization (f)) differ.

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CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF TRANSITION METAL COMPLEXES POSSESSING FLUORINE-CONTAINING ARYL-β-DIKETONE LIGANDS

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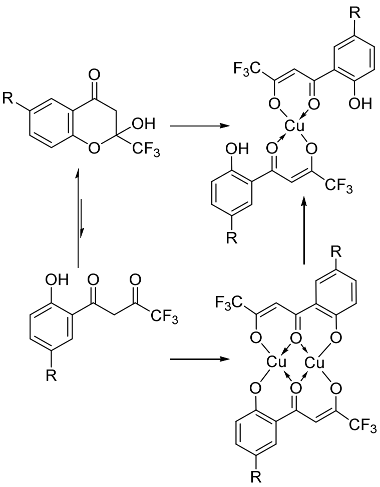
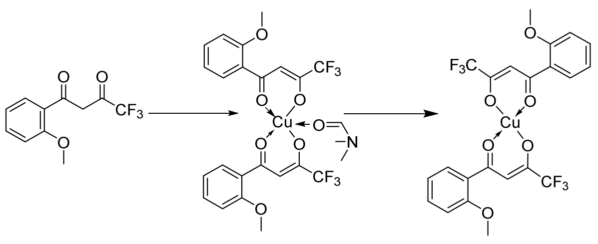
Bioinorganic chemistry has generated significant interest in the design of metal complexes as potential therapeutic agents. Such compounds have attracted considerable attention as metallodrug candidates because metal ions are essential in many natural biological processes. There are several metal complexes that are already in use for these purposes and this has encouraged further research on new metallodrugs such as metal-mediated antibiotics.

β-Diketones and their transition metal complexes are of current interest because of their ability to form metal complexes, which may play an important role in biological functions of the compounds. Those compounds, which are not biologically active, can become active upon coordination.

Keeping in view the biological importance of β-diketones and the role of metals in biology, we herein report the synthesis, crystal structure and biological activity of a series of β-diketone derivatives.





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SYNTHESIS AND CRYSTAL STRUCTURES OF THE INCLUSION COMPOUNDS OF A POROUS METAL-ORGANIC POLYMERS WITH PHOTOACTIVE MOLECULES

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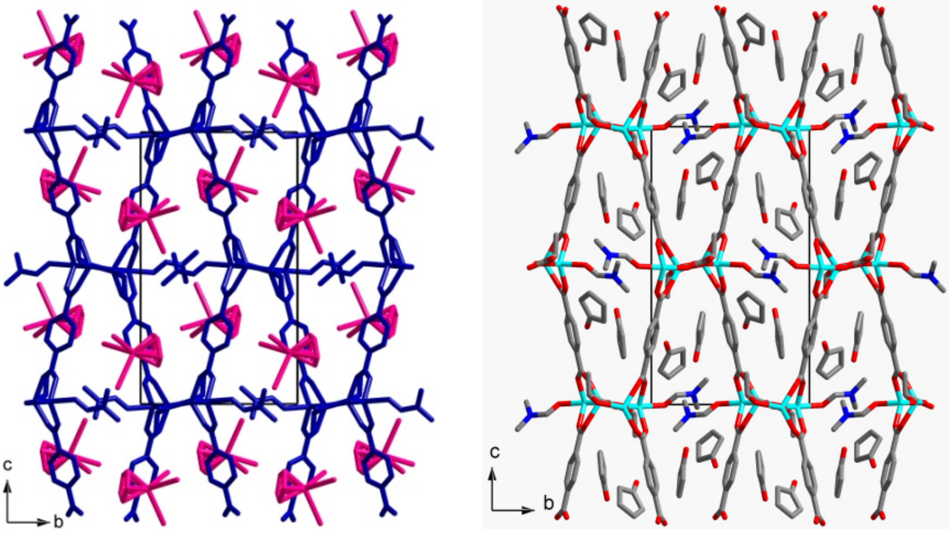
Porous metal-organic coordination polymers (MOCPs) have a number of unique properties, including a high specific surface area. Such compounds have attracted much attention due to numerous possibilities of the structural and functional design of these compounds and prospects for creating new generation functional materials based on them. Nowadays, these are first of all materials suitable for reversible sorption followed by the storage of gases of various nature, materials for selection and purification of various organic compounds, as well as for catalysis. Another new and important aspect being elaborated nowadays is the use of a system of voids and channels in porous MOCPs as nanoreactors to carry out chemical (photochemical) reactions in them. It is also interesting to study the dynamic behavior of guest molecules depending on the size and shape of the channel and on the guest nature. In the present work, we report the synthesis and crystal structure of the inclusion compounds based on previously obtained homochiral porous MOCP ($[Zn_2(dmf)(bdc)(lac)]$) with 2cyclopentene-1-one (C_5H_6O) [1] and cymantrene [2]: $[Zn_2(dmf)(bdc)(lac)]\cdot[Mn(C_5H_5)(CO)_3]$ (1), $[Zn_2(dmf)(bdc)(lac)]\cdot C_5H_6O$ (2) (DMF = N,N′-dimethylformamide, H_2bdc = terephthalic acid, H_2lac = S-lactic acid, C_5H_5 = cyclopentadienyl).



Pic. 1. Packing in crystal of compounds **1** and **2**

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REDOX CHEMISTRY OF O,N-HETEROCYCLIC STANNYLENES

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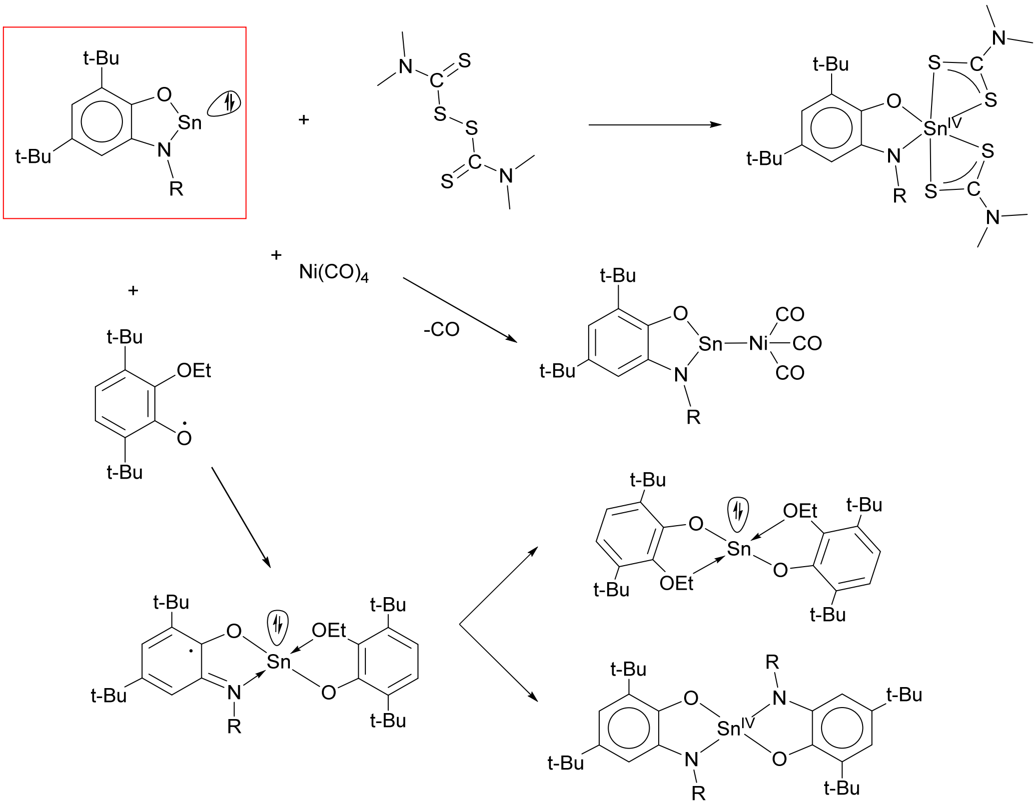
Considerable interest towards the chemistry of the heavier analogues of carbenes has been triggered by the isolation of the first stable N-heterocyclic carbene by Arduengo III in 1991. At present a lot of stable silylenes, germylenes, stannylenes and plumbylenes derived from different heterocycles has been prepared. Redox active ligands such as o-aminophenoles can be used as reservoirs of electrons for bond-making and bond-breaking reactions and can support the multi-electron changes required to promote group- or atom-transfer reactions.

In this work we have investigated redox transformations of heterocyclic stannylenes bearing N-(R)-substituted *o*-aminophenols.



The multiple reactivity modes of O,N-hetecyclic stannylenes supported by redox-active o-amidophenolate ligands was observed. Reaction with TMTD passes through oxidation of tin(II) center and leads to the formation of the new hexacoordinated tin(IV) derivatives. In the reaction with $Ni(CO)_4$ stannylene acts as Lewis-bases giving new bimetallic product. Through a vacant p-orbital metallene compound can react with Lewis-bases such as pyridine. Oxidation of redox-active ligand at tin atom leads to formation of paramagnetic derivatives of divalent tin, which undergo intramolecular redox transformation giving derivatives of tin(IV).

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COMPLEXES OF LANTHANIDE NITRATES WITH BIS(2-BROMOANILIDES) OF 2,2'-BIPYRIDYL-6,6'-DICARBOXYLIC ACID. INVESTIGATION OF LUMINESCENT PROPERTIES

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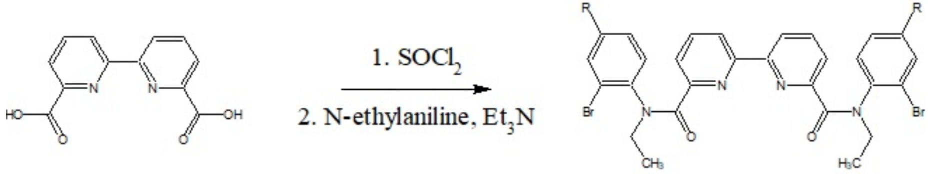
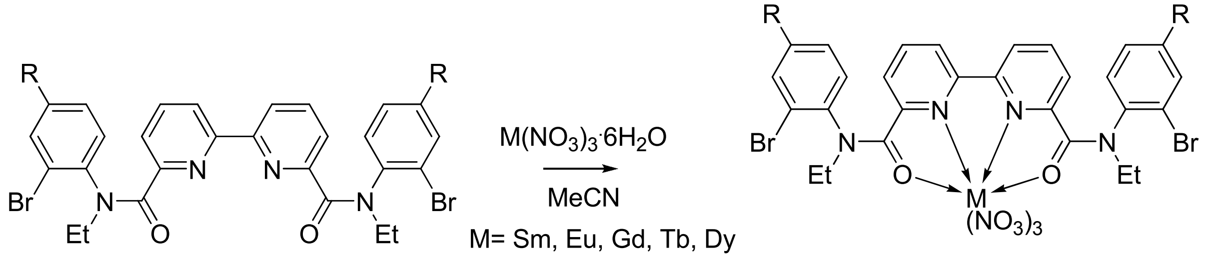
Recently O,N,N,O-type ligands and, in particular, the 2,2'-bipyridyl-6,6'-dicarboxylic acid diamides have been extensively studied for binding of f-elements [1], [2]. As complexes of lanthanides possess potential luminescent materials [3] and the incretion of heavy atoms in the structure of the ligand improves the luminescence of complexes [4], the aim of the investigation was the design of new ligands containing bromine atoms in the structure and the study of the photophysical properties of their complexes with f-block elements. Starting from the substituted 2-bromo-4-R-N-ethylanilines we synthesized a series of diamides of 2,2’-bipyridyl-6,6’-dicarboxylic acid:



R= H, Et, n-Hex, cycloHex

The resulting ligands reacts with lanthanides nitrates in acetonitrile with the formation of the corresponding mononuclear complexes:



M= Sm, Eu, Gd, Tb, Dy

The composition and structure of the synthesized compounds were confirmed by NMR and mass spectrometry. Investigation of the photophysical properties of synthesized complexes showed an increase in the quantum yield of luminescence in comparison with analogous compounds that do not contain bromine atoms in their structure.

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SYNTHESIS AND MOLECULAR STRUCTURE OF O,N-HETEROCYCLIC STANNYLENES

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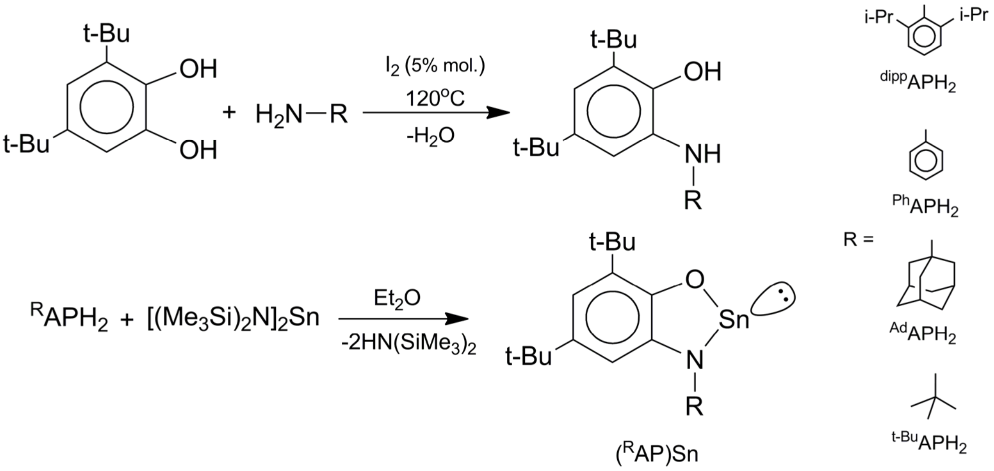
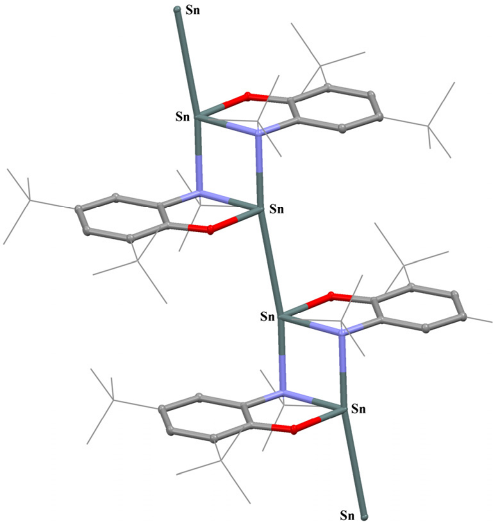
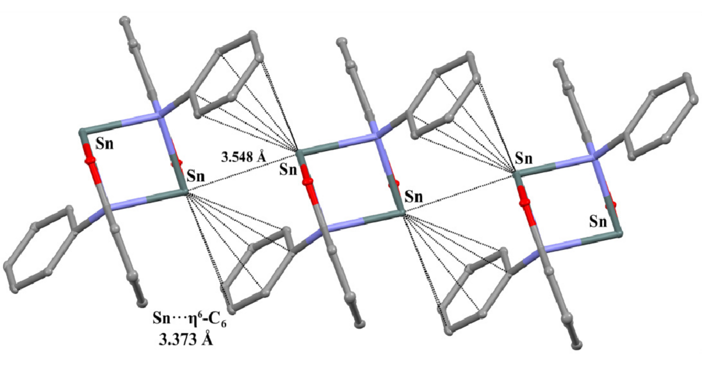
The variation of heteroatoms in the chelating fragment of various metallenes provides a useful means for tuning their reactivity. At present many stable silylenes, germylenes, stannylenes and plumbylenes derived from different heterocycles have been prepared. Interest in these compounds arises from their electronic structures and chemical properties.

In this work we have synthesized and investigated features of molecular structure of heterocyclic stannylenes bearing N-(R)-substituted *o*-aminophenols.







Acknowledgements This work was supported by the Russian Scientific Foundation (Grant 17-13-01428).

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COPPER COMPLEXES OF “BIFACIAL” LIGAND 4,5-DITHIETE-3,6-DI-TERT-BUTYL-O-BENZOQUINONE

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“Bifacial” 4,5-dithiete-3,6-di-*tert*-butyl-*o*-benzoquinone (**1**) [1] contains two coordination sites and able to form both diolate and dithiolate complexes depending from the nature of the metal and auxilliary ligands [1,2].

In this work we present the results obtained from the study of the interaction of the metal copper with a solutions of **1**. The reaction of **1** with compact metal in organic solvents (with the absence of the moisture and oxygen traces) leads to formation of copper(II) bis-*o*-semiquinonate complex (**2**). Two polymorph samples of the complex **2a** and **2b** differing by molecular structure and crystal packing were isolated. Complex **2a** has tetragonally distorted octahedral structure with two *o*-semiquinonic ligand in equatorial plane and two solvated THF molecules in apical sites. In **2b** coordination sphere of the complex do not contain any solvent molecules, and coordination environment of the copper(II) is supplemented by S atoms of neighboring molecules with the formation of a pronounced 1D motif.

The action of “soft” bases on **2** which stabilize the copper(I) state induce a redox-elimination of the one of *o*-semiquinonic ligands forming *o*-semiquinonate Cu(I) complexes (**3**) which were characterized by their isotropic EPR spectra in solution.

Interaction of **2** with neutral diaza-ligands (bpy, phen) leads to formation of paramagnetic copper(II) complexes. Spectral characteristics of their crystalline samples correspond to catecholate structure $(Cat^{OO})Cu^{II}(phen)$ (**4**) or $(Cat^{OO})Cu^{II}(bpy)$ (**5**) with the coordination of the copper ion with dioxa-site of the ligand. In solutions of **4** and **5** the reversible migration of the $Cu^{II}(phen)$ and $Cu^{II}(bpy)$ metallofragments between dioxa- and dithia-sites was found by EPR.

The complexes **4** and **5** may also be formed direct interaction of the metal copper in the solution of **1** with the presence of phen or bpy.

The dissolving of the metal copper in the solution of **1** in THF media in the presence of 1,4-di-*tert*-butyl-di-1,4-azadiene (DAD) leads to formation of diamagnetic *ate*-complex $[(Cat^{SS})_2Cu^{III}]^-[(DAD)_2Cu^I]^+$ (**6**), which structure was established by X-ray difractometry. Contrary to known dioxa-analogs, **6** contains complex copper(III) anion with two dithiolate anions environment. The solutions of **6** in organic solvents are paramagnetic. Their EPR spectra correspond to complex (**7**) with copper cation coordinated to dioxa-site.

$$(Cat^{OO})Cu^{II}(DAD) \quad \Leftrightarrow \quad (SQ^{OO})Cu^{II}(DAD)$$

Observed temperature dependence of the EPR spectra of **7** shows an existence of equilibrium between catecholate (**7Cat**) and *o*-semiquinonate (**7SQ**) redox-isomers in solution.

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SYNTHESIS AND X-RAY DIFFRACTION ANALYSIS OF HEXA(ISOTHIOCYANATE)CHROMATES(III) OF SOME NICOTINIC ACID LANTHANIDE COMPLEXES

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Double complex compounds (DCC) - hybrid inorganic-organic substances - are promising precursors of various functional materials and nanocomposites. Hexa(isothiocyanate)chromate (III) of lanthanide complexes with neutral organic ligands exhibit the reversible thermochromic properties and their use as chemical sensors in temperature-sensitive devices is of great research interest [1-3].

Ion-type double complex compounds $[M(C_5H_5NCOO)_3(H_2O)_2][Cr(NCS)_6]\cdot nH_2O$, M=Eu (**1**), n=1.15; Dy (**2**), Er (**3**), *n*=1,5; M=Yb (**4**), *n*=2 are synthesized in aqueous solution reacting $M(NO_3)_3$, M=Eu, Dy, Er, Yb, $K_3[Cr(NCS)_6]$ and nicotinic acid (C_5H_5NCOO) in the range of pH 4-6 in yields of 60-65%. DCC **1 - 4** are air-stable pale purple crystalline powder.

IR spectroscopic examination showed the coordination of lanthanide (III) ions through the oxygen atoms of the carbonyl groups of nicotinic acid and the bidentate organic ligand. According to the XRD compounds 1-4 are isostructural to the previously studied set of complexes $[M(C_5H_4NHCOO)_3(H_2O)_2][Cr(NCS)_6]\cdot nH_2O$, where M = Ho [4], La and Nd [5], n = 1–2. In the crystal structures of compounds 1 - 4 the cation has the polymer chain structure. The coordination polyhedra of lanthanide (III) ions are the distorted square antiprisms. The counterions of the polymer cations are the isolated anions $[Cr(NCS)_6]^{3-}$, in which the coordination chromium (III) polyhedron consists of nitrogen atoms of six thiocyanate ions and has the typical octahedral environment with the minor deviations from the ideal geometry. The polymer chains are packed one against another according to the law of hexagonal *bc*-plane rod setting, the space between the chains is filled with the island complex anions and the crystallization water molecules. In addition, the structure is stabilized by intermolecular hydrogen bonds between crystallization water molecules and N-H groups of coordinated organic ligands.

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PRODUCTION AND INVESTIGATION OF DOUBLE COMPLEX COMPOUNDS WITH REVERSIBLE THERMO-SENSITIVE PROPERTIES

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The double complex compounds (DCC) – hexa(isothiocyanate)chromates(III) of lanthanide (III) complexes with neutral nitrogen – and sulfur-containing organic ligands are of interest as the precursors of heat-sensitive materials and nanocomposites [1,2].

Hexa(isothiocyanate)chromates (III) of lanthanide (III) complexes are synthesized from aqueous solutions with ε-caprolactam $[LnCpl_8][Cr(NCS)_6]$[1] and nicotinic acid $[M(C_5H_5NCOO)_3(H_2O)_2][Cr(NCS)_6]\cdot nH_2O$, M = La, n=2 ; M = Nd, n=1[3]. While attempting to synthesize such complexes with 8-hydroxyquinoline from aqueous solutions, the DCC of $[Ln(H_2O)_8][Cr(NCS)_6]$[4]compounds were produced. The crystalline and molecular structures of DCC are revealed. The complexes possess the reversible thermochromic properties, changing the color under heating↔cooling in the temperature range 373-483 K [5]. The reversible thermochromism with a change in color from light purple to dark green is characteristic only of ion complexes, DCC with polymeric structures change color irreversibly when heated. The complex of $[Lu\ Cpl_6][Cr(NCS)_6]\cdot 2Cpl$ does not exhibit the reversible thermochromic properties, which is due to the presence of solvated organic molecules, the thermolysis of which proceeds at low temperatures, provoking the further decomposition of the DCC as a whole at temperatures below the thermal discoloration level [6]. Hexa(isothiocyanate)chromates (III) of lanthanides complexes with neutral organic ligands, which have an ionic structure resist many reversible cycles of heating and cooling without changing their physicochemical characteristics. The DCCs are resistant to air, thermally stabile under operating conditions and soluble in organic solvents. Substances are easily applied to the substrates in the form of thin thermochromic films and heat-sensitive coatings, as well as are pressed into the polymer matrices; this fact allows them to be recommended for use in temperature-indicating devices for the visual monitoring of temperatures and temperature fields in various industries. The low-temperature thermo-indicators are promising for use in "smart" packaging of agricultural products [7].

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NEW MOLECULAR TECTONS BASED ON TETRASUBSTITUTED [1111]METACYCLOPHANES WITH DIVERGENTLY DISPOSED QUINOLYL-, CARBOXYL- AND CYANO-GROUPS

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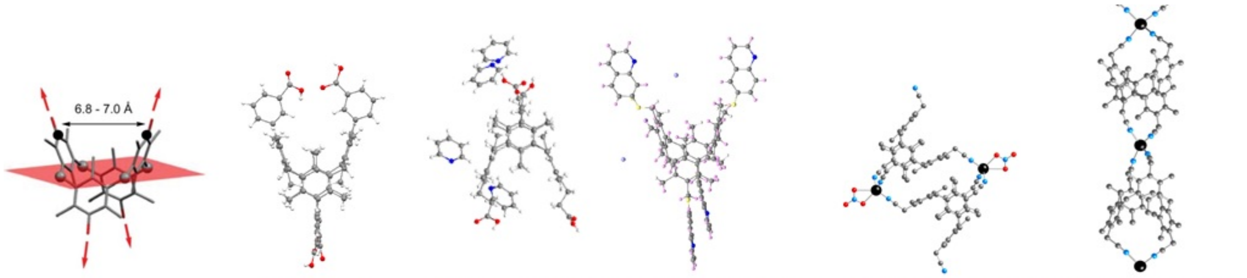
Metal-organic frameworks (MOFs) are still attracting growing interest as functional materials able to find applications in light energy transformation, gas/liquid storage, separation, catalysis etc. [1]. Recently, the chemistry of calix[4]arene based macrocycle compounds have been also intensively developed in order to create new coordination polymers of different dimensionalities [2] using *molecular tectonics* approach [3]. In this study, we were focused on the chemistry of [1111]metacyclophane derivatives displaying a high skeleton rigidity and stability of *1,3-alternate* conformation compared with familiar flexible calix[4]arene backbone [4].

In this contribution, we report the synthesis of new [1111]metacyclophane derivatives bearing divergently disposed *cyano-*, *quinolyl-* and *carboxyl groups* with different spacers (alkyl or phenyl) which presents attractive tetrahedral-shaped molecular tectons for coordinanation or H-bonded networks formation in the crystalline phase (Fig. 1).



$\{C_{68}H_{64}O_8\}$ $\{C_{52}H_{64}O_8, 4C_5H_5N\}$ $\{C_{80}H_{76}N_4O_{4}, 6(H_2O)\}$ $[(C_{48}H_{52}N_4)_2\text{-}(AgNO_3)_2]$ $C_{48}H_{52}N_4\text{-}AgNO_3$

Figure 1. XRD on single crystals of obtained compounds

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THE STRUCTURE FORMATION OF COBALT(II) CARBOXYLATE COMPLEXES: INFLUENCE OF THE R GROUP CARBOXYLATE NATURE

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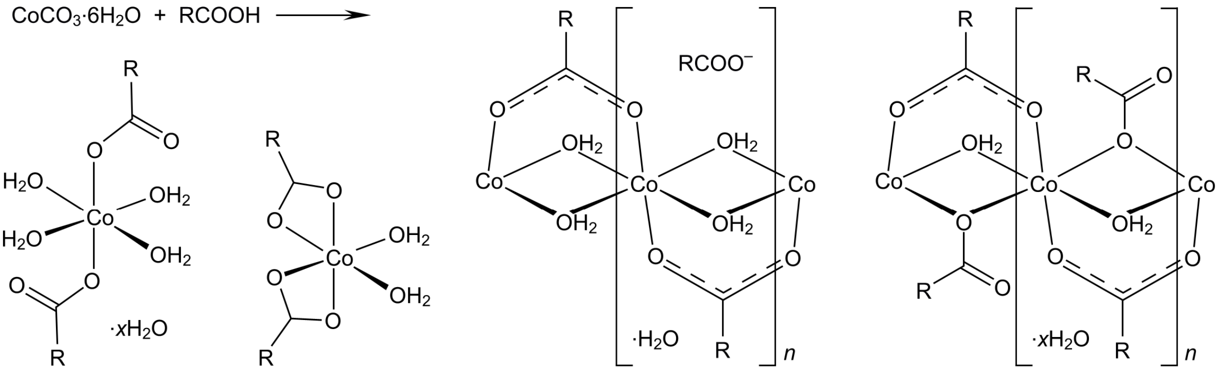
The study of the laws governing the nuclearity and structure motif of *d*-elements coordination compounds refers to the fundamental task of modern chemistry due to their unique chemical, magnetic, spectral and other properties. The direct synthesis of the oligomeric compounds with desired structure and properties still remains the main problem in the preparation of the cobalt carboxylate complexes. The aim of this work is to study the influence of carboxylate $RCOO^-$ R group nature on the nuclearity, structure motif and the properties of the resulting complexes.

By means of single X-ray diffraction analysis our working group have synthesized and characterized the following complex compounds: $Co(RCOO)_2{\cdot}xH_2O$, where R = Et, Pr, Pr^i, Bu^i, Ph, p-$Bu^tC_6H_4$. The complexes have been obtained by the interaction of the corresponding carboxylic acid with $CoCO_3{\cdot}6H_2O$.



R = Me [1], p-$Bu^tC_6H_4$ R = Bu^i R = Ph R = Et, Pr, Pr^i [2]

Despite the identical conditions for yielding of crystalline carboxylates, *p*-(*tert*-butyl)benzoate and isovalerate complexes are monomeric compounds, while propionate, butyrate, isobutyrate and benzoate complexes have a polymeric chain structure, the latter being the ionic compound with the polymer cation which charge is compensated by benzoate outer-sphere anions.

The obtained complexes are the synthons for generation of cobalt carboxylates oxidized forms. Besides, the temperature dependence of magnetic susceptibility has been determined for the compounds.

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SYNTHESIS AND STRUCTURE OF ZINC(II) MALONATES WITH N,N'-CONTAINING LINKERS

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Coordination polymers attract attention of researchers around the world, because, variation of components in the synthesis allows to obtain different compounds with given physicochemical properties, that necessary for use in solving specific problems. For example, coordination polymers of zinc(II) having a framework structure can serve as heterogenous catalysts, capable of sorption of gases, or can be used for storage of substances. Their application in biochemistry and medicine for separation of stereoisomers and delivery of drugs (as «biological capsule») is also described [1-3].

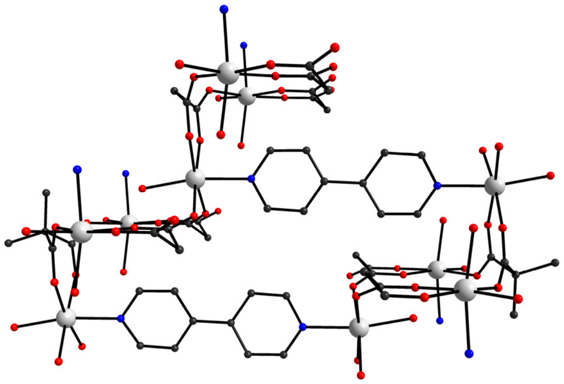

Fig. 1 – Fragment of framework structure of complex **1**

For the first time were synthesized and characterized by X-ray diffraction analysis nine new compounds of zinc(II) with the anions of dimethylmalonic and diethylmalonic acids and with N-donor bridging ligands (4,4'-bypyridyl (bpy), 1,2-bis(4-pyridyl)ethylene (bpe) and 1,2-bis(4-pyridyl)ethane (bpa)): $[Zn_2(H_2O)_2(bipy)(Me_2mal)_2]_n$ (**1**), $\{[Zn(bpa)(Me_2mal)]\cdot H_2O\}_n$ (**2**), $\{[Zn(bpa)(Et_2mal)]\cdot 0.38H_2O\}_n$ (**3**), $\{[Zn(bpe)(Me_2mal)]\cdot H_2O\}_n$ (**4**), $[Zn(bpe)(Et_2mal)]_n$ (**5**), $[Zn(H_2O)_4(bpe)_2]\cdot 2HEt_2mal$ (**6**), $\{[Zn(H_2O)_4(bipy)]\cdot 2HEt_2mal\cdot bipy\cdot 2H_2O\}_n$ (**7**), $\{[Zn(bipy)(bipy)_{0.5}(Et_2mal)]\cdot H_2O\}_n$ (**8**), $[Zn(bpe)(HMe_2mal)_2]_n$ (**9**). Only complex **6** has a molecular structure; the others compounds are polymers – 3D (**1-5**, **8**, **9**) or 1D (**7**).

It was shown that for two compounds with 1,2-bis(4-pyridyl)ethylene the reaction of photoinitiated single-crystal-to-single-crystal [2+2] cycloaddition is possible. UV irradiation of crystals **4** and **6** afforded the 3D→3D and 0D→1D transformations with the $\{[Zn(\mathit{bpe})(Me_2mal)]_2[Zn_2(tpcb)(Me_2mal)_2]\cdot H_2O\}_n$ and $\{[Zn(H_2O\text{-}\kappa O)_4(\mathit{bpe})_2]_{0.15}[Zn(H_2O)_4(tpcb)]_{0.85}\cdot 4HEt_2mal\}_n$ composition (tpcb = tetrakis(4-pyridyl)cyclobutane), respectively.

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NOVEL PSEUDODIPEPTIDE DIAMIDOPHOSPHITES WITH 1,3,2-DIAZAPHOSPHOLIDINE CYCLE

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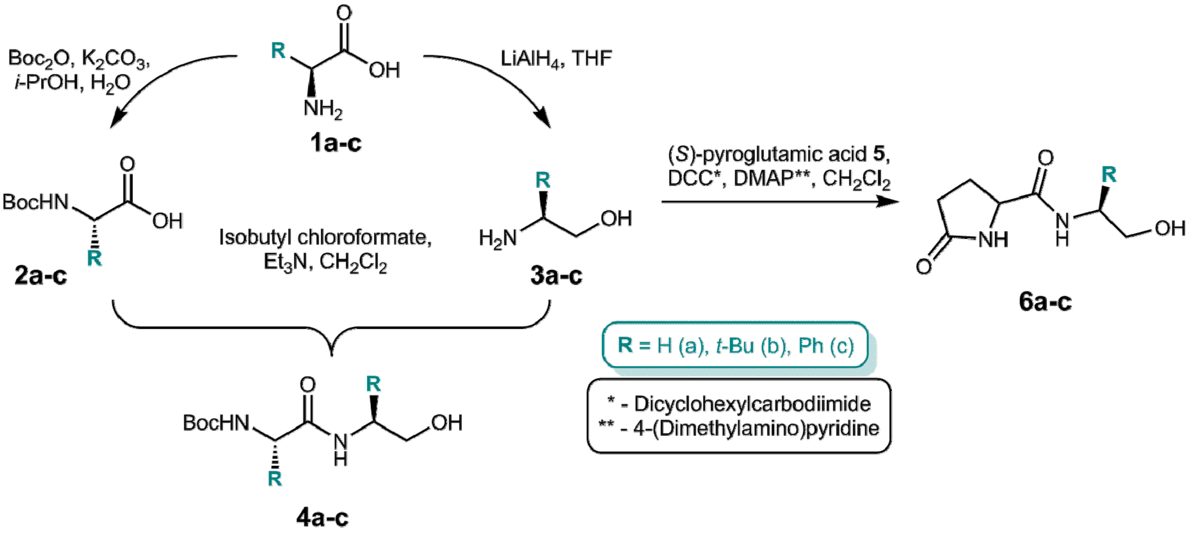
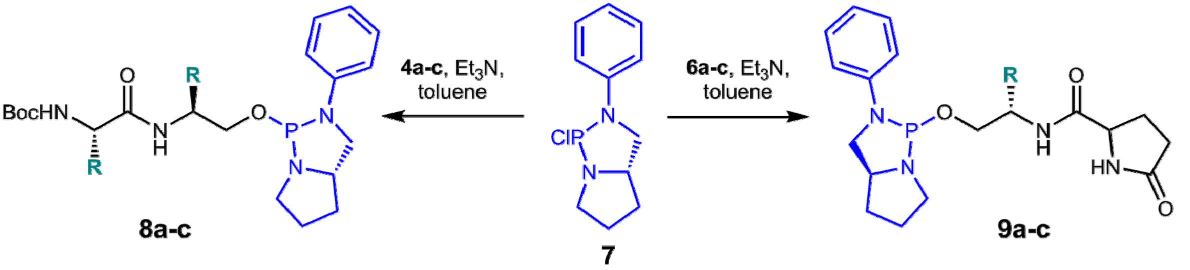
We carried out a three-step synthesis of *N*-Boc-substituted pseudodipeptide amino acids as versatile precursors: the preparation of *N*-Boc (*S*)-derivatives **2a-c** of the corresponding (*S*)-amino acids **1a-c**; the synthesis of (*S*)-1,2-amino alcohols **3a-c** by the reduction of compounds **1a-c**; and the formation of compounds **4a-c** by the reaction between the *N*-Boc derivatives **2a-c** and the corresponding amino alcohols **3a-c**. We also synthesized peptide-like diamido alcohols **6a-c** by the reaction between (*S*)-pyroglutamic acid **5** and amino alcohols **3a-c** in the presence of dicyclohexylcarbodiimide (DCC) with catalytic addition of 4-(dimethylamino)pyridine (DMAP).



We obtained 1,3,2-diazaphospholidines **8a-c** and **9a-c** by condensation of pseudo-dipeptides **4a-c** and **6a-c** with reagent **7**.



These ligands can be recommended for use as stereoinducers in Pd-catalyzed asymmetric allylic substitution of various substrates.

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INTERACTION OF METAL IONS WITH GRAPHENE OXIDE BY THE NMR-RELAXATION PARAMAGNETIC PROBING

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Chemistry of nanomaterials is one of the priority directions in modern science. In this connection, nanomaterials based on graphene oxide are of great interest. It has a unique structure and exceptional physical and chemical properties, which determines the wealth of possibilities for its application. In the literature, there are data on the possibility of using compositions based on complexes of graphene oxide with Gd(III) ions as models of contrast agents for MRI.

Metal ions such as Gd(III), Fe(III) and Mn(II) and an aqueous dispersion of graphene oxide (GO) were chosen as the objects of the study. Optimal modes of ultrasonic treatment of solutions for obtaining stable water dispersions of GO with metal ions were selected. The complexation of Gd(III), Fe(III) and Mn(II) ions with GO in water has been studied by NMR relaxation. The mechanism of proton relaxation for these ions shows that, when bound to large objects (micelles, polymers, etc.), they slow down their rotation, which causes an increase in the relaxation. This fact was used to monitor the state of Gd(III), Fe(III), and Mn(II) in GO solutions.

For all metal ions, it was found that with a large content of GO, a considerable sharp increase in the relaxivity (up to 5 times) is observed, starting with a strong acid medium, and passing through a maximum at pH 6-7 with a decrease in alkaline solutions according to the scheme on the Figure.

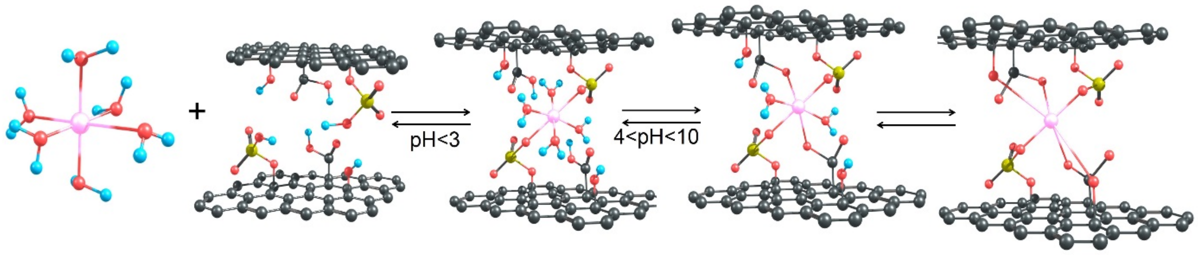

Figure. Possible scheme for binding metal ions to graphene oxide.

The growth of the relaxation in a strongly acidic medium is observed due to the binding of metal ions to the sulfate groups present in the GO composition in a small amount due to the synthetic procedure. The maximum in a neutral medium is observed due to the binding of metal ions to carboxyl groups. The decrease in the relaxation in the alkaline region can be caused by the partial replacement of oxygen atoms of carboxyl groups GO by hydroxyl groups in the first sphere of the metal ions (see Figure).

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PORPHYRIN NANOTUBES BASED ON N-CONFUSED N-METHYLATED TETRASULFOPHENYLPORPHYRIN

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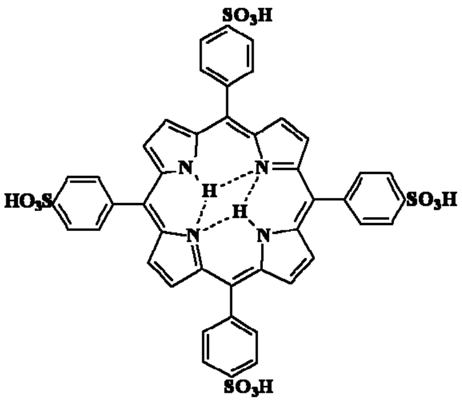
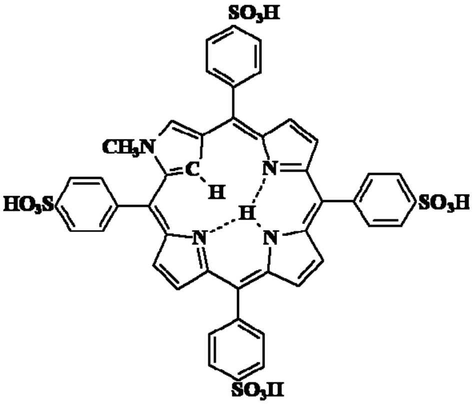
Inverted porphyrins (2-aza-21-carbaporphyrin) since the discovery in 1994 by two independent groups of researchers [1,2], attract a great interest through the unique physical and chemical properties. Inverted porphyrins are quite similar to regular ones, but have a crucial structural difference-one pyrrole carbon atom located inside macrocyclic cavity, whereas a nitrogen atom occupies an external position of the ring. Water soluble N-confused porphyrin derivatives are particularly interesting objects for researchers due to their potential medical and biological application. Well-known water-soluble tetrasulfophenyl porphyrin **H_2P**($PhSO_3H)_4$ possessed the unique ability to pH-depended tubular J-aggregates supramolecular self-assembly as a result of porphyrinic platform transannular diprotonation [3].



$H_2P(PhSO_3H)_4$



$H_2MeIP(PhSO_3H)_4$

Inverted N-metylated analogue of tetrasulfophenyl porphyrin **H_2MeIP**($PhSO_3H)_4$ obtained for the first time [4], and protolytic equilibrium of J-aggregates self-assembly monomer formation was investigated by means of synchronous UV-Vis absorbtion, fluorescence and potenciometric titration technique and also quantum-chemical calculations. Combination of invertation and methylation leads to dramatic increase of porphyrinic platform basicity. As a result, obtained J-aggregates are quite stable in neutral aqueous solutions, whereas J-aggregates of tetrasulfophenyl porphyrin are stable only at low pH values. This peculiarity creates the new possibilities for porphyrin nanotubes applications. Computational model of tubular J-aggregates, based on **H_2MeIP**($PhSO_3H)_4$, was also suggested.

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2,2′-AZOPYRIDINE IN THE PHOSPHORUS COORDINATION CHEMISTRY.

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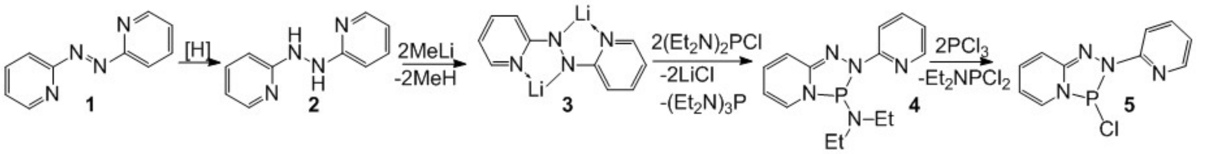
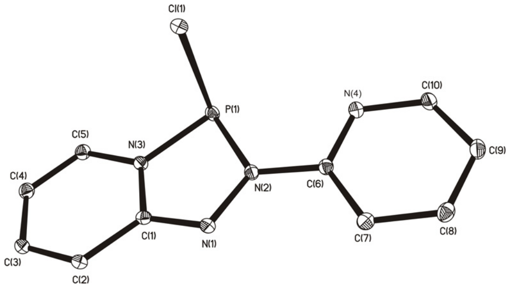
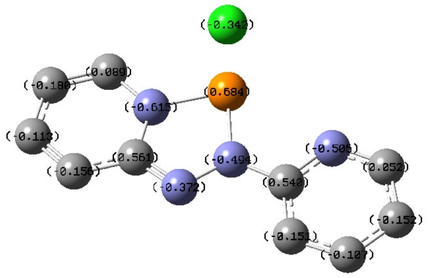
2,2′-Azopyridine may be considered as a promising ligand in coordination chemistry and starting material for synthesis of heterocyclic compounds with different heteroatoms [1] and in particular phosphorus atom. We report here the synthesis of 1,2,4,3-triazaphospholes starting from 2,2′-azopyridine. Azopyridine **1** was reduced to the hydrazopyridine **2** with hydrazine-hydrate. The treatment of **2** with MeLi gives the dilithium salt **3** that was used *in situ*. Interaction of **3** with $(Et_2N)_2PCl$ resulted in the formation of triazaphosphole **4**. Subsequent addition of PCl_3 to **4** results in the substitution of NEt_2-fragment by chlorine atom and the formation of compound **5.** $^{31}P\{^1H\}$ NMR spectrum of **5** shows single resonance at 115 ppm. According to the X-ray data the phosphorus atom in **5** has a pyramidal configuration. Nitrogen atom of pyridyl fragments in **4** and **5** turns to phosphorus atom due to their Coulombic attraction.

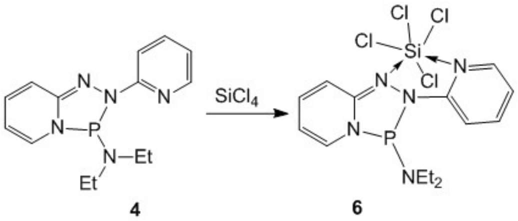




Molecular structure of **5.**



(B3LYP)/6-31+G(d) optimized structure of **5.**



To our surprise, interaction of **4** with $SiCl_4$ did not lead to cleavage of the P-N bonds. Instead, ligand **4** coordinated to the $SiCl_4$ with formation of hexacoordinate silicon compound **6**. Five-membered annulated heterocycles in **6** are not planar and bent relative to each other. Four-valent six-coordinated silicon atom adopts octahedral geometry with chlorine atoms in the axial and equatorial positions.

[1] M. Bardaji, M. Barrio and P. Espinet, *Dalton Trans.,* **2011**, *40*, 2570-2577.

This work was supported by Russian Science Foundation (grant no. 14-13-01015-P).

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NEW WAY TO MIXED NIOBIUM CONTAINING POLYOXOTUNGSTATES

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Chemistry of polyoxometalates (POM) is a rapidly growing area of modern coordination chemistry. Among numerous polyoxocomplexes Nb/W mixed-addendum POMs explored by Klemperer, Hill, Finke et al., including Lindqvist-type $[Nb_xW_{6-x}O_{19}]^{(2+x)-}$, Keggin-type $[XW_9Nb_3O_{40}]^{n-}$ (n = 7, X = SiIV, GeIV; n = 6, X = PV, AsV), and Dawson-type $[P_2W_{12}(NbO_2)_6O_{56}]^{12-}$, $[P_2W_{15}Nb_3O_{62}]^{9-}$, and $[P_2W_{17}(NbO_2)O_{61}]^{7-}$, attracted attention because of their unique characteristics. Such derivatives have good stability in acidic media owing to the presence of the peroxide groups. Finally, inheriting the properties of polyoxoniobates, the Nb/W mixed-addendum POMs also possess high nucleophilicity especially on O_t(Nb), after elimination of the peroxide groups. Such complexes demonstrate photocatalytic activity toward water oxidation process, can be used as precursors for hydrodesulfurization catalysts or can be active in the process for preparing linearly-extended polyalkylenepolyamines. Traditional synthetic way to primary Nb/W mixed POMs is the reaction of Nb-peroxo compounds prepared in situ by solubilizing of $[Nb_6O_{19}]^{8-}$ in H_2O_2 with lacunary polyoxotungstates or sodium tungstate. This methodology was also used to produce unique Ta/W complexes.

In this research we have found a new efficient way to the synthesis of a wide range of mixed Nb/W complexes. Thinking along the way of using niobium peroxocomplexes gave us the new idea to found new niobium precursor because of synthesis with H_2O_2 has some disadvantages limiting the range of reactions in which this method can be used. So we have set out to develop an alternative approach based on the use of a niobium oxalate complex, $(NH_4)[NbO(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ (Nb-Ox), as a Nb precursor. Two anions were synthesized by the reaction of $[AsW_9O_{33}]^{9-}$ and Nb-Ox: $[\{AsW_9O_{33}\}_2(NbO)_2(H_2O)]^{12-}$ and $[\{AsW_9O_{33}\}_2(NbO)_3(H_2O)]^{9-}$, which were isolated in the composition of single phase and detected in water solution by coupled HPLC-ICP-AES technique. The reaction of $[SbW_9O_{33}]^{9-}$ with niobium oxalate leads to selective formation of $[\{SbW_9O_{33}\}_2\{Nb(C_2O_4)\}_2]^{12-}$ anion. In the reaction of $[PW_{11}O_{39}]^{7-}$ with this niobium oxalate selective formation of $[PNbW_{11}O_{40}]^{4-}$ was observed by NMR and EDS. Reactions of bi- and tri-lacunary phosphotungstate with Nb-ox or self-assembly reactions of the niobium oxalate complex, sodium tungstate and phosphoric acid give a mixtures of niobium substituted Keggin $[PW_9Nb_3O_{40}]^{6-}$ and $[PW_{10}Nb_2O_{40}]^{5-}$ anion, formed as all possible niobium positional isomers [1].

[1] P.A. Abramov, A.A. Shmakova et al, *New J. Chem.*, **2017**, *41*,256-262.

Acknowledgements -This work was supported by Russian Science Foundation (grant number 14-13-00645-П).

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SYNTHESIS, STRUCTURE AND PROPERTIES OF {Cd(II)-Ln(III)} COMPLEXES WITH ANIONS OF MONOCARBOXYLIC ACIDS

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E.A. Varaksina[b,c,d], I.V. Taydakov[b,c] and I.L. Eremenko[a]

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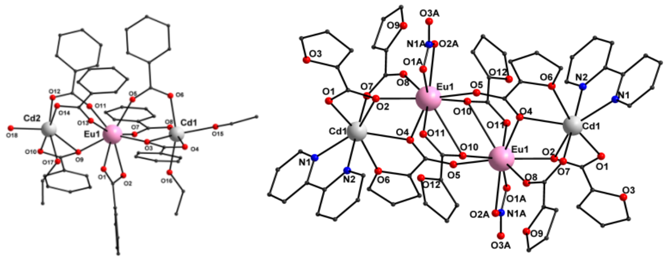
Carboxylate heterometallic complexes of $3d^{10}$ metals with lanthanide atoms draw the notice of investigators due to the possible demonstration of unusual photoluminescence properties. The synthetic method based on the variation of N-donor ligand and the anion of monocarboxylic acid allows us to reveal the patterns of the obtainment of compounds with the predetermined structure and to follow the change of their properties simultaneously.

Using the 3,5-di-*tert*-butilbenzoic acid anion (Hbenz), a new trinuclear heterometallic complex $[Cd_2Ln(benz)_7(EtOH)_x(H_2O)_{4-x}]$ (**1**) (Ln(III) = Eu (**1**), Tb, Dy, Sm, La) was obtained. Involving of the monodentate (L = pyridine, 2,4- lutidine, phenanthridine, 2,3-cyclododecenopyridine), chelating (L = 2,2'-bipyridine, 1,10-phenanthroline) or bridging (L = pyrazine, 4,4'-bipyridine, 5-methylpyridin-2-amine, 1,2-di(pyridin-4-yl)ethene) ligand into the system allowed us to either fully or partly substitute coordinated solvent molecules in the structure of the complex (**1**) by molecules of N-donor ligand. Synthesized {Cd(II)-Ln(III)} (Ln = Eu, Tb) compounds possess photoluminescence activity. Also on examples of obtained complexes with monodentate ligands (2,4- lutidine) the contrast of the Cd (II) chemistry from earlier received {Zn(II)-Ln(III)} analogues was shown.

Involving of the 2-furoic acid (Hfur) salts in the reaction leads to the reorganization of the metal core and in the presence of 2,2'-bipyridine (bpy) the tetranuclear complex $[Cd_2Eu_2(Fur)_8(NO_3)_2(bpy)_2]$ (**2**) was isolated.

In case of using salts of pentafluorobenzoic acid (Hfbenz) at the same conditions we managed to isolate only homometallic Cd(II) complex $[Cd(fbenz)_2(bpy)(H_2O)]_n$, in which the pentafluorobenzoate-anion appears to be a bridging ligand. However, it was revealed that in the presence of the lanthanide salt excess the formation of the new heterometallic complex $[Cd_2Ln(fbenz)_6(NO_3)(bpy)_2]$ takes place.



Pic. 1. The molecular structure of the complex **1** (a) and **2** (б) (*tert*-butil substitutes are omitted)

Acknowledgements - this work was financially supported by the RSF *(project 16-13-10537)*.

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FIRST EXAMPLES OF COORDINATION OF CYCLIC AMINOPHOSPHINES TO TRINUCLEAR MOLYBDENUM SULFIDE CLUSTERS

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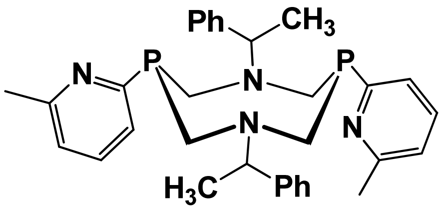
1,5-Diaza-3,7-diphosphacyclooctanes (cyclic aminomethylphosphines) are known since the 1980s [1]. Such compounds have phosphorus and nitrogen atoms included in one cyclic system consisting of eight atoms and can be coordinated to a metal center as bidentate P,P-chelating ligands. Nitrogen atoms are not usually coordinated but rather act as pendant amine in the secondary coordination sphere of the corresponding metal. It has recently been found that metal complexes with cyclic aminophosphines can catalyze some reactions such as hydrogen evolution and oxidation, reduction of oxygen, electrochemical oxidation of formate and Suzuki-Miyaura cross-coupling [2].



L

Fig. 1. View of cyclic aminomethylphosphine used for coordination to Mo_3S_4 cluster.

In this work we describe for the first time a coordination of 1,5-bis(1-phenylethyl)-3,7-bis(6-methylpyridin-2-yl))-1,5-diaza-3,7-diphoshacyclooctane (L) (Fig. 1) to the Mo_3S_4 cluster core. The reaction of $[Mo_3S_4(H_2O)(tu)_8]Cl_4$ (tu = thiourea) [3] with L resulted in a $[Mo_3S_4Cl_3(L)_3]Cl$ complex where three aminophosphine ligands (L) are coordinated to molybdenum through P atoms. Surprisingly its reaction with KPF_6 on a silica gel column gave a $[Mo_3S_4Cl_3(L)_2(L^*)](PF_6)_2$ complex in which one of the aminomethylphosphines act as tridentate P,P,N-ligand (L^*). To the best of our knowledge such coordination type of cyclic aminomethylphosphines has not previously been observed. The prepared compounds have been characterized by IR, UV-vis and NMR spectroscopy and mass-spectrometry. The ^{31}P NMR spectrum of $[Mo_3S_4Cl_3(L)_2(L^*)](PF_6)_2$ contains six different doublet signals which indicates the non-equivalence of all phosphorus atoms in the complex. Further experiments are underway.

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REACTIONS OF AQUACOBALAMIN AND COBALAMIN(I) WITH CYSTEINE-S-SULFATE

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Cobalamins (Cbls) are the most ubiquitous cobalt complexes in living organisms. Their Co(III), Co(II) and Co(I)-species participate in vivo in methyl group transfer reactions, isomerization and dehalogenation of organic substrates. Cbls are able to interact with biological thiols (cysteine, glutathione, homocysteine, etc.): aquacobalamin forms a stable complex with glutathione and is reduced by cysteine to Cbl(II), organocobalamins are dealkylated by thiols [1], and Cbl(II) can reduce dehydroascorbic acid to ascorbate in the presence of thiols via the transient formation of Co(II)-thiol complex [2,3]. Nevertheless, the reactions of cobalamins with oxidized forms of biological thiols have been poorly studied. In this work, the interaction of aquacobalamin and cobalamin(I) with cysteine-S-sulfate ($RS\text{-}SO_3^-$) was investigated.

It is found that Cbl(III) forms an amine complex with $RS\text{-}SO_3^-$. This interaction proceeds at a higher rate than the formation of Cbl(III)-amine complexes with glutamic and aspartic acids, as well as their amides. The reaction is reversible and depends on the acid-base properties of both reagents: deprotonation of the water molecule in aquacobalamin and protonation of the amino group lead to a significant decrease in the rate of the process.

$RS\text{-}SO_3^-$ readily reacts with Cbl(I). The type of product of this interaction depends on the ratio of reagents: when Cbl (I) is taken in 2-fold excess over $RS\text{-}SO_3^-$ in a neutral medium, Cbl(II) formation was observed, whereas Cbl(I) oxidation by higher $RS\text{-}SO_3^-$ concentrations leads to the formation of Cbl(II) complex with thiyl radical.

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REACTION OF GLUTATHIONYLCOBALAMIN WITH HYPOCHLORITE

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Cobalamins (Cbl) are the most ubiquitous biocomplexes of cobalt. They consist of a corrin ring equatorially ligated to cobalt ion, nucleotide loop attached to lower axial (α) site and numerous groups (H_2O, CN, OH, NO, etc.) bound to the upper (β) site [1]. Cobalamins play a crucial role in the metabolism of homocysteine and l-methylmalonyl-CoA in mammals [2]. Glutathionylcobalamin (GSCbl) plays the important role in the process of formation of the B_{12} coenzymes methylcobalamin (MeCbl) and adenosylcobalamin (AdoCbl) [3]. Chlorine oxyanions (ClO^-, ClO_2^-, ClO_3^- and ClO_4^-) have found diverse application in various fields of industry. Hypochlorous acid (HOCl) is a potent oxidant generated by the myeloperoxidase/hydrogen peroxide/chloride system [4]. Hypochlorous acid was reported to destroy cyanocobalamin [5]. This process is accompanied by oxidation of CN^- and liberation of cyanogen chloride (CNCl), a volatile toxic asphyxiant [6]. Recent studies [7,8] report that reduced form of cobalamin, Cbl(II), is extremely reactive toward chlorine oxyanions, including HOCl. The interaction of Cbl(II) with HOCl results in the formation of a mixture of H_2O/HO^-–Cbl(III) and corrin-modified products.

Here we report the results of kinetic and mechanistic studies of the reaction between GSCbl and hypochlorite using conventional and stopped-flow UV–Vis spectroscopies. Rapid interaction of GSCbl with HOCl does not result in the formation of chlorinated products observed in reactions of H_2OCbl or CNCbl with hypochlorite. The stoichiometry of the reaction has been determined (ClO^- : GSCbl = 2:1). It is proposed that the oxidation of GSCbl by HOCl includes formation of glutathione sulfonamide.

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COMPETITIVE AND HETERO-LIGAND COMPLEXATION OF COPPER(II) WITH DIETHYLENETRIAMINE IN SOLUTIONS OF COMPLEXONES

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Hetero-ligand complex compounds are the object of active research to establish the regularities of competitive filling up the coordination sphere with complexing reagents, to determine the compatibility of ligands and the influence of geometric, steric and electrostatic effects on the thermodynamic and kinetic characteristics of the compounds formed, which opens up wide prospects for their use for directional synthesis of functional materials with specified properties. In this work a study of the possibility of forming hetero-ligand compounds of copper(II) with diethylenetriamine (Deta) and complexing reagents of a number of polyaminopolycarboxylic acids: diethylenetriaminepentaacetic (Dtpa), ethylenetriaminetetraacetic (Edta) and nitrilotriacetic (Nta) acids in aqueous solutions using the spectrophotometric method was made. It was found that in the presence of polydentate Dtpa and Edta in the solution of copper(II), which ensure the maximum saturation of the coordination sphere of the central atom, discrimination of chelating ability of Deta takes place even with a 30-fold excess of the polyamine ligand and mononuclear Edta chelate, as well as mono- and binuclear Dtpa-complexonates of copper(II) are formed [1]. In the solutions of the system Cu(II)-Deta-Nta at $\Delta pH = 0–2.4$, the formation of protonated and deprotonated copper(II) chelates occurred, which was confirmed by the complete coincidence of the electronic absorption spectra of the studied and homo-ligand systems. An increase in the pH of the solution in the range of 4.0–6.0 led to the coordination of Deta with the formation of a hetero-ligand chelate with a mole ratio of components Cu(II):Deta:Nta = 1:1:1, for which a characteristic absorption band with $\lambda_{max} = 695$ nm was registered. For the hetero-ligand complex of copper(II) with Nta and Deta an increase in resistance to competing processes of hydrolytic character in strongly alkaline media was observed. The stability constants of protonated and deprotonated diethylenetriaminenitrilotriacetate complexes of copper(II) were calculated by modeling of complexation by the Rossotti method. The numerical value of $\lg\beta$ for the coordination particles of composition $[CuNtaDeta]^-$ was 22.75 [2]. The introduction of Deta into the coordination sphere of the Nta-complex of copper(II) led to an increase in the thermodynamic stability of hetero-ligand coordination particles in comparison with homo-ligand Nta-complexates due to the closure of an additional polyamine cycle with preservation of the octahedral geometry of the coordination polyhedron.

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AMINOCARBONIC AND AMINOPHOSPHONIC LIGANDS ATTACHED TO SILICA IN SEPARATION OF RARE EARTH ELEMENTS

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Technologies of rare earth elements (REE) separation are once again attracting attention in view of government’s plans to restore REE industry in our country. Liquid extraction with various phosphorus containing extragents dominated in this field for decades. But the main trend in hydrometallurgy is a turn to sorption and chromatographic separations as more effective, universal and eco-friendly. The restoration of REE industry gives a good chance to build it on the basis of innovative sorption technologies.

Among sorbents which can be used for this purpose chemically modified silica looks very promising. Such sorbents are widely used as stationary phases in HPLC and in biotechnology and pharma for isolation and purification of proteins, biologically active compounds, medicines, etc. There are precedents of the use of silica with attached organic ligands in hydrometallurgy, in particular, for separation of platinum metals.

In this work we studied two types of silica based sorbents with chemically attached aminocarbonic and aminophosphonic ligands:

$SiO_2)\text{-}(CH_2)_3OCH_2CH(OH)CH_2N(CH_2COOH)_2$ (**I**),

$SiO_2)\text{-}(CH_2)_3NHCH_2P(O)(OH)_2$ (**II**).

Among REE ions La, Eu, Gd, Ho, Dy, Yb and Lu were tested.

REE are sorbed on **I** and **II** in slightly acidic media at $pH > 2$, sorption increases with the increase of pH. For **II** sorption occurs also in high acidic solutions due to complexation with phosphoryl moiety. Sorption on **I** strongly depends on ionic strength of the solution decreasing with its increase. It may be explained by the variation of surface stability constants due to electrostatic interaction between ionized functional groups.

Selectivity of sorption of different REE on **I** perfectly corresponds to the ratio of their stability constants with N-substituted iminodiacetic acid. In contrast to divalent non-ferrous metals, ions of REE form different complexes with attached iminodiacetic acid. Their ratio depends on the distance between attached ligands and therefore on the sorption capacity of sorbent. We have shown that selectivity of sorption can be enhanced by lowering of sorption capacity.

Sorption of REE on sorbents **I** and **II** proceeds rather fast, within 30 min, but considerably slower than in the case of non-ferrous metals due to low rate of REE complex formation. The increase of temperature is one more instrument to increase the performance of REE separation.

Sorbent **I** was used for group separation of light, medium and heavy REE with HNO_3 solutions as an eluent. For complete separation of neighboring REE multistage scheme is needed. Reduction of particle size and, hence, the use of rather high pressure increase the performance of the separation.

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COMPLEX FORMATION OF PALLADIUM(II) WITH ANCHORED THIA-LIGANDS: MACROCYCLES VS. PODANDS

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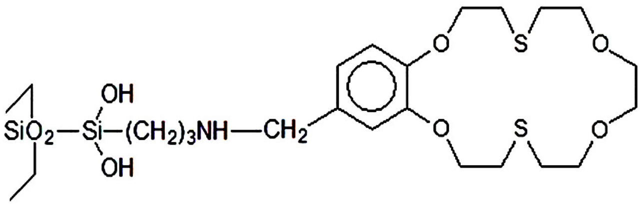
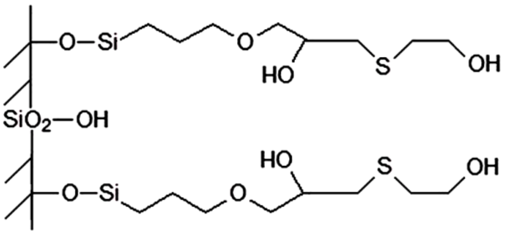
Molecular recognition technology (MRT) is declared as a most prominent approach to selective extraction of rare metals, in particular platinum metals, from aqueous solutions. For technological use the macrocycles responsible for selective binding of metal ions are chemically attached to solid support, i.e. silica [1]. The main barrier for MRT is a high cost of macrocycles with heteroatoms and functional groups in side chains which are necessary for attachment to the support. The alternative is a use of similar linear molecules with the same coordination atoms – podands.

So, we have synthesized a set of dithia crown ethers and attached them to silica surface. Typical structure of such sorbents is defined as **I**. For comparison we have synthesized the sorbent **II** with anchored di(hydroxyalkyl)sulphide. The quantity of anchored ligands for **I** and **II** equals 0.2 and 0.5 mmol/g respectively. The surface density of anchored ligands and the length of spacer in **II** are high enough for coordination of two ligands with one metal ion with the formation of the structure resembling the coordination with dithia crown ether.



I



II

The study of sorption of $[PdCl_4]^{2-}$ from HCl solutions by sorbents **I** and **II** revealed the identity of their properties. Sorption proceeds very quickly, during 10-30 min, in wide range of HCl concentration – 0.1-5 M. The binding is caused by the formation of complexes of Pd(II) with anchored ligands, their composition being M:L = 1:1 and 1:2 for sorbents **I** and **II** respectively. At high Pd(II) concentration in solution (> 1 g/l) sorption stimulates the formation of polynuclear Pd(II) complexes on the surface which is proved by UV-VIS spectroscopy.

The results obtained show that in view of $[PdCl_4]^{2-}$ binding sorbents which anchored macrocycles have no advantage over sorbents with analogous podands. Moreover, sorbent **II** possesses even higher selectivity for Pd(II) binding in the presence of Pt(IV), Rh(III) and Cu(II) as compared to sorbent **I**. This enabled us to achieve selective extraction of Pd(II) from complex technological solutions containing above mentioned metal ions.

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NOVEL HETERONUCLEAR PLATINUM(II) COMPLEXES

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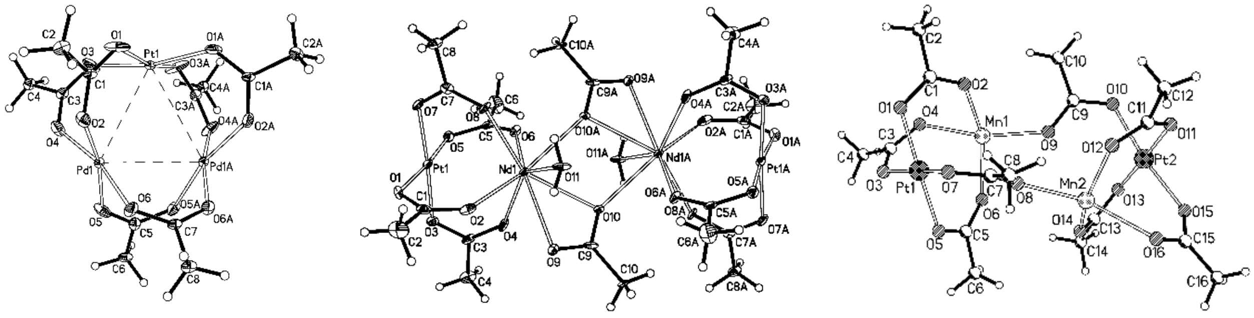
Current studies in platinum chemistry focus attention on medicine and catalysis, placing particular emphasis on Pt-based heterometallic compounds. Herein we report on the synthesis and structure characterisation of new Pt^{II}-based heterometallic acetate complexes containing Pd^{II}, Nd^{III} and Mn^{II} as the complementary metals. Platinum carboxylate chemistry is restricted by low availability and reactivity of the crystalline platinum(II) acetate $Pt_4(\mu\text{-}OOCMe)_8$ as starting material. For this reason we used a readily available non-crystalline platinum acetate blue of the total composition $Pt(OOCMe)_{2.50}$ (PAB) [1] for the preparation of new heteronuclear platinum(II)-based carboxylate complexes. The molecular structure of the obtained complexes $Pd_2Pt(\mu\text{-}OOCMe)_6 \times 2C_6H_6$ (**I**), $Pt_2Nd_2(OOCMe)_{10} \times 2MeCOOH \times 2H_2O$ (**II**) and $Pt_2Mn_2(OOCMe)_8 \times 2C_6H_6$ (**III**) was determined by single-crystal X-ray crystallography with the use of synchrotron radiation.



(I) **(II)** **(III)**

Crystal structures of complexes **I–III** with thermal ellipsoids at 50% probability level

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CORE-SHELL NANOPARTICLES FROM NOVEL BIMETALLIC PLATINUM-PALLADIUM COMPLEX

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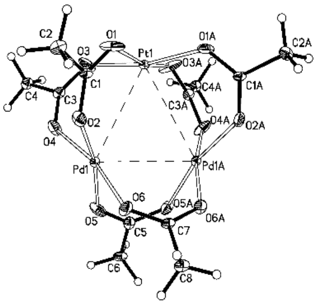
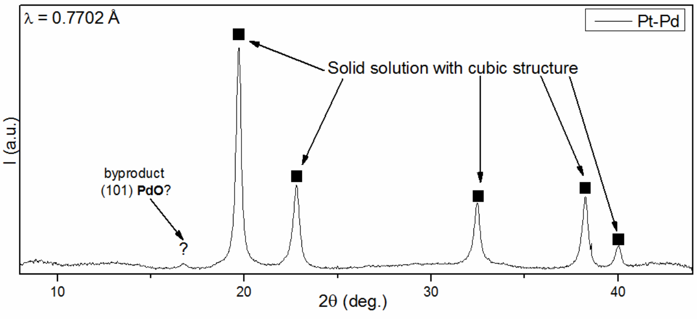
The first acetate-bridged platinum(II)-palladium(II) complex $Pd_2Pt(\mu\text{-}OOCMe)_6{\times}2C_6H_6$ (**I**) recently synthesized in our group was thermally decomposed to give a nanoalloy of composition Pd_2Pt. XRD pattern for this material revealed somewhat different from the known data for Pd-Pt solid solutions.

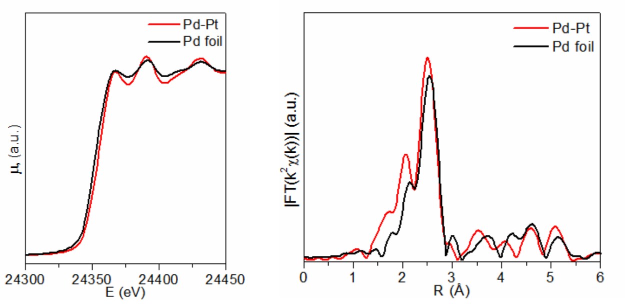


Crystal structure of complex **I**

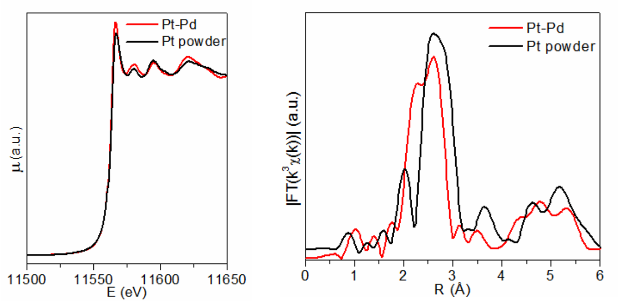


XRD pattern of complex **I** thermolysis products

In this work we studied the Pd_2Pt nanoalloy by XAFS (Pt L_3-edge and Pd K-edge).



XAFS: Pd K-edge



XAFS: Pt L_3-edge

Simultaneous modeling of the Pd and Pt XAFS data showed that the $PtPd_2$ alloyed matter consists of two crystalline phases: a solid Pd_xPt_{1-x} solution as main component and a small admixture (~7%) of PdO. The Pd_xPt_{1-x} phase comprises relatively large nanoparticles (CSR 28 nm) with Pt-enriched interior and Pd presumably as smaller PdO species (CSR ~5 nm) prevailing at their exterior. The lattice parameter (3.9032 Å) and shortest Pd-Pd and Pd-Pt distances (2.74 Å) are close to those for the bulk Pd, suggesting that the solid solution is formed on the basis of palladium matrix by Pt to Pd substitution.

Acknowledgements

The study was supported by the Russian Foundation for Basic Research, project 15-03-07652. This research was performed using the equipment of the JRC PMR IGIC RAS.

THERMAL PROPERTIES, PHASE TRANSITION, AND IONIC MOBILITY IN ANTIMONY(III) PHOSPHATE-FLUORIDE COMPLEX $CsSbF_3(H_2PO_4)$

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Synthesis of heteroatomic compounds enables to prepare substances with diverse chemical and physical properties which change depending on both the composition of the ionic sublattice and that of the coordination sphere of the central atom. It is well demonstrated, in particular, on the example of the fluorine-containing antimony(III) coordination compounds.

Antimony(III) phosphate-fluoride complexes with various F:Sb ratioes in the solid phase are studied unsufficiently. These are: $Rb_2Sb_2F_6(HPO_4)$, $CsSbF_3(H_2PO_4)$, $KSbF_2(HPO_4)$, $MSbFPO_4{\cdot}H_2O$ (M = Na, Rb, NH_4, CN_3H_6), $NaSbFPO_4{\cdot}1.5H_2O$, and $KSbFPO_4$. It is know that the complex phosphate with mono- and trivalent cations are very perspective as polyfunctional materials. Alkali phosphates relates to the superproton conductors group [1], therefore search of compounds with high ionic mobility and conductivity among the above-mentioned antimony(III) fluorine-containing complexes is of an undoubted interest.

The aim of this work consisted in investigation of the thermal properties and ionic mobility in antimony(III) phosphate-fluoride complex $CsSbF_3(H_2PO_4)$ (**I**).

Ionic mobility, thermal properties, and conductivity in $CsSbF_3(H_2PO_4)$ were studied by the ^1H, ^{19}F, ^{31}P NMR (including MAS NMR), thermal analysis, X-ray diffraction, and impedance methods. It was shown that the cardinal changes in the ^1H, ^{19}F, and ^{31}P NMR spectra above 300 K were related to the phase transition in the temperature range 400-420 K (maximum endoeffect at 419 K) when a crystal unordered phase with high ionic mobility in the proton and fluoride sublattices formed. In the same temperature range the transition of $PO_2(OH)_2^-$ – anions from the «rigid lattice» (in the NMR terms) to isotropic reorientations proceeds. The NMR and X-ray diffraction data showed that above 425 K the change of the aggregate state of the compound took place and an amorphouse phase with high ionic mobility, if in a less degree than in the unordered crystal phase, formed in all three sublattices. The types of ionic mobility in the both phases were determined. According to the NMR data diffusion in the proton sublattice in the crystal and amorphous phases which proceeds at cooling of the samples [(420) 450 → 300 K] remained at the room temperature. Such diffusion in the proton and fluoride sublattices of $CsSbF_3(H_2PO_4)$ above 400 K can testify to high ionic mobility in the both crystal and amorphous phases of the compound **I**.

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SYNTHESIS AND CHARACTERIZATION OF ZINC/COBALT ZEOLITIC IMIDAZOLATE FRAMEWORKS

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Zeolitic imidazolate framework (ZIF) materials is rapidly developing subclass of crystalline porous coordination polymers or metal-organic frameworks (MOFs) [1]. The sodalite-type structure constructed by divalent metal atoms (Zn, Co) tetrahedrally connected by the five-membered imidazole rings offers an attractive combination of stability and variability, the features inherited from parental classes of zeolites and MOFs, respectively [2]. ZIF materials possess high surface area of 1617 m^2/g BET [3], thermal resistivity up to 400 °C and excellent solvothermal stability [4]. The combination of high porosity pore with tunable chemistry leads to potential applications in gas sorption, gas separation and catalysis [5].

ZIF materials can be obtained by a variety of fabrication methods including hydro- and solvothermal [6], microwave-assisted [7], sonochemical [8] and electrochemical syntheses. In the present work, we adopted the MW-assisted synthesis in DMF to obtain the set of ZIF materials with different ratios between Zn and Co. Construction of mixed-metal MOFs allows for tuning or improving the properties of such composites due to a synergistic effect [9]. To study the samples, we performed the X-ray powder diffraction to confirm the crystal phase, FTIR to verify the chemical purity of the material, X-ray fluorescence to evaluate the Zn/Co composition, nitrogen sorption isotherms at low temperature to calculate surface area and pore size, thermogravimetry to trace the limit of stability, UV-Vis spectroscopy to follow some metal transitions, and X-ray near-edge adsorption spectroscopy to analyze local structure of the metal centers.

In conclusion, we successfully synthesized the set of Zn/Co-ZIF materials with different ratio of Zn/Co. The complex laboratory diagnostics with different techniques confirmed the high quality and competitive properties of the obtained materials. Zn and Co were found to occupy equivalent sites in the ZIF structure evidencing their homogeneous distribution. These Zn/Co-ZIF materials are useful for selective sorption and catalytic applications.

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COORDINATION COMPOUNDS OF SOME TRANSITIONAL METALS AS BIOLOGICAL ACTIVE SUBSTANCES

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The synthesis of coordination compounds presenting models of natural biological objects and the testing of their action on metabolic processes of microorganisms constitute a promising direction of natural biosynthesis reproduction and control. Since the cobalt dioximates represent models of molecules with vital functions, there was performed the testing of biostimulator properties on some fungal strains. The introduction of cobalt dioximates into the nutrient media of some fungal strains leads to the stimulation of biosynthetic processes (biomass accumulation, enhancement of enzyme activity, reduction of growing period) and stabilizes the enzymeogenesis processes under stress conditions.

There were carried out studies regarding the influence of coordination compounds on physiological processes at a number of fungi: *Aspergillus niger* 33, *Aspergillus niger* 412, *Aspergillus* sp., *Penicillium viride*, *Fusarium gibbosum* CNMN FD 12, *Rhizopus arrhizus*, *Trichoderma koningii* Oudemans CNMN FD 15, etc. For the investigations there were selected mono- and binuclear coordination compounds of different metals (Fe, Co, Cu, Zn) with different degrees of oxidation, containing known dioximes (DH_2 - dimethylglyoxime, $NioxH_2$ - 1,2-cyclohexanedionedioxime) as well as new ones ($DSamH_2$ - disulfanilamideglyoxime). The ratio of metal: dioxime in complexes can be of 1:1, 1:2 or 1:3.

These and other peculiarities give a high degree of diversity of composition, structure and properties among the complexes studied. For example, at the introduction into the medium of the micromycete *Rhizopus arrhizus* Fischer CNMN FD 03L of the compounds $[Co(NioxH)_2(An)_2]_2[ZrF_6]\cdot3H_2O$ and $[Co(DH)_2(An)_2]_2[TiF_6]\cdot2H_2O$, there was recorded lipolytic activity superior to the control in the variants with 1 mg/L concentration for both complexes (by 22.2% and 33.3% superior to the control). The highest pectolytic activity was recorded in the variants with coordination compounds $[Co(DH)_2(An)_2]_2[ZrF_6]\cdot2H_2O$, $[Co(DH)_2(Nia)_2][BF_4]\cdot2H_2O$, at the application of the concentration of 5 mg/L (with 66.6% and 55.5% superior to the control).

Along with the increase of greenhouse effect, air temperature and drought frequency, the problem of increasing the drought resistance of the most important agricultural crops has increased in recent years. An important and yet untapped possibility of increasing the productivity of agricultural crops is the use of physiologically active substances with the effect of regulating the growth, development, modification of various metabolic processes, a fact which leads to the enhancement of the adaptive properties of the vegetal organism to suboptimal environmental conditions. The treatment of seeds for sowing and of the foliage apparatus during the vegetation with aqueous solutions containing cobalt coordination compounds enables the optimization of the functional state, growth and development of maize plants, sugar beet, red beet under favorable humidity conditions as well as in a moderate water deficit. The used coordination compounds have the property of activating the vital processes already at the initial stages of individual plant development, stimulate the growth of the root system and shoot, ensure the homeostasis of water status under suboptimal hydride regime, increase the plant productivity, strengthen the protective functions of the organism, increasing the tolerance to the suboptimal factors. Under the conditions of reduced humidity some coordination compounds have an influence of diminishing the effect of drought on the formation of the assimilation apparatus, the accumulation of biomass, and the plant harvest.

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POLYHEDRAL Ni(II)-CONTAINING METALLASILOXANES: SYNTHESIS, STRUCTURE, LIGANDS EXCHANGE, AND POLYMETALLASILOXANE FRAMEWORK REARRANGEMENT

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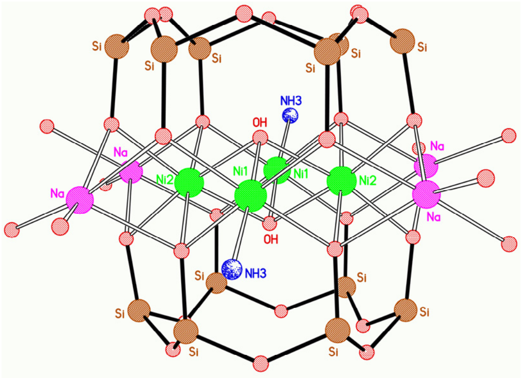
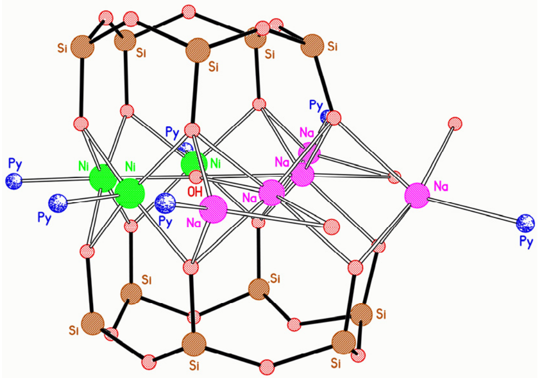
Organometallasiloxanes are compounds whose molecules contain the Si-O-M- groups, where M is the metal ion. This is a very extensive class of compounds, occupying an intermediate place between organosiloxanes and silicates. Polyhedral organometallasiloxanes, the molecules of which contain one or two stereoregular organosiloxanolate cyclic fragments bound to a matrix containing 4 to 10 metal ions, fundamentally different from all other types of organometallasiloxanes are of particular interest [1]. An intriguing feature of bimetallic polyhedral organometallasiloxanes containing transition and alkali metal ions is their ability to rearrange the metallasiloxane framework in aprotic polar solvents, for instance in the presence of 2,2-bipyridyl [2]. In continuation of our studies in this direction, we have obtained phenylnickelsodiumsiloxane (**I**) by hydrolytic condensation of phenyltriethoxysilane in the presence of sodium and nickel ions. The compound **I** has a sandwich-like molecular structure in which the metal ions containing layer ("Ni_4Na_4" assembly) is positioned between two six-membered cyclosiloxanolate macrocycles $[(PhSi(O)O)^-]_6$. In the subsequent treatment of the toluene-ethanol solution of compound **I** with ammonia, the basic polyhedral structure of the molecule is retained, but there is an exchange of the butanol ligands coordinated with nickel ions to form compound **II**. Recrystallization of compound **I** in pyridine led to a complete rearrangement of the polyhedral framework and a new compound **III** was obtained. In the sandwich structure of the compound **III**, the metal ions containing layer ("Ni_3Na_5" assembly) is positioned between six- and five-membered cyclosiloxanolate macrocycles.



Compound **II**



Compound **III**

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VOLATILE COMPLEXES OF IRIDIUM (I) WITH Β-DIKETONES AND CARBONYLS: SYNTHESIS,STRUCTURE AND THERMAL PROPERTIES

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Nowadays, the volatile iridium complexes are widely demanded in the processes of the formation of functional coatings by metal-organic chemical vapor deposition (MOCVD) method. For implementation of MOCVD, such compounds should possess specified thermochemical characteristics: high vapor pressure at low temperatures, thermal stability at vaporization temperatures and others. Using of β-diketonates ligands provides the possibility of wide varying the thermal properties of the complexes by changing of the terminal substituents. Concerning iridium, mixed-ligand Ir(I) complexes is characterized by simpler synthesis than that for Ir(III) compounds. In addition, complexes with carbonyl ligands are of special interest from the point of view of decreasing of the deposition temperature and the reducing of the carbon content in the precursor providing the purity of the coatings obtained. So, the present work describes the synthesis, structure and investigation the influence of terminal substituents on thermal properties of complexes Ir(I) with general formula $[Ir(CO)_2(L)]$ (L = β-diketonate, $R_1C(O)CHC(O)R_2$: $R_1 = CF_3$, $R_2 = CF_3$ (hfac) **1**, Me (tfac) **2**; ^{t}Bu (ptac) **3**, Ph (btfac) **4**, $R_1 = R_2 = {}^t$Bu (thd) **5**, Me (acac) **6**).

All compounds were synthesized in a Schlenk apparatus by CO bubbling through a hexane solution of corresponding cyclooctadiene-1,5 complexes [Ir(cod)(L)]. Complexes **3** and **4** were obtained for the first time. Yields after purification were in the interval 75–95%. Compounds were characterized by elemental analysis, IR and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and powder X-Ray diffraction (XRD). Crystal structures of complexes **1-5** were determined by single-crystal XRD. The compounds under study are monomer molecular complexes; the iridium atom is in the square-planar coordination. The crystal packing is formed by stacks with the shortest Ir...Ir distance between neighboring molecules.

Thermal properties of complexes in condensed phase have been studied by Thermogravimetry (TG/DTA) and Differential Scanning Calorimetry (DSC). According to DSC, the compounds are thermally stable and exhibit only one phase transition (melting) over the studied temperature range (25–*m.p.*)ºC. Also, the thermodynamic parameters of melting were defined. Under TG experimental condition, mass loss for all compounds occurs in single step with residual mass around 1.0%. The following volatility row has been established on the base of 50% mass loss: L = hfac **1** (115ºC) > tfac **2** (135ºC) > ptac **4** (158ºC) > acac **6** (171ºC) ≈ thd **5** (175ºC) > btfac **4** (208ºC). The feature of the series studied is the close volatility for complexes with both Me- and ^{t}Bu-substituents in β-diketonate (**5** vs **6**). For these complexes, temperature dependences of saturated vapor pressure were measured by flow (transmission) method and Knudsen’s effusion one for **5** and **6**, respectively; the thermodynamic parameters of sublimation were defined and the following volatility order have been obtained (80ºC): **5** (0.076 Torr) > **6** (0.053 Torr). The obtained data are demanded to optimize the deposition conditions of MOCVD experiments.

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FORMATION OF THE ADSORPTIVE LAYERS ON THE STEEL SURFACES OF LEAD(II) NITRILO-*TRIS*-METHYLENEPHOSPHONATE COMPLEXES WITH DIFFERENT COORDINATION, THEIR THERMOCHEMICAL BEHAVIOR AND EFFECT ON CORROSION-ELECTROCHEMICAL BEHAVIOR OF STEEL

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The nitrilo-tris-methylenephosphonate complexes of lead(II) with different coordination is synthesized, isolated and X-ray single crystal characterized. In complex $[Pb\{\mu^5\text{-}NH(CH_2PO_3H)_3\}]$ (I) the Pb atom is coordinated by seven atom of oxygen. In complex $Na_4[Pb_2(H_2O)_2\{\mu^3\text{-}N(CH_2PO_3)_3H_2\}_2]\cdot 10H_2O$ (II) atom of lead is coordinated by the six O atom and N atom of ligand. The adsorption layers of complexes (I) and (II) on the steel surface was obtained, by immersion the samples of carbon steel (0.2% C) in the 1% water solution of (I) and (II). Steel samples with adsorbed layers (I) and (II) on the their surface was investigated by XPS *in situ* at thermal action at range from room temperature to 450 °C in work chamber of the X-ray electron spectrometer EMS-3 with double focusing by magnetic field [1]. The same samples subjected to thermal actions at temperature 100, 200 and 300 °C was investigated by potentiodynamic method, was registered the anodic polarization scans at range from –1000 to 1200 mV vs. Ag/AgCl/KCl(sat.) electrode.

It is showed, the complexes (I) and (II), different by coordination of the Pb atom, form on the steel surface the adsorbed layers with different construction and properties. In adsorbed layer of complex (I) lead is present in oxidation state +2, what correspond to binding energy of doublet $Pb4f_{7/2\text{–}5/2}$ E_B = 137.8 и 142.6 eV. At adsorption of complex (II) on steel surface there is a redox process, leading to forming two oxidation state of Pb, correspond to spectral components of doublet $Pb4f_{7/2\text{–}5/2}$ with E_B = 137.8 и 142.6 eV (for Pb^{+2}) and E_B = 136.0 и 140.8 eV (for Pb^0). Under thermal action the adsorbed layer of complex (I) little changed the structure, and at 200°C was destroyed with formation of the $PbPO_x$ layer on the steel surface. The adsorbed layer of complex (II) is by kept on the steel surface until 450°C, at the same time forming the $(Pb,Fe)PO_x$ layer. Formed protective layer contain Pb in oxidation state 0.

Anodic polarization scans of steel samples with adsorbed layers of complex (I) subjected to thermal actions at temperature 100, 200 and 300 °C, not showed of great changed in corrosion-electrochemical behavior of the steel surface. Was observed only small increase (+40 mV) of currentless compromise corrosion potential. Adsorbed layers of complex (II) in temperature range from room temperature to 200 °C also little changed the corrosion-electrochemical behavior of the steel surface. However at 300 °C layers of complex (II) over 100 mV raised the currentless compromise corrosion potential and over 10 times lowered corrosion current in anodic area. It shows that the steel corrosion inhibition the adsorbed layers is based on the secondary inhibition mechanism, and opens a way to creation of new methods of nanothickness protective layers formation on the steel surface.

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STUDY OF FORMATION FEATURES OF THE BINUCLEAR PHENANTHROLINE COMPLEX WITH CORE (V)V-O-V(IV): SYNTESIS, X-RAY ANALYSIS AND QUANTUM CHEMICAL DFT MODELING

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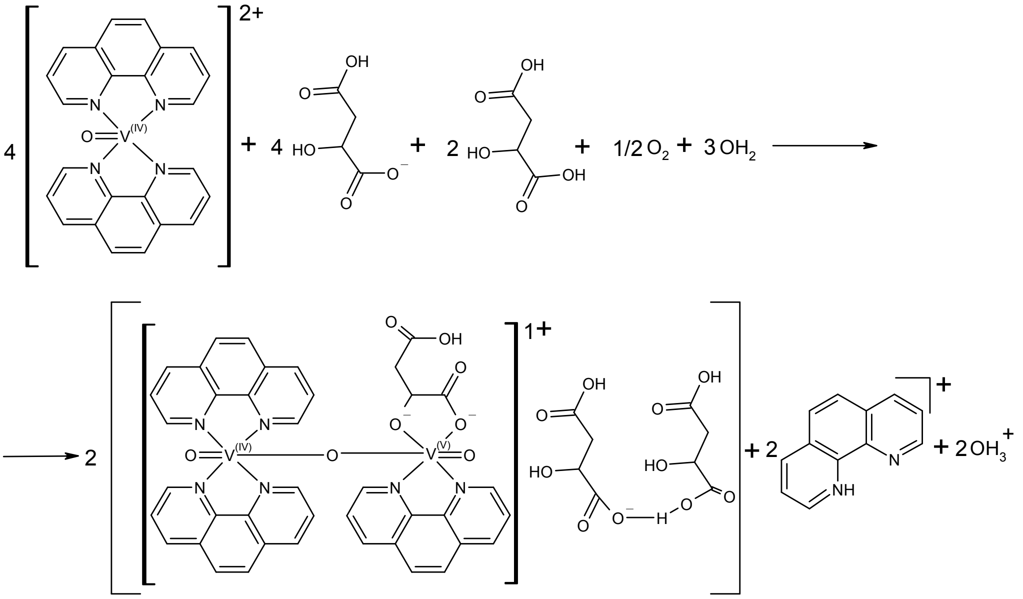
Synthesis of coordination compounds is inevitably bound to an assessment of influence of possible factors on reaction products formation. Their analysis is necessary for formation of a basis of the so-called "directional synthesis" of compounds including catalytically and biologically active ones.

The method of synthesis and results of a X-ray diffraction analysis of new mixed-valence binuclear coordination compound of vanadium $[(O)(phen)_2V^{IV}(\mu\text{-}O)V^V(O)phen)(mal^{2-})]$ $(malH^-\cdot malH_2)\cdot 5H_2O$ as a product of interaction of mononuclear cation $[(O)V^{IV}(phen)_2]^{2+}$ with malic acid are presented:



Quantum chemical modelling by DFT M06/6-31G (d,p) method allowed to receive the geometrical arrangements of polyhedrons with parameters which are in a good agreement with X-ray data. For an assessment of various possible paths of formation of binuclear compound in the framework of DFT method changes of thermodynamic characteristics ΔG^0 accounting influence of solvent in reaction of formation of paramagnetic coordination cation $[(O)(phen)_2V^{IV}(\mu\text{-}O)V^V(O)(phen)(mal^{2-})]^+$ were calculated.

Comparison the quantum chemical and the experimental results allowed making the following conclusions:
1. Binding between vanadium fragments has the oxo-bridge nature;
2. Process of oxidation of $V^{IV} \rightarrow V^V$ in the reaction of binuclear compound formation is preferably initial and facilitating further replacement of ligands;
3. Subsequent combination of particles happens by the donor-acceptor mechanism – an acceptor is cation $[(O)V^{IV}(phen)_2]^{2+}$, the donor is an anion $[(O)V^V(O)(phen)(mal)]^-$.

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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF COMPLEXES OFCOBALT, COPPER AND ZINC WITH 5-(2-HYDROXYNAPHTHALENYL)-6-PHENYL-3-(2-PYRIDYL)-1,2,4-TRIAZINE

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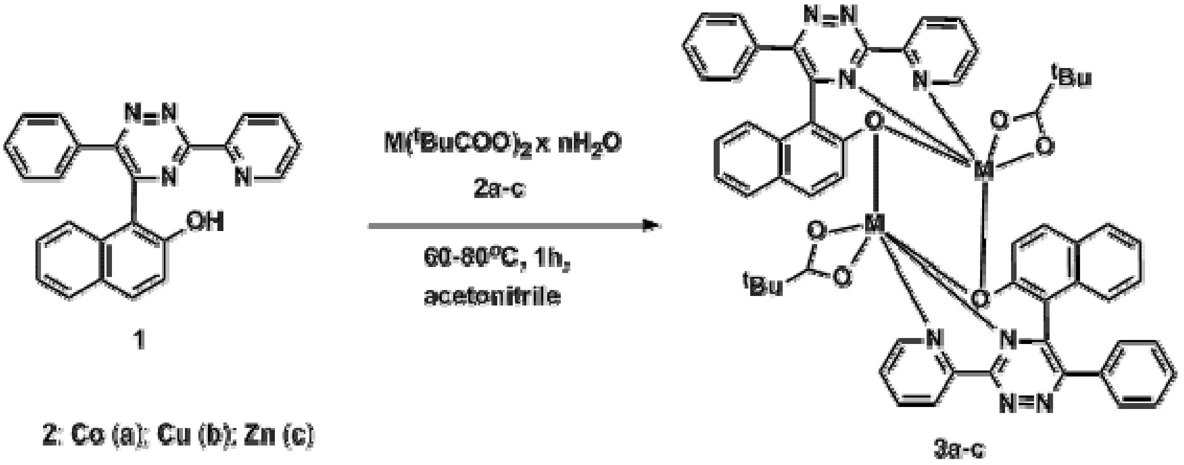
3,5,6-Trisubstituted-1,2,4-triazines ligands are important structural moieties in the synthesis the transition metals complexes reveal bioactive and anti-cancer properties [1]. On the other hand, they can be used for obtaining materials with subsequent application in optical technologies [2]. We succeeded to get 5-(2-hydroxynaphthalenyl)-6-phenyl-3-(2-pyridyl)-1,2,4-triazine (**1**) by direct metal-free cross-coupling of 2-naphthol with 6-phenyl-3-(2-pyridyl)-1,2,4-triazine. In this work, the reactions of pivalates of cobalt (**2a**), copper (**2b**) and zinc (**2c**) with **1** are reported (Scheme 1).



Scheme 1. Synthesis of complexes **3a**-**c**

Binuclear complexes $M_2(\mathbf{1})_2(^t\text{BuCOO})_2$ (**3a**-**c**) were formed. The structure of obtained compounds are confirmed by X-ray analysis, FTIR analysis, elemental analysis and ^{1}H NMR for **3c**.

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SYNTHESIS AND THERMOLYSIS OF SOME SALTS OF POLY-5-VINYLTETRAZOLE

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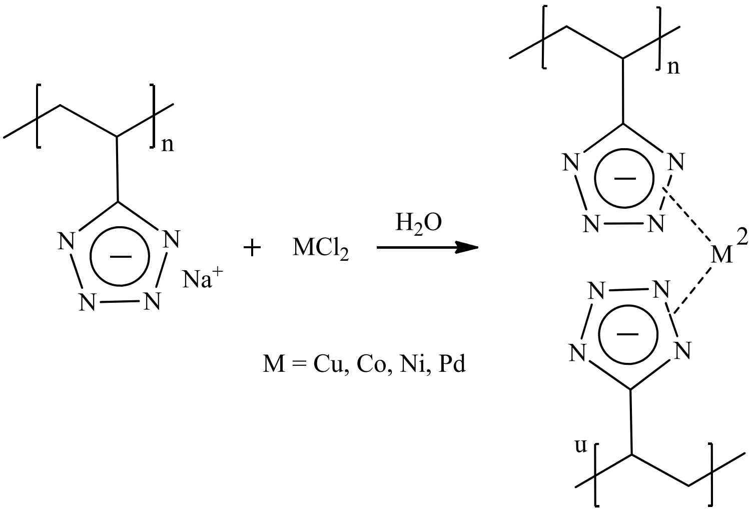
The methods for preparation of tetrazole-containing polymers and their thermochemical properties are relatively well-researched, that is primarily due to the prospects of their use as components of different kind combustible and thermally decomposed energetic systems [1, 2]. However, despite of the high ability of tetrazole ring to form metal salts and complex compounds, the methods for the preparation of metal-containing polyvinyltetrazoles and investigation of their thermal decomposition have scarcely been studied [3].
The reaction between sodium salt of poly-5-vinyltetrazole (PVT) and Cu, Co, Ni, Pd chlorides in aqueous solutions was found to be a convenient way to obtain poly-5-vinyl-tetrazolates of these metals. This approach allows to prepare at a definite conditions the target products with close to the theoretical metal content.
Self-propagating thermolysis of synthesized Cu and Ni poly-5-vinyltetrazolates in air leads to formation of the metal nanoparticles incorporated into the porous matrix. Thermolysis of Pd-PVT under the same conditions leads to the formation of nanoscale $PdH_{0,3}$ that is also incorporated into the porous matrix. The nanoparticles formed do not exceed 20 nm in all cases. Co_3O_4 nanoparticles are formed as the result of thermolysis of Co-PVT.



The products of thermal decomposition of investigated poly-5-vinyl-tetrazole salts are promising for study as heterogeneous catalysts for various chemical processes including cross-coupling reactions, click- and hydrogenation reactions. In particular, the obtained Cu-containing nanocomposite demonstrated high activity in the cross-coupling synthesis of 1,4-diphenylbutadiyne-1,3 at room temperature.

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HETEROMOLECULAR INSERTION OF CO_2 WITH PhNCO, PhNCS OR (HEX)N=C=N(HEX) INTO Ti-O(R) BONDS OF $Ti(OPr^i)_4$

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Early we have found that several molecules, e.q. acetonitrile – sulphur dioxide [1] or isocyanates [2,3], not only stimulated each other to be inserted into bond Ta-Cl,but also leads in formation of chain of inserted molecules of different types – heteromolecular insertion [4].

We uncovered that tetraisopropoxide Ti(IV) can efficiently catalyze an attachment of phenylisocyanate in combination with carbon dioxide (2:1) into four Ti-O(Pr^i) bonds to form products of heteromolecular insertion, which is the first example of these reactions for the compounds of transition metals of group IV of the periodic system.

In contrast, phenylisothiocyanate does not form stable addition products, and enables only a reversible insertion under the action of acetonitrile, stimulating a heterocyclization of embedded fragments. We discovered the ability of combinations of dicyclohexylcarbodiimide in combination with carbon dioxide to joint implementation (at a ratio 2:1) when Ti - O(Pr^i) . Confirmation of our assumptions about the nature of the incorporation of ligands into the reaction product(s) came from the results of the IR-, NMR- and mass-spectroscopy studies of the products of the hydrolyze isolated compounds.

The reaction of the derived tetraisopropoxide with N,N1-phenylenediamine, however, proceeds quite differently. In this case, phenylisothiocyanate in combination with carbon dioxide for two relations going on easily and evenly, giving a stable product insertion, while accession combinations or carbodiimide does not occur evenly and does not lead to the formation of stable products introduction.

Furthermore, we were able to maintain the produced compound in a crystalline state and perform an x-ray analysis of organic side-reaction products, providng us with essential insights into the first stages of the reaction of an insertion of phenylisocyanate organic compound: the earlier structurally characterized triphenylcianyrate.

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SUPRAMOLECULAR COMPLEXES OF ZINC(II) BIS(DIPYRROMETHENATE)S WITH AROMATIC LIGANDS

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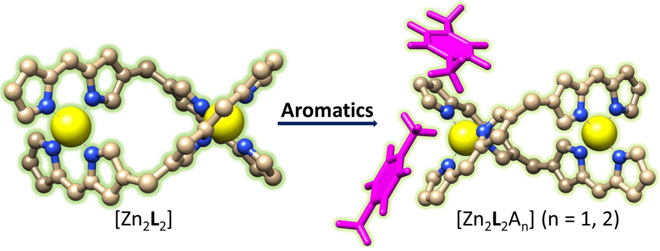

In recent years, aromatic hydrocarbon discharges received large coverages because of bulking oil, gas production, and making from arenes of many organic compounds. Therefore, the search of fluorescent methods for aromatic toxicants rapid detection in various media is currently under way. From this point of view, the alkylsubstituted binuclear zinc(II) helicates ($[\mathrm{Zn_2}\mathbf{L}_2]$) are able to become one of the promising platforms for the development of fluorescent sensors. There is a considerable interest to $[\mathrm{Zn_2}\mathbf{L}_2]$ helicates due to the high fluorescence quantum yield (to 100%) and fluorescence sensitivity to the medium properties. For example, fluorescence quantum yield (φ_o) of $[\mathrm{Zn_2}\mathbf{L}_2]$ helicates amounts to 100% in nonpolar saturated hydrocarbons. The complexes fluorescence is significantly quenched (to 60 %) in aromatic hydrocarbons solutions. In this case, fluorescence quenching of $[\mathrm{Zn_2}\mathbf{L}_2]$ can be due to the formation of $[\mathrm{Zn_2}\mathbf{L}_2\mathrm{A}_n]$ supramolecular systems (A – aromatic molecular ligand) by π – stacking of chromophore aromatic systems with solvent molecules. In this abstract, we report the results of experimental and theoretical studies of $[\mathrm{Zn_2L_2A}_n]$ supramolecular structures with toxic aromatic hydrocarbons (A = benzene, toluene, *o*-, *m*-, *p*-xylenes). The methylsubstituted (tetra-, octa-, and deca-) zinc(II) bis(dipyrromethenate)s were used as luminophores. The solid samples of $[\mathrm{Zn_2}\mathbf{L}_2\mathrm{A}_n]$ were obtained by the slow crystallization from the saturated solutions of $[\mathrm{Zn_2}\mathbf{L}_2]$ helicates in A at temperature about 300 K. Composition, stability, and spectral-luminescent properties of the $[\mathrm{Zn_2}\mathbf{L}_2\mathrm{A}_n]$ crystal solvates were studied by means of FT-IR, PXRD, thermal, mass spectral, quantum chemical, absorption, and fluorescence analyses. Spectroscopic studies showed that in cyclohexane the φ of $[\mathrm{Zn_2}\mathbf{L}_2\mathrm{A}_n]$ is lower (to ~ 1.2–3.9 times) than φ_o for the $[\mathrm{Zn_2}\mathbf{L}_2]$ helicates. It was shown that fluorescence quenching efficiency of helicates increases with decreasing molecular ligands aromaticity. The thermal dissociation processes of $[\mathrm{Zn_2}\mathbf{L}_2\mathrm{A}_n]$ have been investigated in an argon atmosphere. Crystal solvates are stable up to a temperature ~ 369–477 K. The $[\mathrm{Zn_2}\mathbf{L}_2\mathrm{A}_n]$ solvates stability increases with decreasing alkyl substituents number in pyrrole rings of complex domains. It is demonstrated that high π-π-intermolecular interactions energies in $[\mathrm{Zn_2}\mathbf{L}_2\mathrm{A}_n]$ are the main cause of the fluorescence quenching of $[\mathrm{Zn_2}\mathbf{L}_2]$ luminophores in the aromatic hydrocarbons presence. The results obtained provide theoretical and experimental basis for the development of a new direction of the trace aromatic hydrocarbons fluorescent detection by means of $[\mathrm{Zn_2}\mathbf{L}_2]$ as highly selective fluorescent sensors.

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SYNTHESIS AND X-RAY STRUCTURE OF THE BORON-CAPPED COBALT(II) TRIS-PYRAZOLOXYMATES WITH (DECACHLORO)-*CLOSO*-BORATE AND BROMIDE COUNTERIONS

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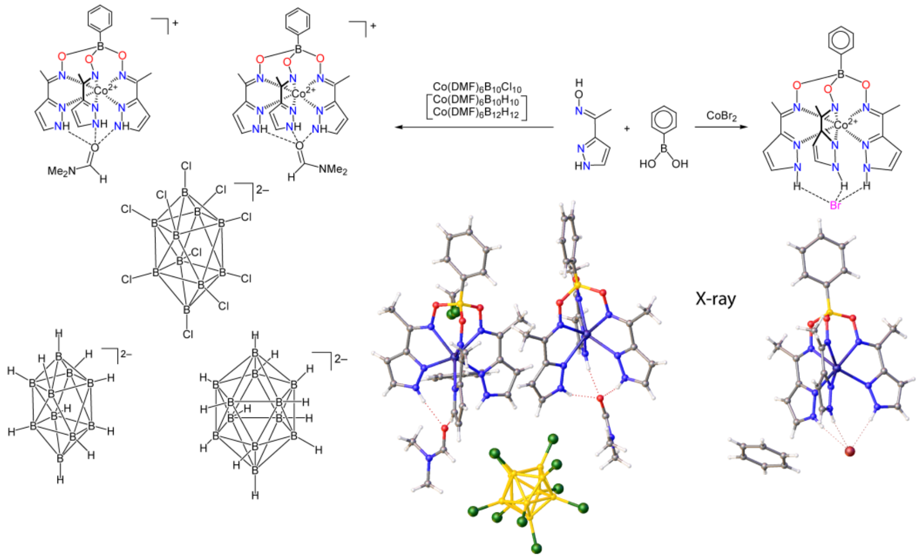
Earlier, chloride ion-aided template self-assembly of a mixed pyrazoloxime ligand with phenyl- or hexadecylboronic acids on a corresponding metal(II) ion as a matrix afforded the boron-capped zinc, cobalt, iron, and manganese pseudoclathrochelate tris-pyrazoloximates [1,2]. The presence of a pseudocross-linking hydrogen-bonded chloride ion is reported to be critical for their formation. The cobalt(II) tris-pyrazoloximate with a pseudocapping bromide ion was obtained by the analogous direct procedure using $CoBr_2$ as an initial cobalt(II) salt. As follows from the single crystal X-ray diffraction data, this pseudomacrobicyclic complex is capped by bromide ion forming three N−H···Br hydrogen bonds and, thus, stabilizing its pseudocage framework. The template reaction with cobalt(II) decachloro-*closo*-borate $[Co(DMF)_6](B_{10}Cl_{10})$ also gave the monocapped pseudomacrobicyclic complex: as follows from X-ray diffraction data, one DMF molecule acts as a capping group, oxygen atom of which forms N−H···O hydrogen bonds with three pyrazole groups of the ribbed pyrazoloximate fragments. The encapsulated paramagnetic cobalt(II) ion is in its high-spin state in the temperature range of 4−300 K in all these compounds, showing a single-molecule magnet behaviour.



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IRON AND COBALT(II) TRIS-DIOXIMATE COMPLEXES WITH PHOTOACTIVE FRAGMENTS

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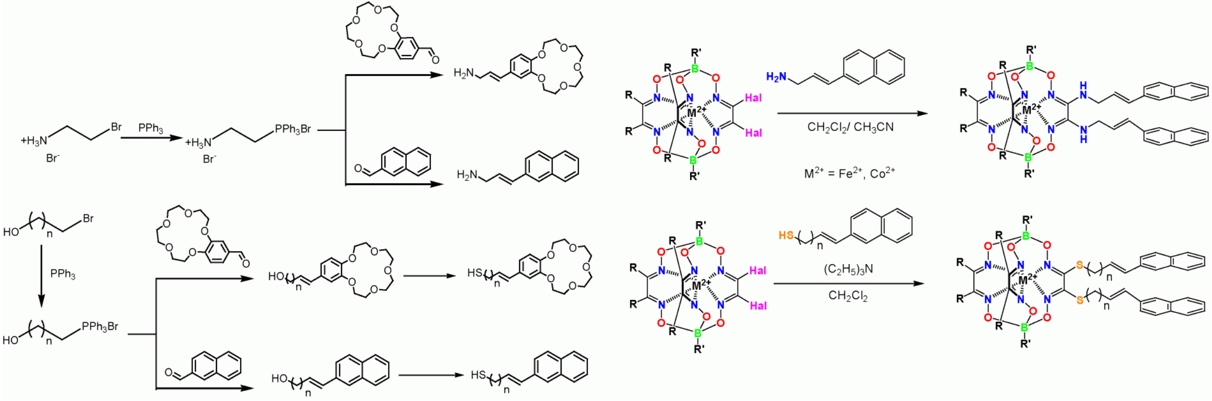
Macrobicyclic cage complexes with encapsulated metal ion (clathrochelates) have unusual chemical properties and physical and physicochemical characteristics, suggesting their practical usage as functional materials [1]. Ribbed functionalization of clathrochelate complexes allow to change their chemical and physicochemical properties directly. Introducing photoactive fragments into clathrochelate molecule can expand their usage in various fields of science and technology by creating molecular switches based on them, with managing their properties by light emission.



Synthesis of photoactive functionalizing nucleophiles was implemented from corresponding aromatic aldehydes using Wittig reaction or its modifications by Scheme. Iron and cobalt(II) halogenoclathrochelates undergo nucleophilic substitution of their reactive halogen atoms with photoactive naphthalene-containing amines and thiols as *N*- and *S*-nucleophiles.

The presence of olefine double bond in the ribbed fragment will allow to change the properties of the clathrochelates obtained due to pericyclic [2+2]-photocycloaddition. For the naphthalene-containing clathrochelates it is possible to stacking interactions formation between prolonged aromatic systems in *vic*-position in the ribbed chelate fragment. Irradiation of intramolecular ensembles obtained will lead to reversible formation of cyclobutane derivatives of these clathrochelate precursors.

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MOLECULAR PEROVSKITE CRYSTALS APPLIED IN MESOSCOPIC SOLAR CELLS: ELECTRONIC STRUCTURE AND X-RAY PHOTOELECTRON SPECTRA

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Molecular crystals with perovskite structure based on s^2-ions are of great interest in terms of their application for quantum electronics devices and modern energy sources [1-3]. It is known that these crystals possess luminescent, thermochromic and nonlinear optical as well as dielectric properties, which makes it possible to use them in mesoscopic solar cells, hole conductors, double-perovskite semiconductors, ferroelectric ceramics with perovskite structure [4-9]. A huge interest in this class of crystals in recent years is due to the discovery of ferroelectric, ferroelectric and ferroelastic phases [10, 11].

These crystals have not only covalent bonds but ionic and metallic ones that contribute to the fact that the total electron density becomes more asymmetric and, as a consequence, shifts to the anion-forming agent. In this case, a larger range is observed between the maximum and minimum value of the periodic potential in the crystal field [12]. Binding to cations the perovskites form clusters with tight packing of layers, where some of them demonstrate polymorphism and phase transitions caused by the dynamics of rotation of organic cations. However, luminescent properties are not observed in certain crystals where halogen ligands F, Cl, Br, I are bound to s^2-ions or metals (it is known that these properties are mostly determined by metal ions with mercury-like electron configuration ns^2). The transitions between sp-excited ^3P_j and s^2-ground $^1S_0$ states are considered responsible for the luminescence process, so luminescence has an intraionic character [13].

An important role in luminescence is also played by the correlation of the Jahn-Teller effect with the spin-orbit interaction, and the presence of an anomalously large Stokes shift, which can reach from 20 000 cm^{-1} to 30 000 cm^{-1}. The probability of optical transitions in crystals depends mainly on the nearest environment of the s^2-ion and its structure. In this case, the unshared electron pair, due to the spin-orbit interaction, leads to mixing of electronic transitions of various types, which further complicates their interpretation.

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POLYOXYETHYLENE CONJUGATES OF CALIXRESORCINARENES AS A NEW SUPRAMOLECULAR NANOCONTAINERS FOR BIOLOGICALLY ACTIVE SUBSTRATES

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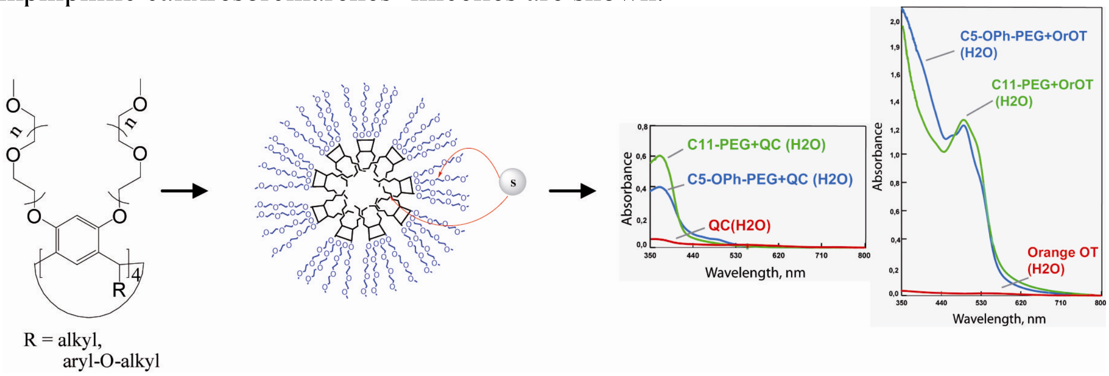
The design of nanocontainers as new nanomaterials is a major challenge in biomedical applications for drug delivery carriers, diagnostic agents, sensing probes, and tracking labels. For example, the incapsulation of the drugs into the nanocontainers allows preventing their premature biodegradation, decrease their toxicity, and increase their solubility. Despite of the different examples of nanocontainers in literature, searching of new systems with high therapeutic effect, low toxicity, appropriate sizes and high loading of biologically active substrates, remains relevant.

One of the potential ways to increase of targeted substrate concentration in the nanocontainer is using of the synthetic receptor molecules, in particular, amphiphilic calixresorcinarenes. The most practically important characteristic of amphiphiles is the ability to form nanocontainers by their self-association, capable of controlled binding/release of various substrates. Wherein the question about safety of using these systems *in vivo* remains open.

Our idea is the using of preorganized structure of amphiphilic calixresorcinarenes, functionalized with non-toxic poly(ethyleneglycol) chains, as a bilding block of nanoassociates, capable to effective binding of substrates.

Now we have been synthesised a few new calixresorcinarene derivatives, modified with eight polyethyleneglycol groups at the upper rim. Hematoxicity assessment for obtained macrocycles showed that they practically don’t lead to the erythrocytes’ destruction. The parameters of their self-association have been studied. Preliminary data showed that these nanoassociates effectively incapsulate the water-insoluble organic substrates (optical probe Orange OT, flavonol Quercetin). The similarities and differences of solubilisation behaviour of amphiphilic calixresorcinarenes’ micelles are shown.



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QUENCHING OF THE PHTHALOCYANINE AND PORPHYRINE LUMINESCENCE BY C_{60} IN TOLUENE SOLUTION. SYNTHESIS OF NEW PHTALOCYANINES.

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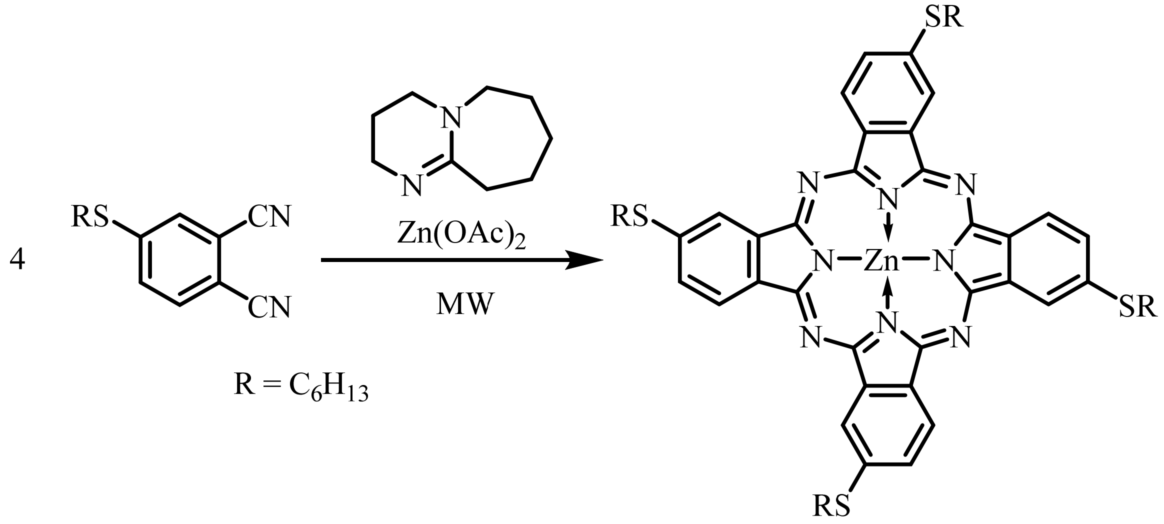
The interaction of C_{60} with the substituted phthalocyanines, porphyrines and their metal complexes had been investigated. We studied the luminescent spectra ($\lambda_{\text{excitation}}$= 360 nm, $\lambda_{\text{emission}}$ = 510–735 nm) of the titled compounds in toluene solution using C_{60} as a quencher in visible region. The quenching appears to be caused by the resonance interaction of the macrocyclic systems and their metal complexes (e.g. Zn) with fullerene C_{60}. The dependence of the relative intensity of the emission on the quencher molar concentration corresponds to the Stern-Volmer equation with $K_q = (3.7–32.6)\cdot 10^3$ l·mol^{-1}. Week dynamic charge transfer complexes with C_{60} are therefore formed.



Scheme 1

The investigation of charge transfer mechanisms in such type of systems is very important as a step in development of organic photovoltaic materials because it allows to find out the correlation between structure and properties. Based on these data and calculations (DFT, semi-empirical) the range of compounds for photovoltaic use (e.g. for solar cells) was obtained, for example new tetrahexylsubstituted phtalocyanine and its zinc complex (Scheme 1).

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NEW AZAHETEROCYCLE DERIVATIVES OF PHOSPHONIC ACID AS PERSPECTIVE LIGANDS IN BIOGENIC METALS COMPLEXES

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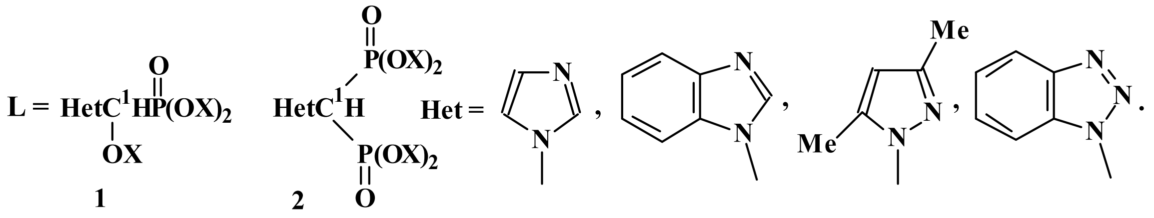
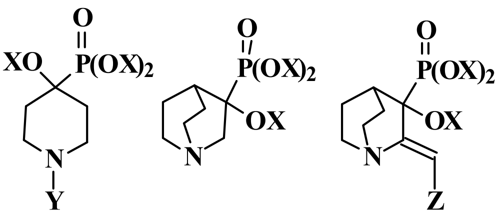
Functionalized organophosphorus acids and their derivatives with heterocyclic moieties are of great interest as effective chelating ligands and perspective bioactive substances with various properties. These acids are well-known biomimetics of hydroxy- or aminocarboxylic acids and natural pyrophosphates, and some of them such as zoledronic, risedronic, and minodronic acids are widely used in medicine [1]. We have synthesized the new functionalized phosphonic acids and their derivatives **1-5** including azaheterocycles *via* addition of tris(trimethylsilyl) phosphite to azaheterocyclic formamides and ketones [2,3] as well as new complexes of functionalized organophosphorus acids and their derivatives including P-C-N moieties with various biogenic metals as potential cell-penetrating substances.

M_nL_m, M = Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Fe^{2+}



1 **2**



3 **4** **5**

X = H, Me_3Si, Na; Y = H, Me, Bn, Ac, $MeSO_2$;
Z = 4-BrC_6H_4, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, Fc.

The resulting complexes with complicated structure are the perspective biologically active substances with versatile properties and the promising precursors for multitarget drug discovery.

This work was financially supported by the RFBR (grants numbers 15-03-00002 and 17-03-00169).

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PERSPECTIVE DIORGANOTIN DIHALIDES COMPLEXES WITH NEW FUNCTIONALIZED MONO- AND BISPHOSPHONATES

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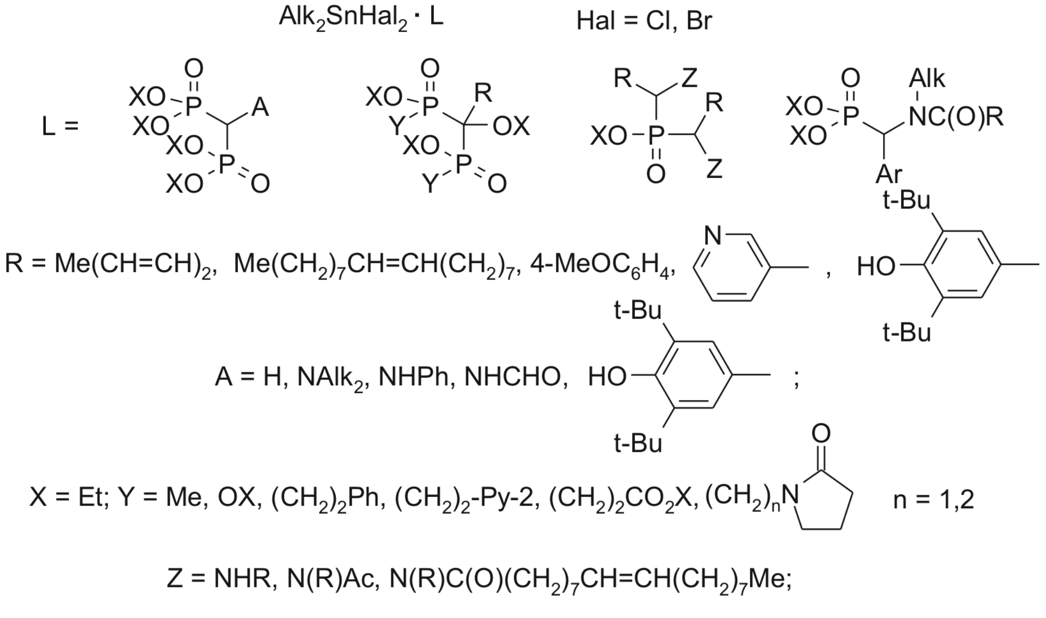
Functionalized organophosphorus acids and their derivatives with heterocyclic and unsaturated fragments are of great interest as effective chelating ligands, perspective bioactive substances, and well-known organophosphorus biomimetics of hydroxy(amino) acids or natural pyrophosphates [1]. The series of diorganotin dihalides complexes with new functionalized mono- and bisphosphonates are synthesized by us and characterized *via* NMR spectroscopy and X-ray structural analysis. We have developed the convenient methods of synthesis of new functionalized mono- and bisorganophosphorus acids and their derivatives using as starting compounds the trimethylsilyl esters of several trivalent phosphorus acids and functionalized alkenes, aldehydes, and carboxylic acids. The obtained complexes are presented below.



The complicated complexes of diorganotin dihalides with functionalized mono- and bisphosphonates possess antitumour and antioxidant activities with multifactor mode of action [2,3].

This work was supported by the Russian Foundation for Basic Research, grants № 15-03-00002 and 17-03-00169.

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THE FEATURES OF COPPER(II) COMPLEX FORMATION WITH ISOMERS OF 3(5)-AMINO-5(3)-METHYL-2-CHLOROPYRIDINE IN THE ACID MEDIUM

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Various pyridine derivatives are promising classes of ligands for the synthesis of a number of novel compounds with transition metals, possessing magnetic, chemical, and biological properties. Complexes of copper(II) are widely known for its physical properties, such as ferromagnetism, piezoelectric effects and thermochromism, they are often used as catalysts.

Coordination compounds of Cu(II) with isomers of 3(5)-amino-5(3)-methyl-2-chloropyridine (L^1 and L^2) of different composition: $(HL^1)_2[CuCl_4]\cdot H_2O$ (yellow), $(HL^1)_2[CuCl_4]\cdot 2H_2O$ (green) (Fig. 1), $(HL^2)_2[CuCl_4]$ (yellow), have been synthesized. Shown that L^2 in the last complex is able to enter a condensation reaction with acetone under synthesis conditions, forming a new complex $[Cu(L^{2*})Cl_3]$ (green) (Fig. 2). Coordination compounds have been investigated by X-ray diffraction analysis, IR spectroscopy, thermal analysis, and DSC.

Magnetochemical investigation of the complexes reveals in them ferromagnetic exchange interactions between paramagnetic copper(II) ions, which is due to strong hydrogen interactions in the crystals.

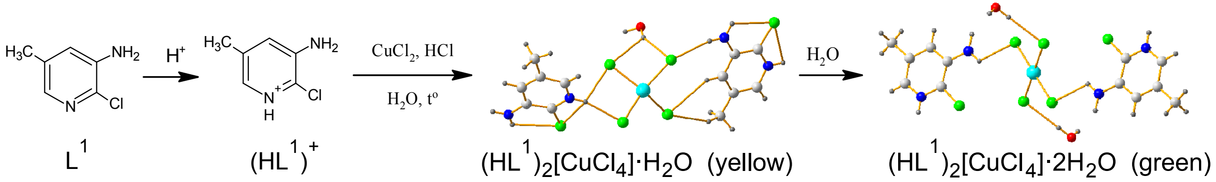

Figure 1. Protonation of L^1 and synthesis of copper complexes

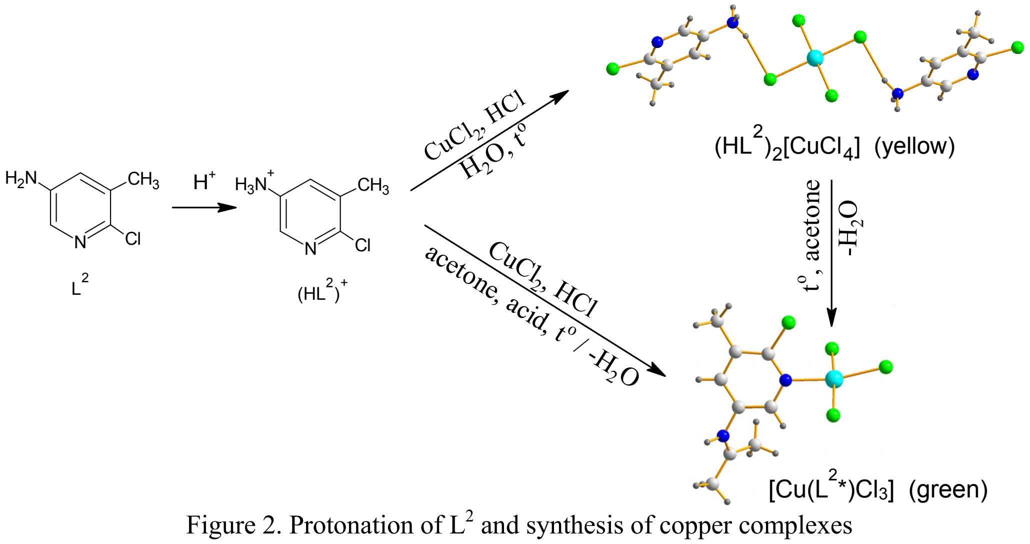

Figure 2. Protonation of L^2 and synthesis of copper complexes

Shown that the processes of complex formation in acidic media can be associated with processes of protonation and conversion of ligand, preferably leads to formation of acidocomplexes and their hydrates. The trans angle of Cl-Cu-Cl varies widely in the range from 180° to 142°, depending on the structure of the halide complexes of copper(II). Complexes are capable of exhibiting thermochromism as the energy costs of changing structures are small. Thermochromism is a characteristic phenomenon for this class of compounds.

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Cu(II), Mn(II) COORDINATION COMPOUNDS WITH CONDENSATION PRODUCT OF «HYDAZEPAM» AND ISATIN

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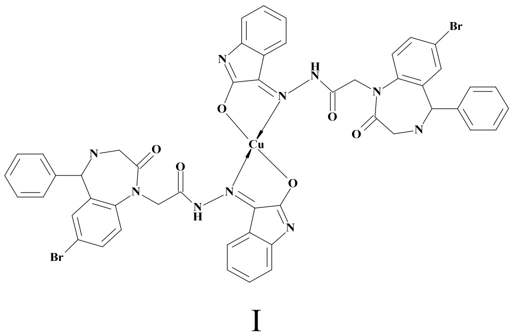
The creation of new drugs based on the coordination compounds of biologically active metals and organic ligands is one of the topical trends in modern bioorganic chemistry. Particularly promising is the use as bio-ligands used in medical practice of pharmaceuticals.

For the first time the coordination compounds of copper(II), manganese(II) ("metals of life") with hydrazone – the condensation product of the daily tranquilizer "hydazepam" – 2-(7-bromo-2-oxo-5-phenyl-3H-1,4-benzodiazepin-1-yl)acetohydrazide (Hydr) with isatin (HIz) have been synthesized and studied.

By self-assembling in the systems $Cu(CH_3COO)_2$ – Hydr – HIz – 2-propanol, $Mn(CH_3COO)_2$ – Hydr – HIz – 2-propanol the complexes $[Cu(HydrIz)_2]$ (I), $[Mn(HydrIz)_2]$ (II) have been synthesized. Their composition is determined by elemental analysis, measurement of electroconductivity, mass-spectroscopy, thermogravimetry. Ligand coordination mode in the complexes was determined by comparison of IR spectra of initial Hydr, HIz and the corresponding complexes I and II. Schemes for the structure of complexes are proposed:



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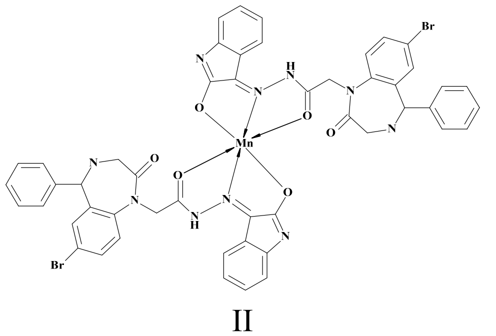

II

Their validity was confirmed by X-ray absorption spectroscopy (EXAFS), EPR spectroscopy, and magnetic susceptibility. Based on the analysis of the Cu*K*-edge (for I) and the Mn*K*-edge (for II), the composition of the first coordination sphere (CS) including nitrogen/oxygen atoms is determined: for I – two with a distance R = 1.92 Å and two with R = 2.00 Å ; for II – two with R = 2.10 Å, two with R = 2.20 Å and two with R = 2.27 Å.

The EPR spectrum of a polycrystalline sample II is satisfactorily modeled by a spin Hamiltonian (SH) with a thin interaction, characteristic for rhombic symmetry, with parameters: g = 2.00; D = 0.0281 cm^{-1} (total spin S = 5/2). The ESR spectrum of complex II in ethanol at T = 293 K is described by an isotropic SH of spin ½ and includes the Zeeman and hyperfine interaction. The parameters of the SH are: g = 1.99; A = $8.062 \cdot 10^{-3}$ cm^{-1}.

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SYNTHESIS, RAMAN SPECTRA AND STRUCTURE OF COMPLEX COMPOUNDS $FeCl_3$ WITH MONO- AND DIVALENT METAL CHLORIDES

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The investigation of interaction of $FeCl_3$ with mono- and divalent metal chlorides in practical and theoretic attitude is important. The known complex compounds of Fe(III) type $MFeCl_4$ (M = Cs, Rb, K, Na, Li), $Ba(FeCl_4)_2$, $M_3Fe_2Cl_9$ and M_3FeCl_6 (M = Cs, Rb) have been synthesized earlier by melting of anhydrous chlorides either from aqueous HCl solutions or in a medium of $POCl_3$ [1–4]. We found that the complex compounds of Fe(III) could be obtained by new non-traditional method – oxidation of $FeCl_2$ in his fusion cakes with mono- and divalent metal chlorides by means of anhydrous liquid chlorine. According to this method, the dry powder-like $FeCl_2$ fusion cakes with MCl and $M'Cl_2$ with different correlations of components were exposed during 1–7 days in the medium of liquid Cl_2 at room temperature.

The reaction run could be observed by changing powders colour or to change the intensity of the characteristic lines in the Raman spectra. For the identification reaction products the analyzed samples after removing of chlorine were placed in the special hermetic microcuvettes and were investigated under microscope of Raman spectrometer “Microprobe MOLE” or “Renishaw U1000” using an argon-ion laser with wavelength $\lambda = 514.5$ nm as the excitation source. The elaborated method allows to synthesize as all known the above-mentioned complex compounds of Fe(III) and obtain a number of new ones: M_3FeCl_6 with M = Cs ÷ K; $M_3Fe_2Cl_9$ with M = Cs, Rb; $MFeCl_4$ and $M'(FeCl_4)_2$ with M = Cs ÷ Li, Ag and M' = Ba ÷ Mg, Cr, Mn, Co, Ni, Cu, Cd, Pb. The largest is the type of compounds containing tetrahedral grouping $[FeCl_4]^-$ with the vibration frequencies (assuming T_d symmetry): $\nu_1(A_1) = 331–344$, $\nu_2(E) = 114–119$, $\nu_3(F_2) = 374–420$ and $\nu_4(F_2) = 131–159$ cm^{-1}. They are thermally more stable compared with complex compounds containing groupings $[FeCl_6]^{3-}$ or $[Fe_2Cl_9]^{3-}$, where the coordination number of Fe (III) is 6. Raman active vibrational modes of these groupings lay in the following frequency intervals: $[FeCl_6]^{3-}$ (assuming O_h symmetry) – $\nu_1(A_{1g}) = 290–294$, $\nu_2(E_g) \sim 278$, $\nu_5(F_{2g}) = 162–169$ cm^{-1} and $[Fe_2Cl_9]^{3-}$ (D_{3h}) – $\nu_1(A_1') \sim 340$, $\nu_2(A_1') \sim 269$, $\nu_3(A_1') \sim 142$, $\nu_4(A_1') \sim 130$, $\nu_{10}(E') \sim 310$, $\nu_{12}(E') \sim 188$, $\nu_{15}(E'') \sim 303$, $\nu_{16}(E'') \sim 260$ and $\nu_{17}(E'') \sim 162$ cm^{-1}. However the additional lines in Raman spectra appear at distortions of these groupings for some compounds. The spectroscopic characterizations and geometrical structures of all synthesized complex compounds are analyzed and systematized.

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CATION-INDUCED SUPRAMOLECULAR DIMERIZATION OF YTTRIUM(III) CROWNPHTHALOCYANINATE STUDIED BY DIFFUSION-ORIENTED NMR SPECTROSCOPY AND SINGLE-CRYSTAL X-RAY DIFFRACTION ANALYSIS

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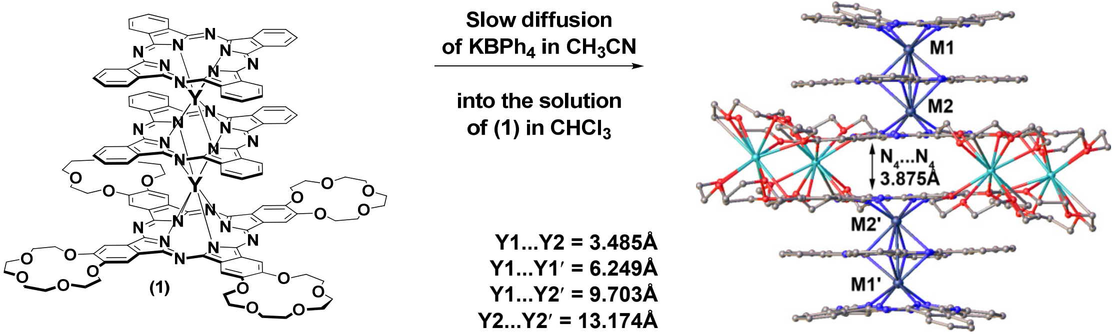
Double- and triple-decker lanthanide phthalocyaninates reveal single-molecular magnetic (SMM) behaviour, which is characterized by exceptionally high energy barriers and blocking temperatures [1]. Further improvement of SMM properties of sandwich lanthanide complexes can be achieved by the increase of the number of decks, which provides multinuclear complexes with *f-f* coupling between proximal Ln^{3+} ions.

Among the ways to form extended complexes based on sandwich phthalocyaninates, cation-induced assembling of crown-substituted complexes attracts special attention. In the present work we have firstly shown that this method affords formation of supramolecular assemblies, whose architecture is the same both in solution and in solid state. This investigation was performed on the example of the previously synthesized model complex **(1)**, which contains one terminal crown-substituted deck capable of cation-induced dimerization in the presence of potassium ions [2].

The interaction of **(1)** with KOAc in solution was studied using UV-Vis and NMR-titrations together with NMR DOSY, the results were consistent with the formation of the dimer. Finally, the structure of the dimer was *firstly* proved by single crystal XRD of solvates **$(1)_2*(KBPh_4)_4\cdot 4(CH_3CN)\cdot 7(CHCl_3)$**, which were obtained by slow diffusion of $KBPh_4$ in CH_3CN into the solution of **(1)** in $CHCl_3$ at 25 °C. Comparison of the hydrodynamic radius deduced from NMR DOSY and molecular size from XRD analysis revealed that these data are in good agreement with each other.

The structural characteristics of the dimer suggest the possibility of the magnetic-dipolar *f-f* interaction between the ions at M1 and M2 cites, as well as additional weaker coupling between ions at M2 and M2' cites, which can be observed in the case of isostructural complexes with Tb(III) and Dy(III).



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DEVELOPMENT OF ULTRAPOROUS CATALYSTS FOR THE PROCESS OF PHOTOOXIDATION OF HYDROCARBONS IN SOFT CONDITIONS

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The study of the processes of oxidation of hydrocarbons, with using the polymeric metal complexes deposited on organic or inorganic substrate, creates the prerequisites for the search of new technologies for the chemical processing of oil and gas hydrocarbons in important oxygen-containing products. As an alternative technology of catalytic oxidation can be used the heterogeneous photocatalysis using semiconductor photocatalysts in normal conditions. The process of preparation of catalysts consists of several stages.

While creating highly efficient catalysts for the oxidation of hydrocarbons it is necessary to provide a specific chemical composition, structure, and valence states of individual ions.
Furthermore, for the catalyst an optimal macrostructure (pore size) should be created which would not change under the influence of reaction conditions (stability to overheating and adsorptive action) and not destroyed (mechanical strength).

The acid-base modification of the TiO_2 surface was carried out using solutions of NaOH and H_2SO_4. After that, the titanium dioxide slurry was washed to a neutral pH by repeated centrifugation. The application of metal salts and oxides on the titanium dioxide was carried out by impregnation. Chemical deposition of Cu was carried out in an aqueous suspension by mixing TiO_2 with a solution of $CuCl_2$ and then reducing it with excess of $NaBH_4$. The concentration of metal salts was calculated in such a way that after synthesis the metal content was not more than 0.5 wt. %. Then, the catalyst was separated from the solution by centrifugation and further repeated washing to pH ~7.

For study of the mechanism of reaction of photocatalytic oxygenation of o-xylene a flow-type demountable reaction cell with a quartz window was used. The working volume was 1.25 cm^3. A bactericidal quartz lamp with a wavelength interval of 230-400 nm was used as the light source.
The products of the UV oxidation were examined by IR spectroscopy using an spectrometr Alpha Eco-ATR Bruker. Based on the spectral analysis of the solution it has been established that the main product of the oxidation reaction of o-xylene is aldehyde. In the IR spectra there is a characteristic absorption band in the field 1730 cm^{-1} which corresponding to vibrations of the –COH group of the aldehyde and the characteristic middle band at 1270 cm^{-1} corresponding to the deformation vibrations of the –CH bond.

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HETERONUCLEAR GOLD(III)-MERCURY(II) COMPLEXES COMPRISING ALKYLENEDITHIOCARBAMATE LIGANDS: CHEMISORPTION SYNTHESIS, SUPRAMOLECULAR SELF-ORGANISATION AND THERMAL BEHAVIOUR

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Novel heteronuclear gold(III)-mercury(II) complexes comprising alkylene dithiocarbamate ligands have been synthesised and preparatively isolated: $[Au\{S_2CN(CH_2)_5\}_2]_2[Hg_2Cl_6]$ (**I**), $[Au\{S_2CN(CH_2)_6\}_2]_2[HgCl_4]\cdot H_2O$ (**II**) and $[Au\{S_2CN(CH_2)_4O\}_2]_2[Hg_2Cl_6]$ (**III**). Crystal structure of the prepared compounds contains either two ('A' and 'B' for III) or three ('A', 'B' and 'C' for I and II) isomeric square-planar cations $[Au(S_2CNR_2)_2]^+$ (playing different structural functions and having intraorbital *dsp*^{2} hybrid state of the central gold atom) and complex anions $[HgCl_4]^{2-}$ or $[Hg_2Cl_6]^{2-}$ (with *sp*^{3} hybrid state of the central mercury atom).

At the supramolecular level, various species of structural self-organisation appear in compounds I–III: they all arise due to the relatively weak intercationic Au···S secondary bonds (Fig. 1). In complex I, isomeric gold(III) cations (*i.e.*, the noncentrosymmetric 'A' and the centrosymmetric 'B') form trinuclear moiety of $[\text{'A'}\cdots\text{'B'}\cdots\text{'A'}]^{3+}$ (Fig. 1*a*); while centrosymmetric cations 'C' are structurally isolated. In compound II, the secondary Au···S interactions arising between noncentrosymmetric cations 'A' result in the formation of binuclear moieties of $[Au_2\{S_2CN(CH_2)_6\}_4]^{2+}$, which in turn interact in a similar manner with two neighbouring centrosymmetric cations 'B'. These lead to the construction of zigzag polymeric chains of the type of $(\cdots[\text{'A'}\cdots\text{'A'}]\cdots\text{'B'}\cdots)_n$ (Fig. 1*b*); centrosymmetric discrete cations 'C' are located between these polymeric chains. Supramolecular structure III is characterised by linear polymeric chains of $(\cdots\text{'A'}\cdots\text{'B'}\cdots)_n$, which comprise two kinds of isomeric gold(III) cations 'A' and 'B' alternating along the chain length (Fig. 1*c*).

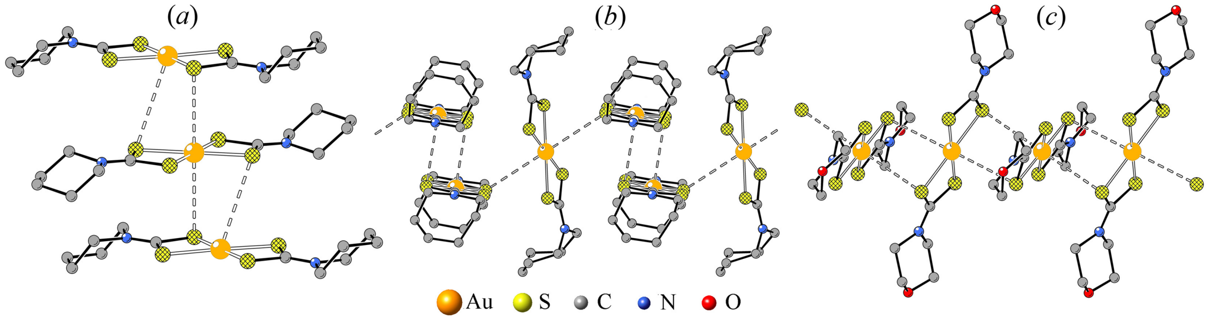

Fig. 1. Trinuclear cation of **I** (*a*), four-membered fragments of the polymeric chains of **II** (*b*) and **III** (*c*). Dashed lines show the secondary bonds Au···S.

The thermal behaviour of polycrystalline samples of I–III was studied by simultaneous thermal analysis (STA). It was shown that thermal decomposition of the aforementioned compounds is accompanied by a quantitative reduction of gold(III) to elemental gold and the liberation of $HgCl_2$ along with its partial transformation to HgS.

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THE QUANTUM-CHEMICAL ESTIMATION OF THE ACIDITY OF H-PHOSPHONATES COORDINATED WITH THE Cr(CO)$_5$ CORE

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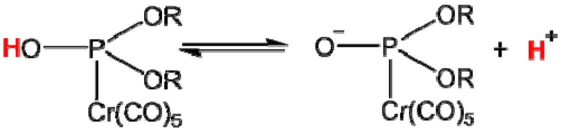
Previously we have found that the H-phosphonates coordinated with the M(CO)$_5$ (M = Cr, Mo, W) core reveal the vast acidity due to its isomerization into the hydroxyl-tautomeric form [1]. To reveal the trends in the acidity of the hydroxyl-tautomeric form of the coordinated H-phosphonate we held the quantum-chemical calculations that allowed us to estimate the static (positive charge located on hydrogen atom) and dynamic (the constant values for dissociation depicted on caption 1) for the organochromium modelled compounds.



Caption 1. The scheme of the coordinated H-phosphonate dissociation (in hydroxy-form).

R	pK_a
CH_3	-1.06
C_2H_5	+0.54
n-C_3H_7	+1.12
i-C_3H_7	+0.48
n-C_4H_9	+2.01
n-C_5H_{11}	+3.12

Table 1. Dissociation constants of coordinated H-phosphonates (in hydroxy-form).

Analyzing results depicted in the table 1 we can see that the adding of one methylene group to of the alkoxyl substituents decreases the value of the dissociation constant on one order of magnitude (the only exception are diethyl- and di-*iso*-propyl(H)phosphonates having nearly equal pK_a values for coordinated hydroxyl-form). The reasons of the observed trends are being discussed.

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HYDROAMINATION OF 2-VINYLPYRIDINE, STYRENE, AND ISOPRENE WITH PYRROLIDINE CATALYZED BY ALKALI AND ALKALINE-EARTH METAL COMPLEXES

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Complexes (dpp-bian)Mg(thf)$_3$ (**1**) [1], (dpp-bian)Ca(thf)$_4$ (**2**) [1], (dpp-bian)Mg(pyr)$_3$ (**3**) (dpp-bian = dianion of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene; pyr = pyrrolidine) containing the dpp-bian dianion, the complex (dpp-bian)Mg[N(SiMe$_3$)$_2$] (**4**) [2] containing its radical anion, as well as a mixed lithium-sodium salt [(dpp-bian)Li{N(SiMe$_3$)$_2$}][Na(C$_7$H$_8$)] (**5**) were tested for intermolecular hydroamination reactions with different substrates (see scheme 1). Molecular structures of complexes **3** and **5** are shown in figure 1 and 2 respectively.

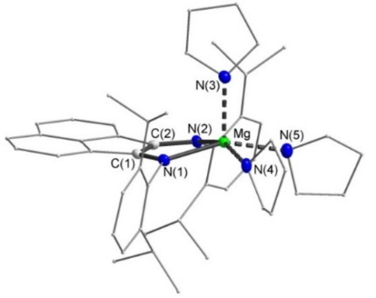


Figure 1. Molecular structure of complex **3**.

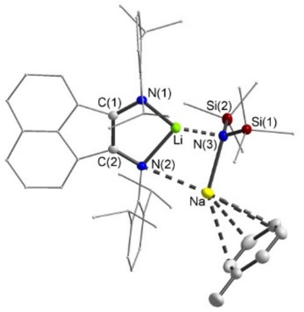
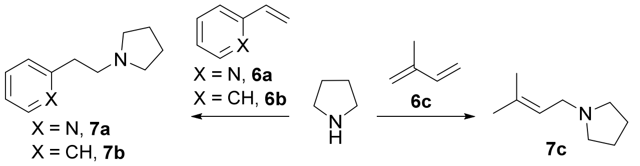


Figure 2. Molecular structure of complex **5**.



Scheme 1

Complexes **1**, **2** and **3** serve well as catalyst for the addition of pyrrolidine to 2-vinylpyridine (**6a**) at ambient temperature to give product **7a**. The reactions with magnesium catalysts **1** and **3** require longer time than with the calcium analog **2**. However, the high reactivity of calcium derivative **2** leads to the formation of poly-2-vinylpyridine as a by-product. Compound **4** containing the dpp-bian radical-anion catalyzes addition of pyrrolidine to styrene (**6b**) at 60 °C to give **7b**. The mixed lithium-sodium salt (**5**) is an active catalyst for the addition of pyrrolidine to styrene (**6b**) as well as to isoprene (**6c**) at 60 °C to give **7b** and **7c** respectively. In all the cases the catalyst loading was 1 to 2 mol %. With styrene and 2-vinylpyridine the reactions proceed to afford *anti*-Markovnikov product while with isoprene 1,4-addition product has been obtained.

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ТЕОРЕТИЧЕСКИЕ ИССЛЕДОВАНИЯ МЕЖМОЛЕКУЛЯРНЫХ ВЗАИМОДЕЙСТВИЙ ВОДНЫХ РАСТВОРОВ ГАЛЛОВОЙ КИСЛОТЫ

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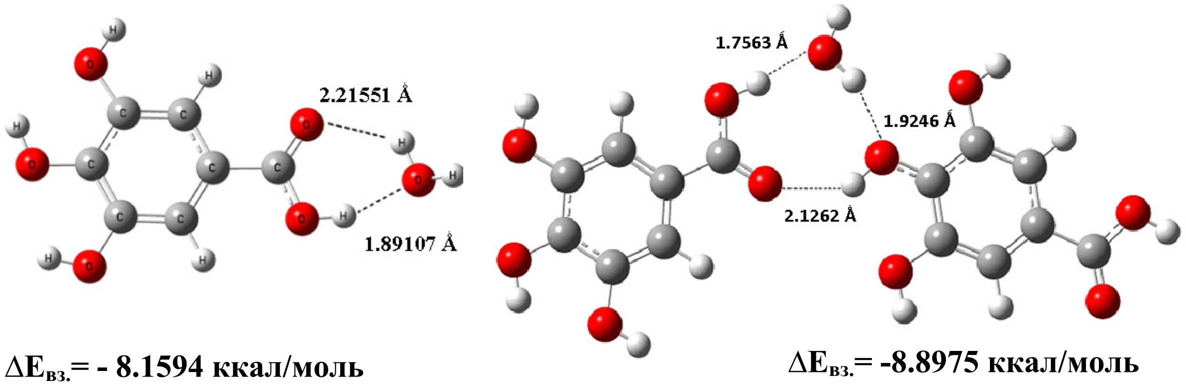
Галловая кислота (3,4,5-тригидроксибензойная кислота – ГК) и производные ГК являются биологически активными веществами. Они принадлежат к классу легко гидролизируемых натуральных полифенольных соединений. Предпочтительные межмолекулярные взаимодействия в водных растворах полифенольных соединений влияют на реакционную способность этих соединений, что важно для регулирования взаимодействий ГК с биомолекулами. Информацию о предпочтительных межмолеклярных взаимодействиях можно получить, используя как экспериментальные, так и теоретически методы исследования [1, 2].

В работе представлены результаты теоретических исследований димера ГК, а также структур возможных комплексов ГК-H_2O, ГК-H_2O-ГК, как в вакууме, так и в присутствии растворителя - воды (ε_{H2O} = 78.36).

Неэмпирическим методом *ab initio* (HF/6-311+G*) рассчитаны структурные и энергетические характеристики димера ГК, комплексов ГК-H_2O, ГК-H_2O-ГК в вакууме и водных растворах. Оценка влияния среды на форму и устойчивость комплексов ГК была выполнена в приближении самосогласованного реакционного поля SCRF в рамках модели Онзагера. Определены наиболее стабильные структуры возможных комплексов (рис.), их геометрические параметры, электрические свойства и рассчитаны колебательные спектры.



$\Delta E_{вз.}$= - 8.1594 ккал/моль

$\Delta E_{вз.}$= -8.8975 ккал/моль

Рис. Структуры стабильных ГК-H_2O и ГК -H_2O-ГК комплексов.

Однако, из результатов расчетов водных растворов ГК следует, что в присутствии растворителя наиболее стабильным из конкурирующих взаимодействий является взаимодействие типа ГК-ГК ($\Delta E_{вз}$= -12.9758 ккал/моль) по сравнению с ГК-H_2O и ГК-H_2O-ГК взаимодействиями.

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RARE-EARTH METAL AND CALCIUM ALKYL COMPLEXES CONTAINING SUBSTITUTED DIPHENYLMETHYL LIGANDS: SYNTHESIS AND REACTIVITY IN ISOPRENE POLYMERIZATION AND INTERMOLECULAR HYDROPHOSPHINATION

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Rare earth and calcium complexes, in recent decades, have a great interest due to their unique properties in high reactivity. Along with high reactivity in stoichiometric reactions rare-earth and calcium hydrocarbyl complexes demonstrated great promise in catalysis of a wide range of transformations of unsaturated substrates such as polymerization, hydrogenation, hydrosilylation, hydroamination, hydrophosphination, hydroboration and alkyne dimerization. Thier stability and reactivity are depend on a spectator ligand nature and also on the nature of the alkyl group used. In target of design and synthesis of new σ-bonded metal alkyl complexes and their application for hydrocarbons activation and alkanes functionalization we offer to use substituted diphenyl methyl ligands, containing additional heteroatoms (N, P), able to coordinate to the metal center.

The synthetic procedure toward novel substituted diphenylmethyl ligands cntaining imidazolyl, diphenylphosphine oxido and diphenylphosphine sulfido groups in orto-positions of the phenyl rings. This compounds can be synthesized by c-c cross-coupling reaction of aryl halides and tributyltin imidazole$[4\text{-tBu-2-(1-MeC}_3\text{H}_2\text{N}_2)\text{C}_6\text{H}_3]_2\text{CH}_2$ (**1**) or by oxidation of $[4\text{-tBu-2-(PPh}_2)\text{C}_6\text{H}_3]_2\text{CH}_2$ (**2**) by H_2O_2 $[4\text{-tBu-2-(POPh}_2)\text{C}_6\text{H}_3]_2\text{CH}_2$ (**3**) or sulfur or sulfur$[4\text{-tBu-2-(PSPh}_2)\text{C}_6\text{H}_3]_2\text{CH}_2$ (**4**).

It was found out that equimolar reactions of **1** with $\text{Ln(CH}_2\text{SiMe}_3)_3(\text{THF})_2$ or $[\text{Amd}^{\text{OMe}}]\text{Y(CH}_2\text{SiMe}_3)_2(\text{THF})$ (Ln =Y, Nd) go with activation of one CH-bond of methylene group, SiMe_4 elimination and resulted in formation of heteroleptic yttrium alkyl derivatives $\{[4\text{-tBu-2-(1-MeC}_3\text{H}_2\text{N}_2)\text{C}_6\text{H}_3]_2\text{CH}\}\text{Ln(CH}_2\text{SiMe}_3)_2(\text{THF})$ (**5**, **6**) and $\{[4\text{-tBu-2-(1-MeC}_3\text{H}_2\text{N}_2)\text{C}_6\text{H}_3]_2\text{CH}\}\text{Y(CH}_2\text{SiMe}_3)[\text{Amd}^{\text{OMe}}]$ (**7**) containing two different Ln-C σ-bonds. Bis(alkyl) Ca and Yb complexes $\{[4\text{-tBu-2-(PPh}_2)\text{C}_6\text{H}_3]_2\text{CH}\}_2\text{M}$ (M = Ca (**8**), Yb (**9**)) were synthesised by salt exchange reaction of $\text{MI}_2(\text{THF})_2$ with potassium derivative of **2**.

Mixed alkyl complexes **5-7** have found to efficient catalysts for isoprene polymerization in composition of ternary catalytic systems together with $\text{Al}i\text{Bu}_3$ and $[\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]$ or $[\text{HNMe}_2\text{Ph}][\text{B(C}_6\text{F}_5)_4]$ (ratio [Y]/[Al]/[B] = 1/10/1). While bis(alkyl) complexes **8** and **9** was found to be active in intamolecular hydrophosphination of alkene and acetylenes.

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MOLECULAR RELAXATION IN BINARY NITRATE–PERCHLORATE SYSTEMS

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Investigation of the processes of molecular relaxation by the methods of vibrational spectroscopy provides a wealth of information on the structural and dynamical properties of condensed systems [1]. Such studies are based on the fact that the widths of bands in the vibrational spectrum are inversely proportional to the molecular relaxation times [2]. The purpose of this study is to analyze and compare the processes of molecular relaxation in individual crystals and binary solid systems, as well as to determine the possible additional mechanisms of relaxation of vibrationally excited states of molecular ions in binary solid systems (as compared to individual crystals). In accordance with the purpose of this work, the objects of investigation were chosen as follows: crystalline $LiNO_3$, $LiClO_4$, $NaNO_3$, $NaClO_4$, KNO_3, $KClO_4$, as well as equimolar binary solid systems $LiNO_3$–$LiClO_4$, $NaNO_3$–$NaClO_4$, KNO_3–$KClO_4$.

The processes of molecular relaxation in the binary nitrate–perchlorate solid systems $LiNO_3$–$LiClO_4$, $NaNO_3$–$NaClO_4$, and KNO_3–$KClO_4$ have been investigated using Raman spectroscopy. It has been found that the relaxation time of the $\nu_1(A)$ vibration of the NO_3^- anion in the binary solid system is shorter than that in the pure metal nitrates. It has been shown that an increase in the relaxation rate is caused by the existence of an additional mechanism of relaxation of vibrationally excited states of the nitrate ion in the system. This mechanism is associated with the excitation of a vibration of another anion (ClO_4^-), as well as with the "creation" of a lattice phonon. It has been established that the condition for the realization of the relaxation mechanism is that the difference between the frequencies of the aforementioned vibrations should correspond to the range of sufficiently high densities of states of the phonon spectrum.

Thus, it was found that there are factors that are favorable for an increase in the relaxation rate of intramolecular vibrational modes in the binary solid systems as compared to the relaxation rate in the individual crystals. In our opinion, this experimental fact can be explained if it is assumed that there is an additional mechanism of relaxation of vibrationally excited states in the binary solid systems. The implementation of this mechanism implies the existence of a possible exchange of vibrational quanta between different molecules or molecular ions with the close values of the frequencies of intramolecular vibrations. Such an inelastic intermolecular exchange should be accompanied by the "creation" of a lattice phonon, which takes itself the difference between the energies of the relaxing excited vibrations. Therefore, the proposed mechanism of relaxation of vibrationally excited states is effective when the difference between the frequencies of these vibrations is less than the maximum frequency of the phonon spectrum of the system.

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ZINC PHTHALOCYANINE BEARING FOUR META-(3,5-DIMETHYL-1*H*-PYRAZOL-1-YL)PHENOXY SUBSTITUENTS: SYNTHESIS AND SPECTRAL PROPERTIES

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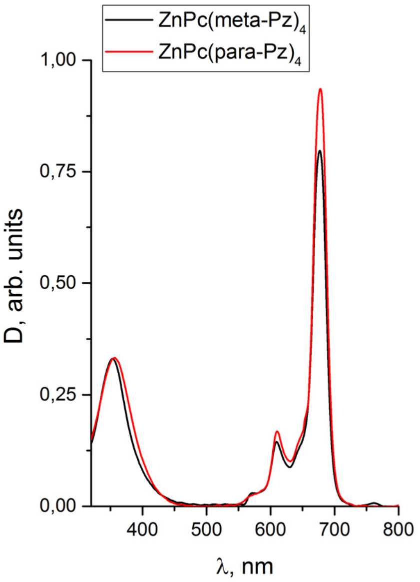
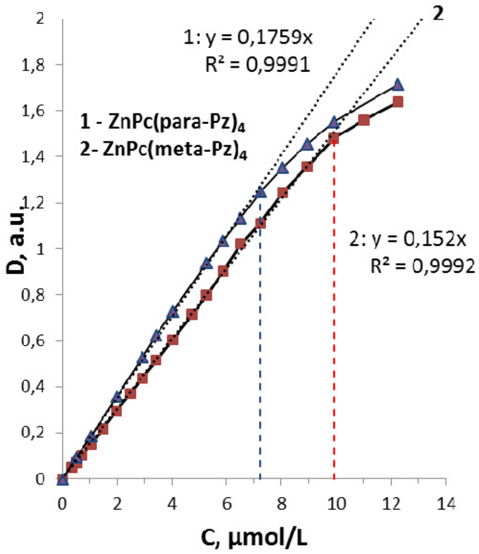
Substituted zinc phthalocyanines have intensive red-visible region absorption with high extinction coefficient, both high singlet and triplet quantum yields and high singlet oxygen quantum yield. These properties make them important candidates as potential agents for fluorescence imaging and photodynamic therapy of cancer. Recently [1] we published a paper devoted to synthesis and isolation practically pure *C*s regioisomer of zinc 2,9,17,23-tetrakis[*para*-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenoxy]-phthalocyanine. In the present work, we have synthesized new zinc phthalocyanines bearing *meta*-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenoxy groups. The synthesized compounds were characterized using different analytical techniques. The effects of the pyrazole fragments position in the substituents on the spectral properties were also studied.





As in the case of the *para*-isomer we have isolated practically pure *C*s regioisomer but with lower yield. Position of pyrazole fragments don't practically influence on spectral properties of substituted zinc phthalocyanines. The Bouguer-Lambert-Beer law is fulfilled in the concentration range at 0-7.3 μmol/L for ZnPc(*para*-Pz)$_4$ and 0-10 μmol/L for ZnPc(*meta*-Pz)$_4$. At the same time coefficients of extinction were practically identical – lg(ε) ammounts to 5.24 for ZnPc(*para*-Pz)$_4$ and 5.18 for ZnPc(*meta*-Pz)$_4$.

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THE INDIVIDUAL AND MIXED COMPLEX COMBINATIONS OF PLATINUM (II) WITH THIO- AND AMINOTHIO ACIDS

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The complexes with mixed ligands of platinum that contain nitrogen or sulfur atoms have been obtained and learned [1, 2]. The complexes of the biologically active ligands have been investigated finitely. Therefore, to obtain and investigate different biologically active ligands that contain nitrogen or sulfur atoms and to learn their biological activity practically are very important.

In the presented paper the individual and mixed complex combinations of platinum (II) with ethylenediaminediacetate (EDDA – $HOOCH_2CNH_2CH_2CH_2NCH_2COOH$) and mercaptoacetate ($HSCH_2COOH$) acids has been synthesized and studied their composites, structures and other properties by physicochemical methods. And their biological activity has been investigated. $[Pt(ЕДДА)(NH_3)_2]Cl_2$(1), $[Pt(SCH_2COOH)_2(NH_3)_2]$(2) and $[Pt(ЕДДА)(SCH_2COOH)]$(3) complexes with above-mentioned ligands have been synthesized recarding the nature of the platinum salts that taken for synthesis in beginning, the stoichiometric ratios of the ligands, temperature, pH of medium and other conditions.

The IR-spectrums of the ligands, platinum salts and synthesized complexes have been studied comparatively. The diacetate aminoion existing in the IR-spectrum of EDDA disodium salt is characterized by one asymmetric $\vartheta^{as}_{coo^-} = 1582\ cm^{-1}$ adsorption band. Two 1686 and 1690 cm^{-1} asymmetric bands observing in IR-spectrum of EDDA belong to free COOH groups. This is same with the one 1690 cm^{-1} adsorption band that belongs to free carboxyl group of the ligand in IRS of the complex 1. Therefore, we can say that the carboxyl group of the ligand does not participate in coordination. Other observing wide adsorption bands of 3300-3280cm^{-1} belong to coordinated NH-group. 3400-3350cm^{-1} adsorption band is special for free NH-group. Thus, in complex 1, EDDA is coordinated with nitrogen atom bidentally and forms pentahedron metallic chelate ring. The specific adsorption band for SH-group of 2562 cm^{-1} in the IRS of free ligand HSH_2COOH was not recorded in the IRS of the complex 2 [3]. Instead of it, one adsorption band of 368cm^{-1} that special to ϑ_{pt-s} valence bond was observed. Two valence bonds are observed by one adsorption band, it means that they locate in trans-position. The carboxyl groups of ligands in complex 3 do not participate in coordination. The proof of this is existing one adsorption band of 1686 cm^{-1} in IRS of complex 3. In complex 3 EDDA is coordinated bidentally in cis-position with two nitrogen atoms, therefore, the imperative cis-coordination of the mercaptoacetate acid happens. The proof of cis-coordination of EDDA in complex 3 is existing of adsorption bands of 453 and 470cm^{-1} in IRS that are special to ϑ_{pt-N} valence bond.

Complexes 1, 2, 3 are stable at 276, 315, and 240^{0}C, respectively. Upwards of these temperatures the complexes undergo decomposition.

The element analysis of 1-3 complexes and the results of electroconductivities of $1\cdot10^{-3}$M solutions prove presented coordination structures.

The antimicrobic properties of 1–3 complexes have been studied on microbes and proved that antimicrobic properties are changed in order of 3>2>1.

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REACTION OF METAL-BOUND ISOCYANIDES WITH NITRONES – THEORETICAL INVESTIGATION OF THE CHEMICAL DIVERSITY

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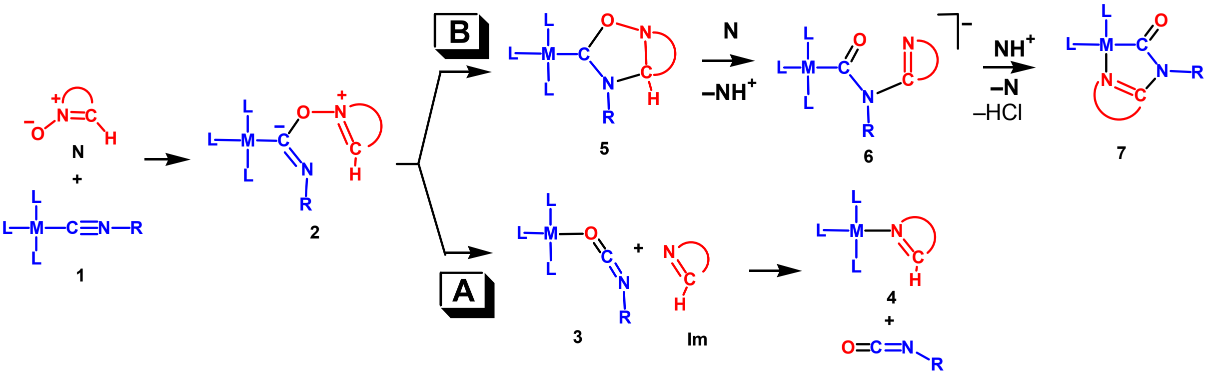
Metal coordinated isocyanides [M]–C≡NR exhibit very rich chemical activity towards 1,3-dipoles of the allyl anion type, *e.g.* nitrones $R_2C{=}N^+(R){-}O^-$. Different products are formed depending on the nature of the metal centre, dipole and isocyanide substituent, *i.e.* heterocyclic products of cycloaddition, isocyanates + imines or metallacycles [1–3]. The origin of such diversity and details of the reaction mechanism were investigated using theoretical DFT methods. The mechanism of the reaction includes the nucleophilic addition of the nitrone at the C atom of the C≡N group (Scheme). Further, depending on the metal centre, either oxygen transfer with subsequent ligand substitution to give **4** and isocyanate or cyclization of **2** to **5** could occur. Cycloadduct **5** is not stable when the metal centre is Au(III) and R is Cy or Xyl, and it is converted further into the metallacycle **7** that includes deprotonation of the endocyclic C–H group, simultaneous N–O bond cleavage and cyclization. The formation of cycloadduct **5** is controlled by the $\mathrm{LUMO}_{\pi^*(C\equiv N)}$ of C≡NR. The main driving force of the formation of the imine + isocyanate products is the N–O bond cleavage in **2**. The main factor controlling the formation of the metallacycle is acidity of the endocyclic C–H group in **5**.



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SYNTHESIS AND LUMINESCENT PROPERTIES OF IONIC DINUCLEAR COMPLEXES OF IRIDIUM(III) WITH 1,4-BIS[2-(2-PYRIDYL)BENZIMIDAZOLATO]BUTANE AS A BRIDGING LIGAND

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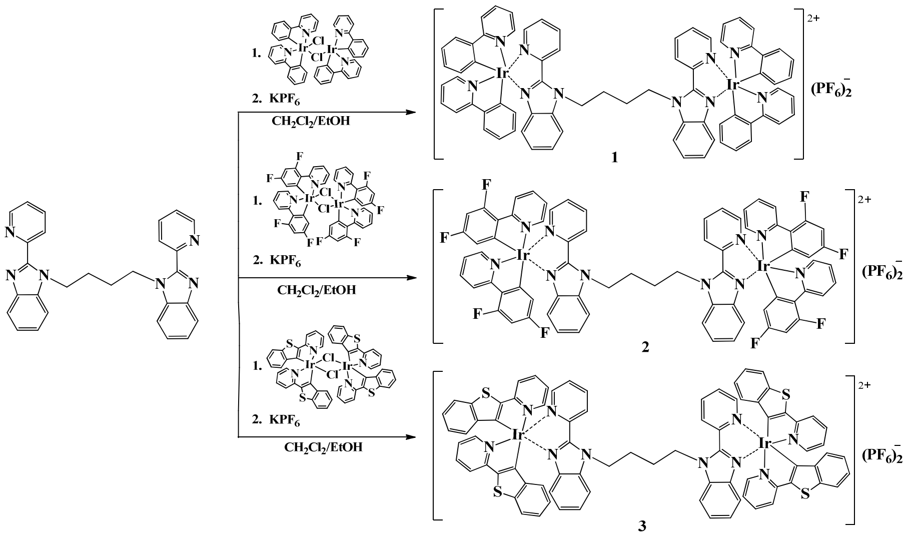
New ionic binuclear complexes of iridium(III) containing 1,4-bis[2-(2-pyridyl) benzimidazolato]butane as a bridging ligand were synthesized:



The resulting compounds exhibit intense photo- and electroluminescence (OLED-configuration: ITO/Ir-комплекс:PVK/BATH/Alq_3/Yb) of yellow-green, green-yellow and pink colors.

Complex	Turn-on voltage (V)	Brightness (cd/m^2)	Current efficiency (cd/A)	Power efficiency (lm/W)	CIE (x; y)
1	8	4565 (24 V)	7.69 (22 V)	1.10 (22 V)	0.40; 0.54
2	12	516 (26 V)	6.2 (24 V)	0.84 (22 V)	0.34; 0.54
3	14	1013 (30 V)	2.0 (28 V)	0.22 (28 V)	0.54; 0.36

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DFT INVESTIGATION OF STRUCTURE FEATURES OF BINUCLEAR NICKEL(II) CARBOXYLATE $[Ni_2(\mu\text{-}OH_2)(\mu\text{-}CF_3COO)_2(tmeda)_2(CF_3COO)_2]$

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The purpose of this present work is to study the binuclear tetramethylethylenediamine (tmeda) nickel(II) complex with trifluorocarboxylate ligands and water molecule in bridging position. Comparison of results of quantum chemical modeling by DFT PBE0/def2-TZVP method with X-ray diffraction (XRD) data allowed to obtain information about the nature of chemical bonds in this compound, as well as its magnetic properties. The last are particularly important for the $3d^8$ Ni(II) compounds capable of forming coordination structures of different multiplicity, singlet, triplet or quintet, depending on the strength of the ligand field surrounding the ions of this metal.

The most stable structure is a polyhedron with four unpaired electrons from two metal ions in d^8 configuration, which is a quintet structure according to the optimization of the geometry of the binuclear carboxylate $[Ni^{II}_2(\mu\text{-}OH_2)(\mu\text{-}CF_3COO)_2(tmeda)_2(CF_3COO)_2]$ [1] in different spin states. The triplet structure with spin-nonequivalent metal ions is essentially less stable (about ~67.5 kJ/mol). The singlet state with all coupled electrons exceeds the triplet state by ~241 kJ/mol and is therefore the most unstable one.

In addition to energy differences, the formation of the most stable quintet structure of the coordination compound is supported by its geometric characteristics. In the optimized structure of the binuclear polyhedron in the singlet state each Ni(II) ion is in the plane-square environment of two N atoms of the tmeda ligand, the bridging O atom of the coordinated H_2O molecule and one O atom of the trifluoroacetic acid anion. The reason for the plane-square structure of the singlet coordination structures of Ni^{2+} ions is usually explained by the repulsion of binding electron pairs of ligands in axial positions and electrons of an elongated ellipsoidal singlet d^8-shell of the metal ion. At the same time, XRD data indicate the presence of an octahedral environment of Ni(II) ions with two coordinated O atoms of carboxylate ligands in the structure of the coordination compound under study. The most stable optimized structure with four unpaired electrons of nickel (II) ions corresponds exactly to this structure. Thus, quantum-chemical modeling of the coordinating polyhedron of $[Ni_2(tmeda)_2(\mu\text{-}OH_2)(\mu\text{-}CF_3COO\text{-}k O,O`)_2(CF_3COO\text{-}k O`)_2]$ in combination with the X-ray diffraction data led to the conclusion that the experimentally obtained complex is in the paramagnetic quintet state.

The frequencies of the normal vibrations obtained as a result of the DFT calculation correlate well with the characteristic bands of the experimentally obtained FTIR spectrum and will be used to classify the IR spectral characteristics of the binuclear nickel(II) carboxylates with terminal amine ligands.

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SPECTROSCOPIC STUDIES ON THE INTERACTION OF A PROTOPORPHYRIN WITH CETYLTRIMETHYLAMMONIUM BROMIDE AND ALBUMIN

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Porphyrinmacrocycles are very promising objects for medicine and pharmacology and, taking into account the specific requirements for drugs, colloidal porphyrinnanoassociates of optimal size, are of particular interest.Most hydrophilic porphyrins, including natural ones, do not form discrete associates in neutral media (pH 7-8) without any special stabilizers. At the same time, it is known that the processes of the association of aromatic macrocycles can be initiated by various anti-charged surface-active substances, and the interaction of these molecules with proteins, especially those that provide delivery through the bloodstream, is of paramount importance for the formulation of safe drugs and effective doses. In order to obtain nanoassociates based on protoporphyrin, we studied: (1) the processes of interaction of protoporphyrin IX (H_2PP) with the cationic stabilizer - cetyltrimethylammonium bromide (CTAB) and (2) the interaction of H_2PP with the transport protein in blood plasma - bovine serum albumin (BSA). The interactions of H_2PP with CTAB and BSA were studied as a function of the concentration of the protein or surfactant additive.The formation of colloidal porphyrin associates was identified by absorption and fluorescence spectroscopy.In the case of hydrophilic tetraphenylporphyrins with carboxyl and sulfur groups, the process of their interaction with CTAB goes in two stages.At low surfactant concentrations (stage 1), H-type premicillary aggregates are formed. When the surfactant concentration approaches CMC (Critical MicellarConcentration) [1] (stage 2) the formation of micelle-encapsulated porphyrin monomers occurs. During the interaction of H_2PP with CTAB one family of clear isobestic points in the absorption spectra (Fig. a) and a continuous increase of the yield of fluorescence with an increase in the surfactant concentrationis observed, which indicates the absence of a different preliminary porphyrin association of the H- or J- typein this case.Afinalproduct of the titration ismicellizedmonomer.Changes in the ESP during spectrophotometric titration of H_2PP with albumin (Fig. b) also indicate the formation of a non-covalent porphyrin-albumin complex of the J-associate type, but proceeding in a completely different mechanism.

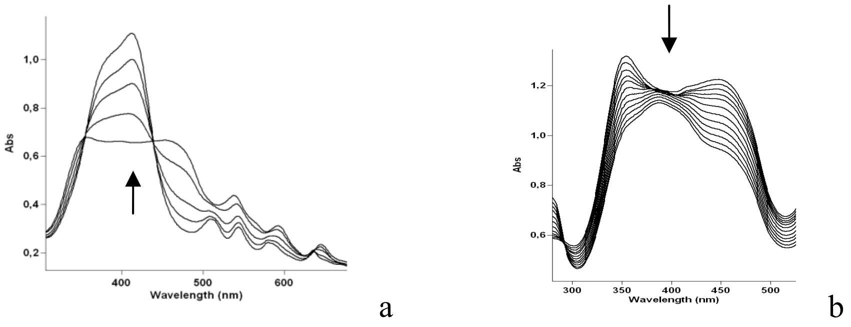

Fig. Titration of H4PP (4.5 μM, pH) 7.4) with CTAB (a) and BSA (b)

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BORON-FLUORIDE DIPYRROMETHENE COMPLEXES: SPECTROSCOPIC CHARACTERISTICS AND APPLICATION IN OPTICAL DEVICES

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Study of dipyrromethene (dipyrrin) complexes with different structure is one of the most successfully developing areas of modern chemistry. The most perspective members of this family are boron fluoride complexes of dipyrromethene (BODIPY). They have effective absorption and emission in the visible spectral region and good photostability [1]. Depending on the introduced substituents, they are widely used, including as active laser media for tunable lasers, laser limiters and optical sensors [2].

In this work we present a spectroscopic study of the physicochemical properties BF_2 dipyrromethene complexes with different substituted which were synthesized at the Institute of Solution Chemistry RAS. The individuality and structure of synthesized compounds were verified using the thin layer chromatography, NMR, and IR spectroscopy methods in accordance with [3]. As solvents, we used ethanol, ethyl acetate, and cyclohexane (reagent grade).

As a result of the research, the spectral luminescent, lasing, and sensor characteristics of BODIPY have been studied. It is found that many of these compounds exhibit stimulated emission in different solvents when excited by the second (532 nm) and third (355 nm) harmonics of a Nd:YAG laser in the range of 548–692 nm. The obtained high values of the efficiency of stimulated emission generation in solutions indicate the prospects of BODIPY as a basis for creating laser-active media [4].

Introduction of halogen atoms as substituents increases the intersystem crossing and phosphorescence yields (the heavy atom effect). The obtained characteristics of long-lived emission from complexes allow us to recommend this compound for study of his interaction with oxygen with aim of creation oxygen sensor. For this BODIPY was incorporated in solid-state matrices on the base of methylcellulose. Measuring dependencies of the intensity of the phosphorescence of the oxygen concentration and plotting the calibration curve (Stern-Volmer dependences have linear portion) can be used to determine the unknown concentration of oxygen. Based on this, the dipyrromethene complexes can use as a basis for creation of optical sensors for oxygen [4, 5].

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NICKEL(II)-MEDIATED REACTIONS OF DISUBSTITUTED CYANAMIDES

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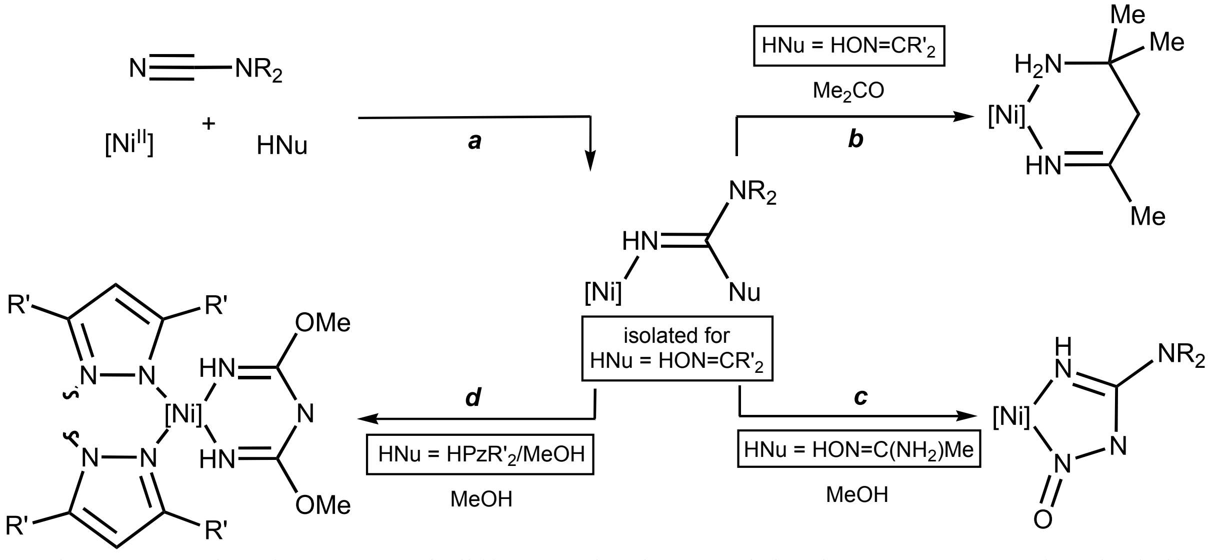
Transition metal mediated reactions of nitriles are of great significance because they allow the synthesis of different classes of nitrogen heterocycles, acyclic imino species, and imino complexes. In particular, nickel(II)-mediated reactions of NCR (R = Alk, Ar) lead to (1,3,5-triazapentadiene)Ni^{II} species and nickel(II) phthalocyanines.

In our work, we focused attention on metal-mediated reactions of disubstituted cyanamides $NCNR_2$, which demonstrated different reactivity than that of conventional nitrile ligands NCR (R = Alk, Ar). Until our work chemistry of disubstituted cyanamides in the presence of nickel(II) salts remained almost unexplored.

We studied reactivity of $NCNR_2$ (R = Alk, Ar) toward different nucleophiles (viz. oximes HON=CR’R”, amidoximes $HON{=}C(NH_2)R''$ and pyrazoles $HPzR'_2$) in the presence of nickel(II) salts in different solvents [1]. In all cases, products of multi-step reactions were obtained, i.e. Busch’s type complexes $[Ni\{NH_2CMe_2CH_2C(Me){=}NH\}_2]^{2+}$ (Scheme, *a* and *b*), nitrosoguanidine species $[Ni\{NH{=}C(NR_2)NN(O)\}_2]$ (*a* and *c*), and bi- and trinuclear complexes $[Ni_n(PzR'_2)_m\{NH{=}C(OMe)NC(OMe){=}NH\}_2]$ (n = 2, m = 2; n = 3, m = 4) (*a* and *d*). The initial step consisted in nucleophilic attack to the coordinated cyanamide with formation of the corresponding nickel(II) imino complex (*a*). Complexes of this type were isolated in the case of reaction with oximes (*a*). In other cases similar complexes was proposed as intermediates of nickel(II)-mediated reactions.



These examples demonstrated difference in the reactivity between conventional nitriles NCR (R = Alk, Ar) and disubstituted cyanamides $NCNR_2$ (R = Alk, Ar). The chemistry of disubstitited cyanamides in the presence of metal centers is rich and allows synthesis of different classes of coordination compounds, which are potentially useful for mastering new materials.

[1] E. V. Andrusenko, E. V. Kabin, A. S. Novikov, N. A. Bokach, G. L. Starova, A. A. Zolotarev, V. Yu. Kukushkin, *Eur. J. Inorg. Chem.*, **2015**, 4894–4904; Andrusenko, E. V.; Kabin, E. V.; Novikov, A. S.; Bokach, N. A.; Starova, G. L.; Kukushkin, Y., *New J. Chem.*, **2017**, *41*, 316–325.

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COMPLEX COMPOUNDS OF VIB GROUP METALS WITH SOME DIHYDROXY AROMATIC LIGANDS

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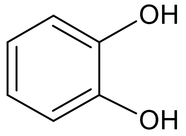
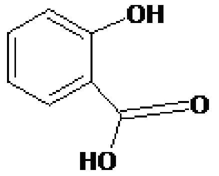
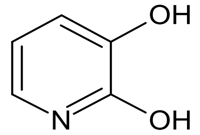
Metal complexes of Ti(IV), Zr(IV) and Hf(IV) with some dihydroxy aromatic ligands were isolated and studied by a set of plysical chemical methods.







The elemental analysis indicates the formation of the compounds of the general composition ML_2. IR and UV-VIS spectroscopic studies illustrate the ionization of hydroxy groups of the ligands at complexation.

The equilibria of the reactions of complex formation in the solutions were studied, and the formation constants of the complexes were calculated.

According to the DFT B3LYP theoretical modeling, the monodentate bridging coordination of the ligands with the formation of polymeric structures is more preferable than the bidentate chelating coordination.

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o-QUINONE WITH ANNELATED DITHIETE: COORDINATION ABILITIES.

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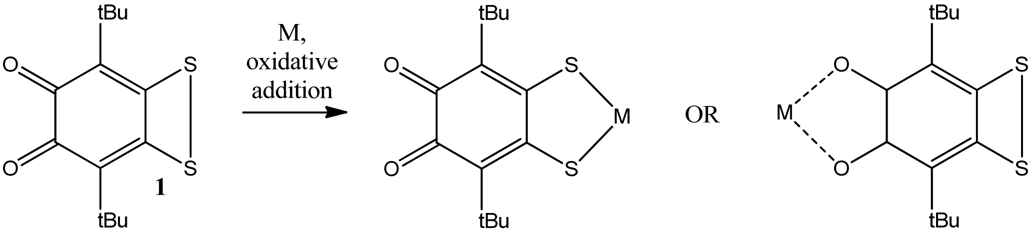
o-Quinone **1**,[1] bears two redox-active and coordinating sites of similar nature. Both these sites are in same oxidation state, therefore ready for oxidative addition to a metal. A dependence of the direction of oxidative addition to a species **1** on the metal nature has been studied.

o-Quinone **1** is a model system providing possibility for estimation of stability of dithiolate or diolate isomers of complexes with different metals. It has been found that metals forming singly charged cations give semiquinonate complexes, whereas for double charged cations there is a diversity in the direction of the oxidative addition. For hard Lewis acid dications diolate (catecholate) isomers are more stable, while soft Lewis acid ions prefer ditiolate addition.[2] Among the systems showing univocal direction for oxidative addition there is a sample of bidirectional behaviour in this reaction. In this case energies of catecholate and dithiolate isomers are quite close, and a ratio of isomers in the reaction mixture is determined by a kinetic control.



A reaction ability of free site in mononuclear dithiolate and catecholate complexes towards secondary oxidative addition to another metal was investigated. Some of these complexes are paramagnetic and have been studied by EPR spectroscopy. A features of spin density distribution across the ligand as well as coordinated metallofragments will be discussed.

[1] V.K. Cherkasov, G.A. Abakumov, G.K. Fukin, S.V. Klementyeva and V.A. Kuropatov, *Chem. Eur. J.*, **2012**, *18*, 13821-13827.

[2] K. A. Martyanov, V. K. Cherkasov, G. A. Abakumov, M. A. Samsonov, V. V. Khrizanforova, Y. H. Budnikova, V. A. Kuropatov, *Dalton Trans.,* **2016**, *45*, 7400-7405.

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SYNTHESIS, STRUCTURE AND ANTIVIRAL ACTIVITY OF BIGUANIDE COMPLEXES OF Co(II), Co(III), Ni(II), Cu(II)

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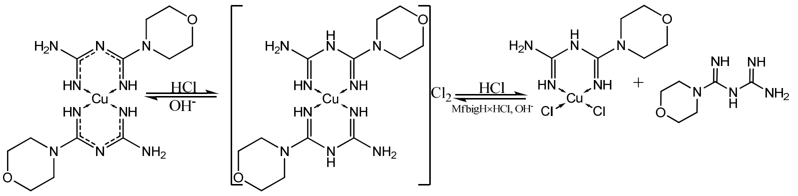
The development of new synthetic antiviral drugs is one of the most important areas of modern medical chemistry. The special attention is given to the viruses, which widespread and are characterised by high pathogenicity and ability with the high speed to be transmitted from one person to another. The influenza and herpes are pertain to such types of viruses. It is known that mutations of many viruses over time make antiviral drugs ineffective, as, for example, occurred with amantadine and rimantadine. The reason for the inefficiency of the amantadine and remantadine is that they contain only one active functional group.

We synthesized complexes Cu^{2+}, Co^{2+}, Co^{3+} and Ni^{2+} with ligands containing several free (uncoordinated) functional groups and investigated their activity against influenza A virus and herpes simplex virus type-2 (HSV-2). As ligands, for the most part, the biguanide derivatives were used, which themselves as drugs (analgetic, antimalarial and antimicrobial agent, lowering of glucose level in the treatment of diabetes and so on) are used.

The complexes were synthesized in water, alcohol or DMSO. Complexes of various types can be formed depending on the pH of the reaction medium, as occurs in synthesis of copper complexes



Most of the synthesized compounds were tested for antiviral activity against influenza A virus and herpes simplex virus type-2. In relation to the influenza A virus the highest activity (IS = 8) showed the complex $[Co(s\text{-}BuHbigH)_3]Cl_3$ (s-BuHbigH – *second*-butylbiguanide). In the table contains data for antiviral activity against herpes simplex virus type-2.

Complex	Toxicity, CD_{50} µg/ml	Efficiency, ED_{50} µg/ml	Therapeutic index IS
$[Cu(PrHBigH)_2]OH_2$	>100	1,5625	>64
$[Cu(s\text{-}BuHBigH)_2]SO_4$	>100	3,125	>32
$[Cu\{(Etyl)_2HBigH\}_2]SO_4$	>100	25	>4
$[Cu(MorphBigH\}_2$	>100	6,25	>16

Complexes $[Cu(PrHBigH)_2]OH_2$ and $[Cu(s\text{-}BuHBigH)_2]SO_4$ are promising for testing *in vivo*.

SYNTHESIS AND STRUCTURE OF IRON(III) COORDINATION COMPOUNDS WITH 2,6-DIACETYLPYRIDINE BIS((ISO)NICOTINOYLHYDRAZONES) AND COORDINATED ISOTHIOCYANATE IONS

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As a result of the interaction of $Fe(NO_3)_3\cdot 9H_2O$, 2,6-diacetylpyridine bis((iso)nicotinoylhydrazone)(H_2L^1/H_2L^2) and NH_4NCS the complexes $[Fe(HL^1)(NCS)_2]\cdot 0.25H_2O$(**I**) and $[Fe(HL^2)(NCS)_2]\cdot 2.33H_2O$(**II**) were obtained. Compounds **I** and **II** were investigated by IR spectroscopy (in the 4000-400 cm^{-1} range) and X-ray diffraction studies. The IR spectra of the compounds are characterized by the absence of the ν(C=O) and ν(NH) absorption bands, which proves the coordination of the Schiff bases in the enolic form. Broad bands in the 2700-2400 cm^{-1} region are attributed to the oscillations of $\nu(NH^+)$, due the protonation of the heterocyclic nitrogen of the hydrazide component. The most intensive absorption bands occur in the 2050-2040 cm^{-1} range and are attributed to the oscillations ν(C≡N) for NCS^- group coordinated to the metal *via* nitrogen. The medium intensity bands 817-815 cm^{-1} are assigned to ν(CS) and those of relatively weak intensity of 480 cm^{-1} to the oscillations δ(NCS) for the same coordination mode of the NCS^- group. The oscillations of $\nu(C = N)_{azomet}$ are observed in the 1636-1629 cm^{-1} range. The average intensity bands in the 600-480 cm^{-1} region are attributed to the ν(Fe-N) and ν(Fe-O) oscillations. Structures **I** and **II** were determined by the X-ray diffraction method. Coordination polyhedra of the metal atoms in **I** and **II** are similar and are difined by the set of O_2N_5 donor atoms, taking the form of a pentagonal bipyramide.

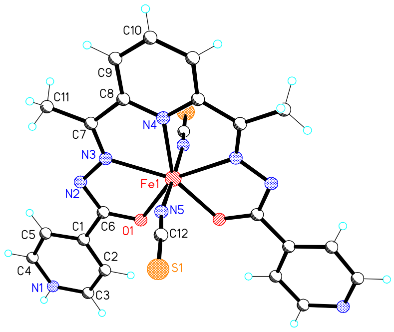
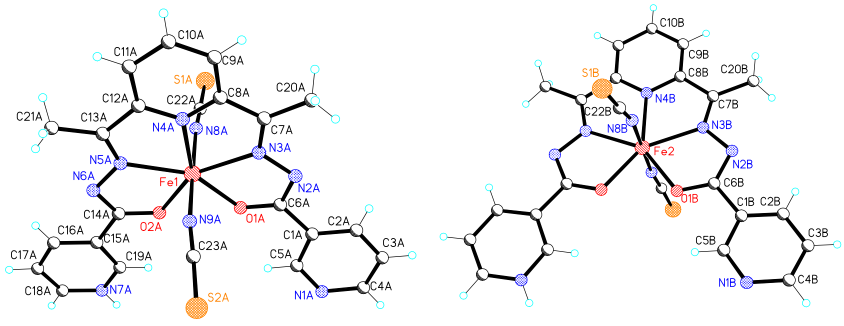


Fig.1 The molecular structure of the complex in I.

As a result, the monodeprotonated HL^1 and HL^2 ligands are located in the equatorial plan of the bipyramides, with NCS^- anions coordinated through nitrogen atom in the axial positions. The analysis of crystal packing established that the in compound **I** molecular complexes are linked in a unidimensional chain through the N-H...N hydrogen bonds, and in **II** the complexes are joined together by means of water molecules.



Complex A Complex B

Fig.2 The molecular structure of the complex in II.

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TETRANUCLEAR AU(I) COMPLEXES WITH *RSSR* ISOMERS OF 16- AND 18-MEMBERED P_4N_2 CORANDS

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Dinuclear Au(I) complexes based on the medium cyclic aminomethylphosphines – 1,5-diaza-3,7-diphosphacyclooctanes were obtained recently. These complexes demonstrated the stimuli-responsive luminescence relatively to VOCs [1,2], which was explained by the changing of ligand conformation in the presence of the guest molecules.

Herein, we present the tetranuclear gold(I) complexes based on the labile macrocyclic aminomethylphosphine ligands – 16- and 18- membered P_4N_2 corands.

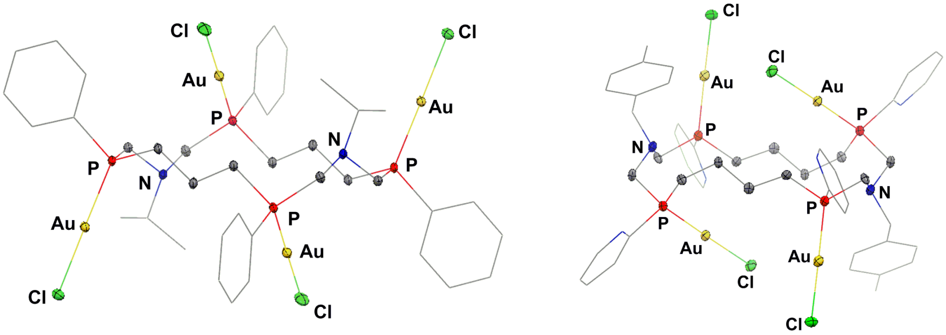

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Figure 1 *The molecular structures of complexes **1** and **2**.*

Complexes **1** and **2** were obtained by the interaction of Au(tht)Cl with *RSSR* isomers of 16- or 18-P_4N_2-corands, respectively, in the ratio of 4 : 1. Compounds **1** and **2** were isolated from the reaction mixture by the removal of the solvent and recrystallization from DMF. The geometry of complexes **1** and **2** is presented in Figure 1.

[1] Shamsutdinova, N.A. and Sinyashin, O.G. *New J. Chem.* **2016**, *40*, 9853-9861
[2] Strelnik, I.D., Musina, E.I. and Grachova, E.V., *CrystEngComm.* **2016**, *18*, 7629-7635

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TWO COMPLEXES OF COPPER(II) WITH ARYLHYDRAZONE OF ACETOACETANILIDE AND AMINOALCOHOLS: CATALYTIC ACTIVITY IN CYANOSILYLATION OF ALDEHYDES

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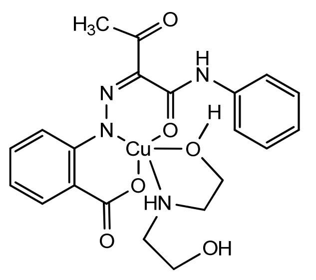
Auxiliary ligands play an important role in synthetic coordination chemistry, usually being used to stabilize particular complexes and/or to modify their properties, such as solubility, acidity, buffer capacity, etc., which are important, *e.g.*, for catalytic applications [1-3]. However, to our knowledge, aminoalcohols such as diethanolamine and *N*-methyldiethanolamine have not yet been used as the auxiliary ligands in the synthesis of copper(II) complexes with arylhydrazones of active methylene compounds [4], and this possibility is explored in this work. Thus, two new copper(II) complexes, $[Cu(HL)(H_3X)]$ (**1**) and $[Cu(HR)_2(H_2L)_2]$ (**2**), were synthesized from copper(II) nitrate and (*Z*)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazinyl)benzoic acid (**H_3L**), in the presence of diethanolamine (H_3X) (for **1**) or *N*-methyldiethanolamine (H_2R) (for **2**). Both complexes are water soluble and are characterized by elemental analysis, IR spectroscopy, ESI-MS and single crystal X-ray diffraction. They act as homogenous catalysts for the cyanosilylation reaction of a variety of both aromatic and aliphatic aldehydes with trimethylsilyl cyanide affording the corresponding cyanohydrin trimethylsilyl ethers in high yields (up to 85 %) and at room temperature.



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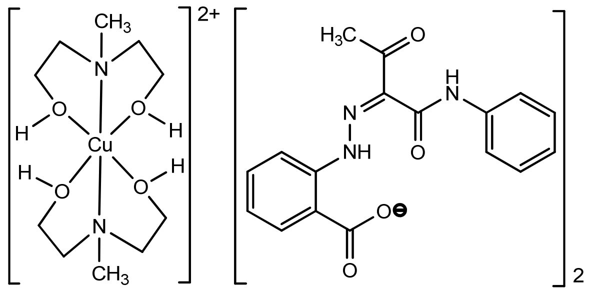

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[1] M. N. Kopylovich, K. T. Mahmudov, M. Haukka, P. J. Figiel, A. Mizar, J. A. L. da Silva, A. J. L. Pombeiro, *Eur. J. Inorg. Chem.* **2011**, *27*, 4175–4181.
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[3] K. T. Mahmudov, M. N. Kopylovich, A. Sabbatini, M. G. B. Drew, L. M. D. R. S. Martins, C. Pettinari, A. J. L. Pombeiro, *Inorg. Chem.* **2014**, *53*, 9946−9958.
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Acknowledgements – Authors are grateful to the Fundação para a Ciência e a Tecnologia: FCT (project UID/QUI/00100/2013), Portugal, for financial support. The work was also supported by the Ministry of Education and Science of the Russian Federation (the Agreement number 02.a03.21.0008).

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MASS-SPECTRAL INVESTIGATIONS OF LEAD (II), MANGANESE (II) AND COBALT (II) CARBOXYLATE COMPLEXES

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Kurnakov Institute of General and Inorganic Chemistry, Moscow, RUSSIA.

Manganese (II), cobalt (II) oxopivalates and lead (II) pivalate were synthesized and studied by the mass-spectrometric analysis. The synthesis of volatile compounds of lead, cobalt and manganese was shown to be quite simple and may be conditional divided into two separate stages. The first stage is a reaction between the freshly precipitated metal hydroxide and pivalic acid with hydrated complexes formation, such as [x $MPiv_2 \cdot y\ H_2O$]. At the second stage hydrated products is dried and vaporized in vacuum (p = 1 Pa) in the temperature range of 150 -300ºC.

The investigations have shown that the thermal behavior of the synthesized pivalate complexes essentially depends on the vaporization conditions of the process. The synthesized complexes except the lead one are generally hydrated. Being heated under atmospheric pressure these cobalt and manganese compounds underwent deep hydrolysis and formed the corresponding metal oxide as a final product. On the other side the thermal behavior in vacuum of the hydrated complexes was completely different: significant amount of crystallization water was removed with the minor hydrolysis leading to the volatile metal oxopivalates M_4OPiv_6. The mass spectrometric investigations of the thermodynamic characteristics were performed on MS 1301 mass spectrometer having a 50–1500 amu mass range using 65 eV ionizing electrons. The complexes were vaporized from a Knudsen effusion cell. The ratio of evaporation surface to surface of the effusion hole was about 600. The cell temperature was measured with a Pt/Pt(Rh) thermocouple (±2). Upon investigation of the temperature dependence of the main ionic currents intensities in the mass spectra of the saturated vapor, the standard enthalpies of sublimation of lead (II) pivalate, manganese (II) and cobalt (II) oxopivalates were calculated by the Clausius–Clapeyron equation using the least squares method. The average means of the data from three independent experiments are presented in Table 1. The enthalpies of sublimation of the cobalt and manganese oxopivalates were found at the first time, the enthalpy of sublimation of the lead pivalate Pb(Piv)2 was shown to correspond sufficiently published data [1]. Low values of the enthalpies, high volatility and monomolecular composition of the gas phase allow us to use these complexes as precursors for oxide films preparation and as materials for MOCVD method.

Table 1. Enthalpies of sublimation of lead pivalate, cobalt and manganese oxopivalates.

Complex	Temperature range, K	$\Delta_sH^o_T$, kJ/mol
$PbPiv_2$	350-382	113 ± 10 (103,5 ± 2,9) [1]
Co_4OPiv_6	380-425	180 ± 10
Mn_4OPiv_6	446-479	161 ± 6.8

[1] Khoretonenko N.M., Rykov A.N, Korenev Y.M., Alikhanyan A.S, Malkerova I.P. "Determination of the composition and vapor-pressure of lead and bismuth pivalates" // Zurnal neorganiceskoj himii, 40(6), 1995, pp. 929-932

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NEW POLYMER NICKEL COMPLEXES WITH N_2O_2 SCHIFF BASES CONTAINING ELECTRON WITHDRAWING SUBSTITUENTS

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Herzen State Pedagogical University of Russia, St.Petersburg, RUSSIA.

Polymer complexes of transition metals with Schiff bases (poly-[M(Schiff)]) are promising functional materials for use in electrochemical energy sources, photoelectrochemical energy converters and sensory devices [1,2]. To adjust the electrochemical and spectral characteristics of polymers, the introduction of electron-donor substituents into the ligand environment of the original complexes is often used. At the same time, there are practically no works in which poly-[M(Schiff)] complexes, containing electron-withdrawing substituents in the ligand environment of monomeric fragments, would be considered. This report contains the results of a study of new complexes poly-(N,N-ethylene-bis(3-nitrosalicylideniminato) nickel (II)) – poly-[Ni(NO_2-SalEn)] and poly-(2,3-dimethyl-N,N'-bis(3-nitrosalicylidene)butane-2,3-diaminato) nickel (II) – poly-[Ni(NO_2-SaltmEn)]:

1. Methods for the electrochemical synthesis of polymers in ionic liquids and alkyl-carbonate solvents, acetonitrile, 1,2-dichloroethane containing tetraethylammonium tetrafluoroborate and lithium tetrafluoroborate have been developed.

2. Electrochemical behavior of polymers in acetonitrile solutions has been studied by cyclic voltammetry. It is established that the region of electrochemical activity of the investigated polymer complexes is shifted by 200 mV in the direction of more positive potential values in comparison with analogous complexes that do not contain nitro groups. Complexes are stable for at least 100 cycles of potential variation in the range of 0 ÷ +1.6 V (AgCl/Ag standard electrode).

3. Using *in situ* quartz crystal microbalance has been established that each [M(Schiff)] fragment of the investigated complexes in the region of positive potential values undergoes reversible two-electron oxidation and reduction, while analogous complexes poly-[Ni(SalEn)] and poly-[Ni(SaltmEn)] are oxidized and reduced by 1.1 and 1.4 electrons per one polymer fragment, respectively.

4. Using in situ spectroelectrochemical method, electronic absorption spectra of polymer films on an optically transparent electrode were recorded. Based on the identification of optical transitions in the investigated polymer complexes, it was found that in both polymers there are two oxidized forms, which are polaron and bipolaron quasi-particles.

[1] I.Chepurnaya, S. Logvinov, M. Karushev, A. Timonov, V. Malev, *Russ. J. of Electrochemistry*, **2012**, *48*, 538-544.

[2] E. Smirnova, M. Besedina, M. Karushev, V. Vasil'ev, A. Timonov, *Russ. J. Phys. Chem. A,* **2016**, *90*, 1088-1094.

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THE INFLUENCE OF HIGH PRESSURE ON THE INTERMOLECULAR INTERACTIONS OF ACETAMIDE WITH WATER

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Acetamide and its derivatives are of great interest due to the presence of amide group in their structure, which can be considered as a model for investigation of peptide bond. The intermolecular interactions of this functional group with water play important role in the structure formation and, thus, determine the properties of many biological systems.

The compressibility coefficients, $k = (V_0 - V)/V_0$ (where V_0 - specific volume at atmospheric pressure p_o, V – the volume at pressure p), of binary aqueous solution of acetamide have been measured within $x_2 = 0 \div 0.4$ (acetamide mole fraction) at 298 K and at pressures from atmospheric one to 100 MPa. The molar isothermal compressibilities of solutions ($K_{T,\mathrm{m}}$), the partial molar volumes of water ($\overline{V}_1$) and acetamide ($\overline{V}_2$), the limiting partial molar volumes of acetamide in water ($\overline{V}_2^{\infty}$), and the limiting partial molar isothermal compressibilities of acetamide ($\overline{K}_{T,2}^{\infty}$) have been calculated.

It was established that the molar isothermal compressibility went down with the first portions of acetamide in water and reached its minimum at $x \sim 0.25$. The concentration dependence of the partial molar volume of acetamide passed through its minimum at $x \sim 0.2$; the extreme depth increased with the pressure growth. The limiting partial molar volumes of acetamide in water ($\overline{V}_2^{\infty}$) decreased with the pressure increase and the limiting partial molar isothermal compressibilities of acetamide ($\overline{K}_{T,2}^{\infty}$) were positive at all state parameters studied. These results agree with the idea about the looser structure of water within the hydration sphere of acetamide as compared with the structure of bulk water.

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GALLIUM COMPLEXES OF THE MONOIMINOACENAPHTHENONE LIGAND (DPP-MIAN): SYNTHESIS AND REACTIVITY

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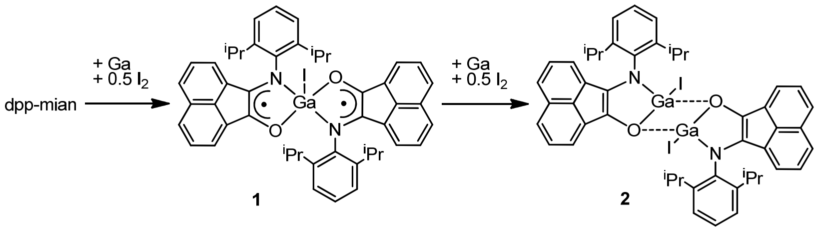
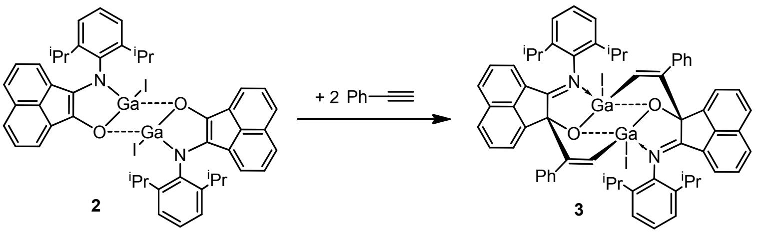
In 2015 we have reported the synthesis of magnesium complexes with a reduced iminoketone ligand: (*E*)-2-(2,6-diisopropylphenylimino)acenaphthen-1-one (monoiminoacenaphthenone = dpp-mian) [1]. This work is devoted to gallium complexes with different anionic types of the ligand. The reaction of dpp-mian with metallic gallium and iodine affords to the bis-ligand biradical (dpp-mian)$_2$GaI (**1**), and then dimeric dianionic [(dpp-mian)GaI]$_2$ (**2**) complexes, through step-by-step reduction of the ligand (Scheme 1).



Scheme 1.

Well known gallium complex [(dpp-bian)Ga]$_2$ is capable of reversibly cycloaddition of alkynes [2]. The dianionic compound **2** also reacts with phenylacetylene to give the adduct (dpp-mianGaI)$_2$(PhCCH)$_2$ (**3**) (Scheme 2).



Scheme 2.

Compounds **2** and **3** were tested as catalysts for the hydroamination of phenylacetylene or *N*,*N*'-dicyclohexylcarbodiimide by 4-chloroaniline and the reaction of phenylacetylene with 1-naphthol. We have shown the complex **2** is less active compare to digallane [(dpp-bian)Ga]$_2$ [2-4] and the adduct **3** does not reveal the catalytic properties.

[1] D.A. Razborov, A.N. Lukoyanov, E. V. Baranov, I. L. Fedushkin, *Dalton Trans.*, **2015**, *44*, 20532-20541.
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NOVEL PHYSIOLOGICALLY ACTIVE METAL COMPLEXES OF SULPHIMIDE

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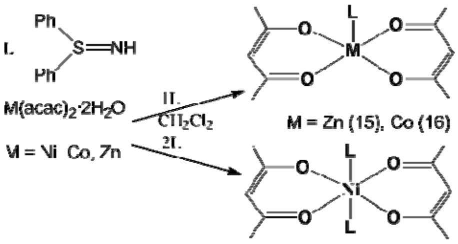
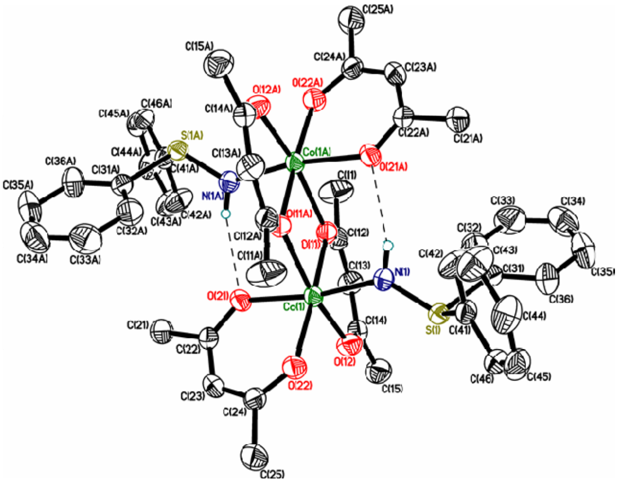
Sulfimides demonstrate a wide spectrum of biological activity due to coordination ability of N and S atoms, and lability of S=N bond. Although their use in medicine is limited by relative toxicity. The aim of present study was the synthesis of new sulfimide complexes and investigation of their antioxidant properties. The novel compounds **1-3** based on the S,S-diphenylsulfimide were synthesized and characterized. The number of coordinated sulfimides depends on the nature of metal. The structure of complex **2** was determined by X-ray diffraction analysis.



1, 2

3



It is known that oxidative stress and excessive level of lipid peroxidation in organism is a main reason of several diseases including neurodeneration. The antioxidant activity of the compounds was evaluated in the processes of Fe^{3+} induced lipid peroxidation of rat brain homogenates. It was shown that the compounds **1, 3** do not possess antioxidant properties while Co complex demonstrats high antioxidant effect. The IC_{50} value was found 3.5 μM for compound **2**. Unlike its Zn and Ni analogues, Co(II) complex is the redox-active one, cobalt atom can reversibly be involved in electron transfer. Apparently, the high activity of **2** may be attributed to electron transfer from Co^{2+} to peroxyl radicals responsible for lipids oxidative destruction.

The financial support of RFBR (grants № 17-03-01070, 15-03-03057) is gratefully acknowledged.

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SYNTHESIS, STRUCTURE AND PROPERTIES OF COMPLEX COMPOUNDS OF ZINC WITH 3,3',4',5,7-PENTAHYDROXYFLAVON

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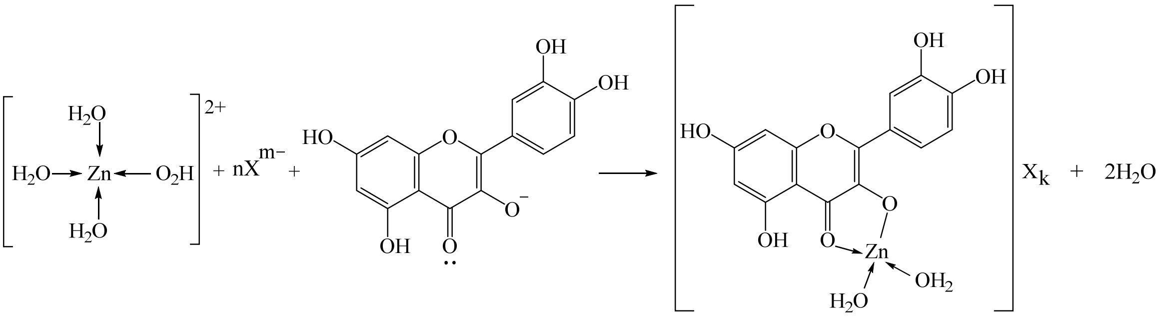
Since the mid-20th century complexes of flavonoids with metals have attracted the attention of scientists due to their unique pharmacological activity in comparison with the activity of initial flavonoids. This will allow to use these compounds in the future to develop new low-toxic, highly effective drugs. Due to the pronounced electron-donor properties, flavonoids are able to bind metal ions and influence their balance in biological systems. Currently, close attention is paid to the study of structural fragments of flavonoid which are involved in the formation of a coordination link [1-3].

The interaction of 3,3',4',5,7-pentahydroxyflavone with zinc salts at pH 6 ÷ 9 and the initial mole ratio of the ligand:Zn^{2+} from 1:1 to 1:2 was synthesized complex compounds. Molecular structure was identified by UV-vis, ESI-MS, IR and 1H NMR-spectroscopy.



X = CH_3COO, NO_3, Cl, SO_4; n = 1,2; m = 1,2; k = 1,2.

Monoligand 3,3',4',5,7-pentahydroxyflavone complexes with zinc ions were formed due to the interaction of the 4-C=O and 3-O-site. The highest yield of the complex is observed at pH = 8, the initial molar ratio of the ligand:Zn^{2+} 1:2 and in the presence of the sulfate anion of the zinc salt. Complex compounds are crystalline powders of green color, soluble in DMSO under ultrasonic irradiation.

The fluorescent properties of complexes were studied. 3,3',4',5,7-pentahydroxyflavone complexes with zinc ions are characterized by green fluorescence. Complex compounds can find wide application as dyes for recognition of living cells.

The use of modern physico-chemical methods of analysis ensures the reliability of the results obtained.

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FUNCTIONAL HYBRID COMPOSITES OF CELLULOSE HYDROGELS AND BIOLOGICALLY ACTIVE Zn(II) 1,10-PHENANTHROCYANINES

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The super-swolen hydrogels based on natural polymeric materials attract considerable attention as scaffolds for medicals for biomedical application. Re-diffusion of biologically active compounds from matrices of the hydrogels mostly defines their prolonged effect. In connection with this, elaboration of methods for preparing the functional hybrid composites by embedding biologically active agents into the polymeric hydrogels and their target desorption is a nowadays problem. In our study cellulose hydrogels obtained by self-assembly of deciduous and flax powder celluloses dissolved in solution of DMAA/LiCl [1] have been used as polymeric matrices. Three types of new electron-rich C(sp^2)-conjugated 1,10-phenanthrocyanine complexes of zinc(II) in hydroacetate forms: Zn^{2+}(μ-phencyanine')Zn^{2+} $(OAc)_4 \cdot HOAc$ (1), (phen)Zn^{2+}(μ-phencyanine')Zn^{2+}(phen)$(OAc)_4 \cdot HOAc$ (2) и [(phen)$_2$$Zn^{2+}$ (μ-phencyanine')Zn^{2+}(phen)$_2$]$(OAc)_4 \cdot HOAc$ (3) containing the bridged chromophor N,N'–N",N"' bis-chelate ligands μ-phencyanine', the derivatives of dihydro-bi-1,10-phenanthrolines (phen–1,10-phenanthroline) have been used as biologically active compounds. They have been synthesized by a new methodology of the metal-mediated non-dehydrogenative C(sp^2)H-coupling of 1,10-phenanthroline ligands in melts of corresponding 1,10-phenanthroline precursors [2]. These complexes exhibit *in vitro* high antibacterial and antitumor activity to the carcinoma cells MCF-7. They can be used as components of transdermal therapeutic systems as well. The hybrid composites of the cellulose hydrogels with the intercalated complexes have been synthesized by the diffusion-sorption method. The diffusion of the complexes 1-3 into the matrices has been carried out from 0.36-1.06% aqueous solutions. Diffusion time and molar ratio cellulose/complex have been varied. We have determined that maximal concentrations of the complexes inside matrices, which were directly proportional to the initial concentrations, have been reached during 5-7 days. To determine what sorts of interaction between the cellulose matrix and the complexes can be expected, FTIR study of the hybrid composites has been performed. We have estimated that the synthesized compounds appeared as a result of bulk diffusion-sorption interplay and chemical interaction between the cellulose and the complexes as well.

[1] N.E. Kotelnikova, A.M. Mikhailidi, Y.V. Martakova, S. Andersson. *Cellulose Chem. Technol.,* **2016***, 50,* 5-6, 545-555.
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BIOLOGICALLY ACTIVE C(sp^2)-CONJUGATED Zn(II) 1,10-PHENANTHROCYANINES: SYNTHESIS, GLASSY SUPRAMOLECULAR STRUCTURE, ELECTRON-RICH NATURE AND ESR SPECTRA

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Biological active electron-rich C(sp^2)-conjugated 1,10-phenanthrocyanine binuclear complexes of zinc(II): Zn^{2+}(μ-phencyanine)$Zn^{2+}(OAc)_4$ (1), (phen)Zn^{2+}(μ-phencyanine)Zn^{2+}(phen)$(OAc)_4$ (2) and [$(phen)_2Zn^{2+}$(μ-phencyanine)$Zn^{2+}(phen)_2$]$(OAc)_4$ (3) containing the bridged chromophoric N,N’–N,N” bis-chelate 1,10-phenanthrocyanine ligands μ-phencyanine – *dihydro-bi-*1,10-phenanthrolines (phen = 1,10-phenanthroline) have been synthesized by new methodology of the *metal-mediated* non-dehydrogenative C(sp^2)H-coupling of 1,10-phenanthroline ligands inside the fusions of the corresponding 1,10-phenanthroline precursors [1]. Then, they have been converted into the form of the corresponding hydroacetates: Zn^{2+}(μ-phencyanine’)$Zn^{2+}(OAc)_4$·HOAc (4), (phen)Zn^{2+}(μ-phencyanine’)Zn^{2+}(phen)$(OAc)_4$·HOAc (5) and [$(phen)_2Zn^{2+}$(μ-phencyanine’)$Zn^{2+}(phen)_2$]$(OAc)_4$·HOAc (6), μ-phencyanine’ – *derivatives* of dihydro-bi-1,10-phenanthrolines. Complexes 1-6 have the complicated supramolecular structure. In the solid state, they have a glassy form while in their solutions, they form complex aggregates. It reflects polymorphism of the forms that form during the synthetic process. The electron-rich nature is typical for the bridged chromophoric 1,10-phenanthrocyanine ligands μ-phencyanine and μ-phencyanine’. These ligands are responsible for the strong bands in the electron absorption spectra of the complexes 1-3 in the visible area ($\lambda_{max.}$ ~ 550 nm). The absorption spectra of the complexes 4-6 have $\lambda_{max.}$ ~ 380 nm (near UV). The complexes 1-6 give the signals in ESR spectra with g-factor 2.0015-2.0055 (180–290 K) in their solid state as well as in their solutions. The ESR signals have been assigned to the bridged electron-rich 1,10-phenanthrocyanine ligands. The proposed mechanisms of generation of the diradical triplet state, in particular thermal excitation, regarding the zinc(II) complexes with 1,10-phenanthrocyanines have been considered as well. Both groups of the complexes 1–3 and 4–6 show *in vitro* the strong antibacterial and antitumor properties to the breast carcinoma MCF-7. The water-soluble compounds 4–6 are especially perspective as active components of the transdermal therapeutic systems.

[1] V.N. Demidov, S.A. Simanova, A.I. Savinova et al., *Russ. Chem. J.*, **2009**, *53*, 128-134.

Recording of the ESR spectra have been carried out at the Resource centre “Magnetic resonance research methods” of Scientific instrument park St.Pb.St.University.

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CATALYTIC INFLUENCE OF BIMETALLIC ADDITIVES ON THE PROCESS OF THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

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Searching for methods of obtaining effective catalysts and studying their properties are subjects of wide theoretical and applied research. One of the new and promising methods for obtaining bimetallic catalysts is the thermal decomposition of binary complex compounds (BCC) consisting of a complex cation and a complex anion of various metals.

In the present work, the catalytic activity of the thermolysis products of BCCs has been studied in the decomposition reaction of ammonium perchlorate (AP). This reaction is well studied due to its great practical importance. AP is one of the components of composite solid propellants. Catalyst samples were obtained by thermal decomposition of BCC $[Co(en)_3][Fe(CN)_6]\bullet 2H_2O$ in a hydrogen atmosphere at 400°C – sample **I**; $[Co(en)_3]_4[Fe(CN)_6]_3\bullet 15H_2O$ in a hydrogen atmosphere at 400°C – **II** and in air at 400°C - **III**; $[Cutn]_3[Fe(CN)_6]_2\bullet 8H_2O$ in air at 300°C - **IV**. Tests of the catalytic activity of the samples were carried out using the AP + 1% catalyst compositions, which were prepared by thoroughly triturating and mixing the corresponding amounts of components. The catalytic activities of the additives were evaluated by decreasing of the outset and complete temperature of AP decomposition. Therefore the thermal analysis of compositions was carried out in air (Fig. 1).

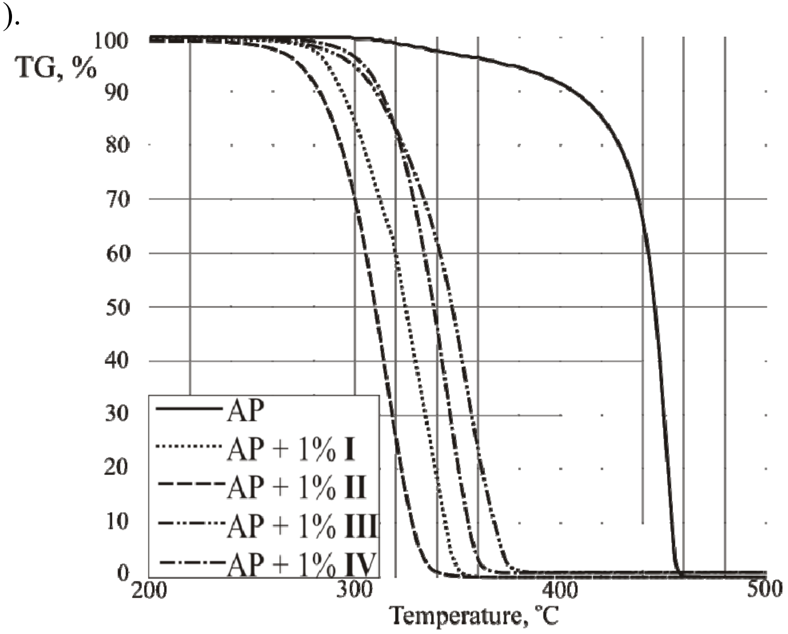

Figure 1. TG curves of pure AP and catalytic compositions.

It is established that all the test samples lower the complete temperature of AP decomposition in the following order **II** > **I** > **IV** > **III**. The decrease of the complete temperature of AP decomposition is from 80 (**III**) to 120°C (**II**). The decrease of the outset temperature of AP decomposition is small and amounts ~ 80°C for the sample **II**, and ~ 50°C for other samples.

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ISOPOLYMOLYBDATE- AND ISOPOLYVANADATE ANIONS IN AQUEOUS AND AQUEOUS DIMETHYLFORMAMIDE MEDIUM AND IN SALTS

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According to the data of pH-potentiometric titration, the complexation processes in $Na_2MoO_4 – HCl – NaCl – C_3H_7ON – H_2O$ and $Na_3VO_4 – HCl – NaCl – C_3H_7ON$ (10-40 vol.%) – H_2O (Cv = 0.01 - 0.1 mol/L; μ = 0.5 mol/L) and the concentration formation constants of isopolymolybdate- and isopolyvanadate-anions were calculated according to the CLINP 2.1 program; the diagrams of isopolyanion distribution are plotted as a function of acidity and concentration, and schemes for their transformation in aqueous dimethylformamide medium are proposed. The pH (acidity) zones of the dominance of isopolymolybdates and isopolyvanadates are established as a function of the concentration of MoO_4^{2} , and VO_4^{3-}- ions; the C_3H_7ON and H_2O ratios in the systems. According to the results of mathematical modeling in aqueous media at a concentration of molybdenum C≤0,05 M in the acidity range Z = 0,5-2,5 the tetraiones of the two compositions $Mo_4O_{13}^{2-}$ and $Mo_4O_{14}^{4-}$ dominate in the solution, and the protonated hexamolybdates $HMo_6O_{21}^{5-}$ and $H_2Mo_6O_{21}^{4-}$ are in minor amounts. In the dimethylformamide medium the effect of increasing the concentration of organic solvent on the composition and distribution of isopolymolybdate-anions is shown, namely: protonated hepta- and octa-ions are formed in dilute solutions, unlike aqueous systems, and octa- and tetramolybdate-anions dominate in decimolar solutions with negligible the content of the other ions $Mo_2O_7^{2-}$, $Mo_6O_{21}^{6-}$, $Mo_4O_{14}^{4-}$, $HMo_7O_{24}^{5-}$.

To confirm the stabilizing effect of dimethylformamide (DMF) on the formation of tetra-, hexa- and octa- molybdate-anions, the synthesis of salts with tetraethylammonium cation in decimolar systems and 25% DMF content was carried out. The composition of crystalline products was determined by chemical, X-ray phase analysis and IR spectroscopy and showed that in the acidity range Z = 1,14 – 1,80 white crystals of octamolybdate $[N(C_2H_5)_4]_4Mo_8O_{26}\cdot nC_3H_7ON\cdot mH_2O$ precipitate after the separation of white crystals of tetramolybdate $[N(C_2H_5)_4]_2Mo_4O_{13}\cdot nC_3H_7ON\cdot mH_2O$ at Z = 1.50 and yellow hexamolybdate crystals $[N(C_2H_5)_4]_2Mo_6O_{19}\cdot nC_3H_7ON\cdot mH_2O$ at Z = 1.80. Salts with hexa-, tetra- and octamolybdate anion, which do not precipitate from water solutions, were obtained from the medium with DMF by precipitation with a cation of the inorganic nature – barium.

In the system with vanadium in the aqueous organic medium, as well as in the aqueous medium, it was possible to detect the existence of three-($V_3O_9^{3-}$) and tetrametavanadates ($HV_4O_{12}^{3-}$) in a narrow range of concentrations (0,01-0,1 mol/L). The decavanadate anion $V_{10}O_{28}^{6-}$ is fixed at Z = 2,50, which is marked by an inflection point on the potentiometric titration curve. There are no tetravanadates of composition $V_4O_{12}^{4-}$ and $V_4O_{13}^{6-}$. In the decimolar solution of sodium orthovanadate such polyoxoanions dominate: $V_4O_{12}^{4-}$, $HV_4O_{13}^{5-}$ and $V_{10}O_{28}^{6-}$ with an insignificant amount of protonated decavanadate $H_3V_{10}O_{28}^{3-}$ and $V_3O_9^{3-}$. With an increase in the DMF concentration of up to 25% by volume, the formation of the unprotonated form of decavanadate anion is stabilized in the system, with the formation of aprotic three- and tetravanadates in larger amounts at Z> 2,5. Crystals of composition: $[N(C_4H_9)_4]_5V_3O_{10}\cdot 4H_2O\cdot C_3H_7ON$, $[N(C_4H_9)_4]_4V_4O_{12}\cdot 4H_2O\cdot 2C_3H_7ON$, $[N(C_4H_9)_4]_6V_{10}O_{28}\cdot 4H_2O\cdot 4C_3H_7ON$; $In_4(V_4O_{12})_3\cdot 7H_2O\cdot 3C_3H_7ON$; $In_2V_{10}O_{28}\cdot 5H_2O\cdot 5C_3H_7ON$ were obtained.

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COMPLEX FORMATION OF METHOTREXATE WITH MONOMERIC AND DIMERIC β-CYCLODEXTRINS: ^{1}H NMR STUDY

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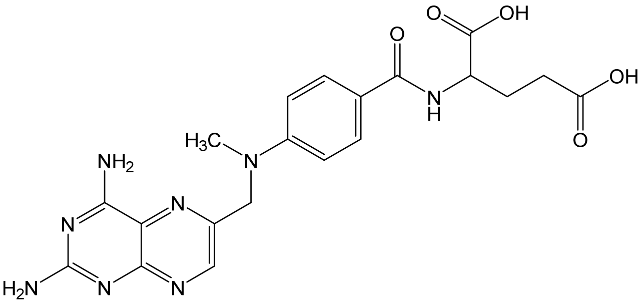
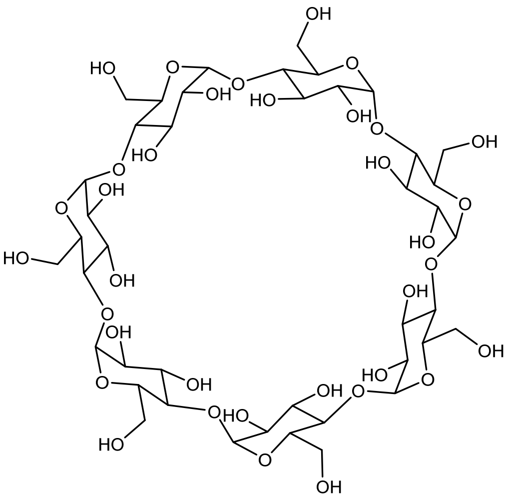
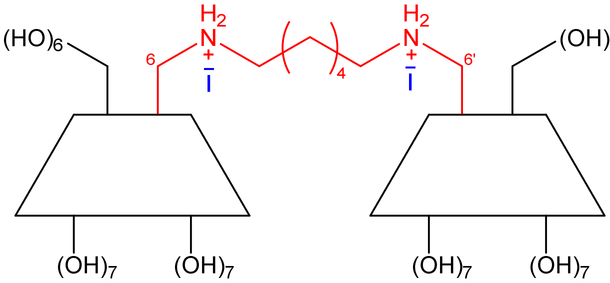
Methotrexate is an effective anti-inflammatory drug widely used in the treatment of cancer diseases, psoriasis and rheumatoid arthritis. Difficulties in the application of this drug are determined by its poor solubility in water, instability in biological fluids and, consequently, low bioavailability. These disadvantages can be partially overcome by complexing methotrexate with cyclodextrins.



methotrexate



β-cyclodextrin



dimeric β-cyclodextrin

In this connection, the complexation of methotrexate with native β-cyclodextrin and its dimeric derivative di-6,6'-dideoxy-6,6'-(hexane-1,6-diyldiaminium)-β-cyclodextrin iodide was studied in phosphate buffer (pH=7.4) using 1D and 2D ^{1}H NMR spectroscopy. Binding mode, stoichiometric composition and stability constants of methotrexate/cyclodextrin complexes were determined on the basis of the experimental data obtained. It was found that native β-cyclodextrin forms 1:1 inclusion complexes with methotrexate, while 1:2 complexation is observed with dimeric β-cyclodextrin. The stability constant of the complexes with dimeric β-cyclodextrin is much higher compared with the native β-cyclodextrin. The deep insertion of methotrexate into cavity of both cyclodextrins was detected. In this case, benzene ring of the methotrexate molecule is included into macrocyclic cavity while its terminal fragments are placed outside and can interact with OH-groups located in the cyclodextrin outer surface.

Acknowledgements This work was supported by Russian Foundation for Basic Research (grant №15-43-03017-r-center-a for study on complex formation of native β-cyclodextrin and grant №16-03-00444 for study on complex formation of dimeric β-cyclodextrin).

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ENERGETIC CHARACTERISTICS OF FREE MOLECULES OF COPPER(I) AND COBALT(II) CARBOXYLATES BY MASS SPECTROMETRY DATA

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The volatile transiton metal carboxylates complexes are of interest due to the opportunity of the determination of structure-properties correlation of these compounds in condensed and gaseous phases as well as their practical application in chemical vapor deposition (CVD) methods for functional materials producing.

Thermodynamic data of studied in the present work complexes Cu(Ac), Cu(Piv) and $Co(Piv)_2$ ($Ac=CH_3COO$; $Piv=(CH_3)_3CCOO$) are not available in the reference literature. Using Knudsen Effusion Mass Spectrometry technique sublimation processes of these substances were investigated in temperature intervals 308-451 K [Cu(Ac)], 373-493 K [Cu(Piv)] and 423-588 K [$Co(Piv)_2$].

The presence of intensive ion currents of metals in mass spectra of the complexes made possible to examine the processes of dissociative ionization and to detect the appearance potential of ions:

$$Cu_2(Ac)_2 + \bar{e} \rightarrow Cu^+ + Cu + 2Ac^\bullet + 2\bar{e} \qquad (1)$$

$$Cu_2(Piv)_2 + \bar{e} \rightarrow Cu_2^+ + 2Piv^\bullet + 2\bar{e} \qquad (2)$$

$$Co_2(Piv)_4 + \bar{e} \rightarrow Co^+ + Co + 4Piv^\bullet + 2\bar{e} \qquad (3)$$

The appearance energies calculation was carried out by the use of the method of extrapolated differences and appearance potential of ion Hg^+ was taken as a standard (Fig.1).

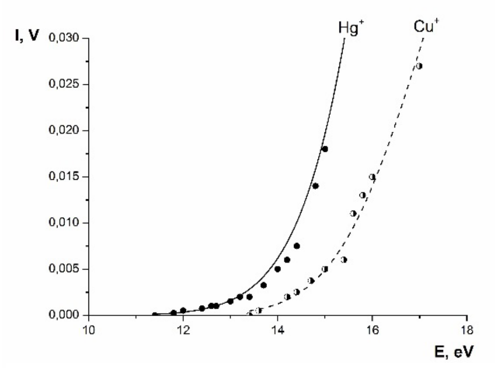

Fig.1. Ionization efficiency curves of standard [Hg^+] and investigated ion [$Cu^+/Cu_2(Ac)_2$].

Using found values of ions appearance potentials upper limit of standard enthalpies of formation of free molecules of studied complexes was estimated (Table 1).

Table 1. Energetic and thermodynamic characteristics of free molecules

Complex	Ion appearance energy, eV	$-\Delta_f H^\circ_{298.15}$, kJ mol^{-1}
$Cu_2(Ac)_2$	12.1±0.3	74
$Cu_2(Piv)_2$	15.3±0.3	772
$Co_2(Piv)_4$	22.7±0.3	1638

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SYNTHESIS AND CRYSTAL STRUCTURE OF NEW DECATUNGSTATES OF COBALT(II), BARIUM(II) AND NICKEL (II)

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The investigation of systems based on the aqueous organic mixture is a important stage towards establishing a systematic link between the composition of the mixed medium and the equilibrium composition of isopolytungstates, especially decatungstates.

To synthesize decatungstates of cobalt(II), barium(II) in the present work aqueous dimethyformamide solution (40 % v/v DMF) of sodium tungstate, acidified to acidity $Z = \nu(H^+)/\nu(WO_4^{2-}) = 1{,}60$, was used. And for nickel decatungstate – aqueous dimethylsulfoxide solution (40 % v/v DMSO) was used. The developed synthetic techniques allowed us to firstly synthesize single crystals: $[Co(C_3H_7NO)_5]_2[W_{10}O_{32}]\cdot$(*CoW₁₀*), $[Ba(H_2O)_2(C_3H_7NO)_3]_2[W_{10}O_{32}]\cdot(C_3H_7NO)_2$ (*BaW₁₀*), $[Ni(C_2H_6SO)_5(H_2O)]_2[W_{10}O_{32}]$ (*NiW₁₀*) with average size 0.15×0.10×0.10mm^3, possessing photochromic properties. The presence of bands at 801 s, 891 s, 960 s cm^{-1} in FTIR-spectra, and also bands at 320-325 nm in absorption spectra of aqueous solutions of the salts confirms the presence of decatungstate anion in the salt composition.

Centrosymmetric anion $[W_{10}O_{32}]^{4-}$ has typical structure (two «square pyramides», consisting of five distorted octahedra WO_6, connected by «bases» through common vertices of four octahedra) (fig. 1). Coordination polyhedron of barium atom in BaW_{10} is monocapped square antiprism, and cobalt in CoW_{10} and nickel in NiW_{10} – octahedron. On the basis of X-ray single crystal analysis of new decatungstates the following characteristics were found: for BaW_{10} triclinic, P-1, a=11.899(3), b = 12.1313(11), c = 13.341(2)Å, α = 70.417(11), β = 64.254(18), γ = 87.185(12)°, V = 1623.7(5) Å^3 at T=293K, Z = 1, ρ = 3.356g/cm^3; for CoW_{10} triclinic, P-1, a=11.2239(7), b = 12.2221(10), c = 13.9184(8)Å, α =71.380(6), β = 89.506(5), γ =72.144(6)°, V = 1713.8(2) Å^3 at T=293K, Z = 1, ρ = 3.100g/cm^3; for NiW_{10} – triclinic, P-1, a=11.9339(7)Å, b = 12.2083(6)Å, c = 12.2083(6)Å, α =75.235(5)°, β = 71.289(6)°, γ =87.785(4)°, V = 1692.44(17)Å^3 at T=293(2)K, Z = 1, ρ = 3.223g/cm^3.

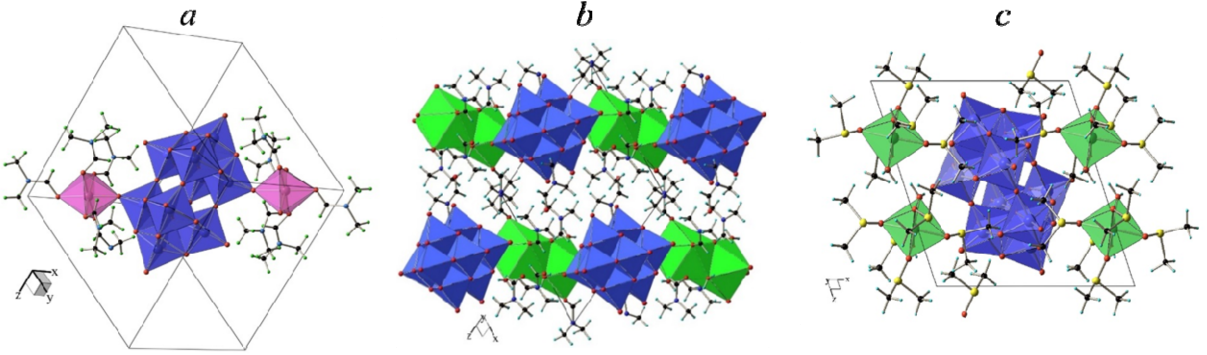

Fig. 1 Structures of new decatungstates: *a* - $[Co(C_3H_7NO)_5]_2[W_{10}O_{32}]$, *б* - $[Ba(H_2O)_2(C_3H_7NO)_3]_2[W_{10}O_{32}]\cdot(C_3H_7NO)_2$, *c* - $[Ni(C_2H_6SO)_5(H_2O)]_2[W_{10}O_{32}]$.

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ZIRCONIUM, YTTRIUM AND CERIUM ALKOXOACETYLACETONATES - COORDINATION COMPOUNDS FOR SOL-GEL OBTAINING OF THIN NANOSTRUCTURED COMPLEX OXIDE SYSTEMS FOR OXYGEN DETECTING

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Alkoxoacetylacetonates are convenient coordination compounds-precursors to obtain thin nanostructured complex oxide systems of a given composition using the sol-gel technology [1]. Changing the composition of the coordination sphere by varying the degree of substitution of the chelating ligand for the alkoxy fragment, it is possible to regulate the hydrolytic activity of the heteroligand complexes obtained. For the preparation of metal alkoxoacetylacetonates, zirconium, yttrium and cerium acetylacetonates were used which, in the desired stoichiometry of the desired oxide, were subjected to a heat treatment in isoamyl alcohol.. Films of the solution of the heteroligand precursors were applied by dip coating to the surface of polycrystalline Al_2O_3 substrates with platinum interdigital electrodes and a microheater on the back side. After the completion of the gelling and polycondensation and drying processes, they were subjected to heat treatment for the crystallization of the oxide phases. As a result, two lines of 2D nanomaterials were obtained: $xZrO_2$-$(1-x)Y_2O_3$ and $yZrO_2$-$(1-y)CeO_2$. The phase composition of the resulting thin films was studied by X-ray phase analysis and Raman spectroscopy, microstructure and dispersion - by scanning electron microscopy. Measurement of gas-sensing properties was carried out on a special installation, as a detectable parameter of the films their resistance was measured on a digital precision multimeter. The films of the $xZrO_2$-$(1-x)Y_2O_3$ system showed some selective sensitivity to large oxygen concentrations at relatively low operating temperatures of 350-450 °C, and $yZrO_2$-$(1-y)CeO_2$ films had high response values over a wide range of concentrations of 0,4-20% O_2 at the operating temperature of 400 °C. Figure 1 shows the dependence of the response magnitude on different concentrations of O_2 for the composition of 90CeO2-10ZrO2. The prospects of this approach for the obtaining of gas-sensing materials were shown experimentally.

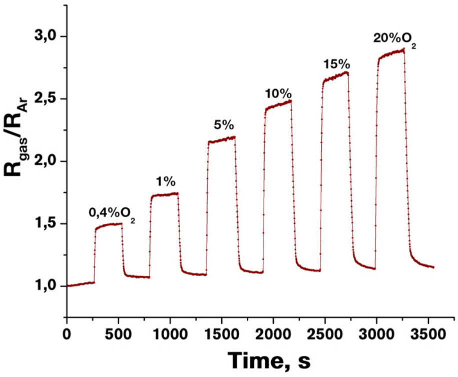

Fig.1 Responses to oxygen of thin films of the composition $90CeO_2$–$10ZrO_2$

[1] N.P. Simonenko, E.P. Simonenko, A.S. Mokrushin, et al., *Russ. J. Inorg. Chem.*, **2017,** *62(6),* 695–701. DOI: 10.1134/S0036023617060213

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MULTIELECTRON REDOX TRANSFORMATIONS OF POLYMERIC TRANSITION METAL COMPLEXES WITH SCHIFF BASE LIGANDS

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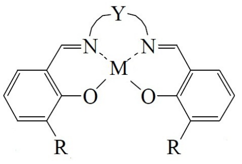
The growing interest in electron-conducting polymers is caused by their possible application as electrochemically active materials for energy storage devices. Polymers capable of multi-electron redox transformations are most interesting for this application because of their high specific capacity. Polymeric transition metal complexes with Schiff-base ligands (poly-[M(Schiff)]) have been previously described as materials that can be reversibly oxidized and reduced by only one electron per a monomer unit. At the same time, every [M(Schiff)] unit (Fig.) potentially has three redox centers: a metal ion and two phenyl rings.

Multielectron redox conversions in compounds containing multiple redox centers are possible if these centers are not in the electronic conjugation. In this work a series of poly-[M(Schiff)] polymers were investigated by cyclic voltammetry (0 – 1.4 V vs. Ag/AgCl/3.0 M KCl; 50 mV/s) and *in situ* electrochemical quartz crystal microbalance (EQCM), and the obtained data was used to calculate the characteristics of redox transformations in the polymers (Table). The polymers used in this work differed by the nature of the metal ion (Ni vs. Co) and the structure of the ligand, which allowed us to vary the degree of electron conjugation between redox centers in the monomer units. As follows from the Table, the maximum number of electrons (per a monomer unit) involved in the polymer oxidation/reduction is determined as 2 for poly-[Ni(Schiff)], and 3 for poly-[Co(Schiff)]. Thus, we have confirmed the ability of poly-[M(Schiff)] polymers to participate in multielectron redox transformations.

Fig. Monomer unit of poly-[M(Schiff)].



M = Ni, Co

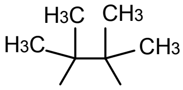
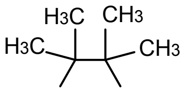
R	Y	
H	-CH_2-CH_2-	M(SalEn)
H		M(SaltmEn)
-OCH_3	-CH_2-CH_2-	M(CH_3O-SalEn)
-OCH_3		M(CH_3O-SaltmEn)

Table. Redox transformations in poly-[M(Schiff)].

Polymer	Number of electrons per a monomer unit (±0.1)	Specific capacity of the polymer, mAh/g (±1)
poly-[Ni(SalEn)]	1.1	93
poly-[Ni(CH_3O-SalEn)]	1.4	99
poly-[Ni(SaltmEn)]	1.3	92
poly-[Ni(CH_3O-SaltmEn)]	2.1	131
poly-[Co(SalEn)]	1.6	130
poly-[Co(CH_3O-SalEn)]	1.8	120
poly-[Co(SaltmEn)]	1.7	113
poly-[Co(CH_3O-SaltmEn)]	3.0	183

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PHOTOACTIVE MOLYBDENUM CLUSTER COMPLEX INCORPORATED IN POLYMERIC MATRIX

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Octahedral molybdenum cluster complexes with the general formula $[\{Mo_6X_8\}L_6]^n$ (X = Cl, Br, I; L = organic/inorganic ligand) can find applications in the fields of biology and medicine due to their superb photoluminescent properties and ability to generate singlet oxygen. However, to use these compounds in living systems they must be stable in aqueous media at physiological pH and have low toxicity. One of the way to achieve this goal is to incorporate the cluster complexes into a water-soluble biocompatible organic matrix.

In this work dextran (natural polysaccharide) with molecular mass of 70 kDa (DEX70) and its oxidised forms, namely dextran polyaldehyde (DPA70-2 и DPA70-15), were selected as water-soluble organic matrix. As for starting cluster complexes we used $(Bu_4N)_2[\{Mo_6I_8\}(NO_3)_6]$, which contains labile nitrate terminal ligands. Incorporation of the cluster complex into matrix was carried out in dimethylsulfoxide. In the course of this work, we chose optimal conditions (reaction time, ratio and concentration of reagents) to produce water-soluble materials with maximum content of the cluster complex.

We determined content of molybdenum in all materials obtained in this work using ICP-AES. From the data we can see, that material based on the most oxidized polymer DPA70-15 contain more molybdenum cluster complex.

In addition, luminescent properties were investigated (Fig. 1). The best photophysical characteristics has material based on DPA70-15. The quantum yield for the solid sample $\{Mo_6I_8\}$@DPA70-15 is 12%.

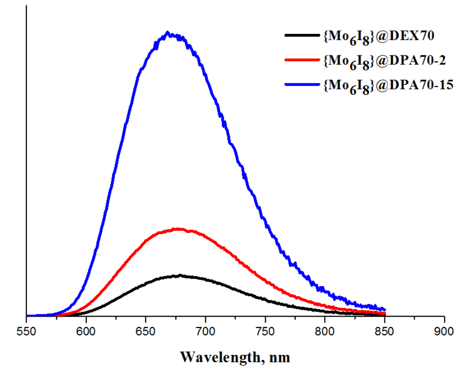

Figure 1. Emission spectra

In order to assess the potential of these hybrid materials in biology and medicine, we also evaluated their biological properties. Cytotoxicity was examined by MTT-assay on tumour cell lines Hep2. All materials demonstrated low toxicity within the whole range of studied concentrations, so the half-maximum inhibitory concentrations (IC_{50}) were not established. Cellular uptake was evaluated using flow cytometry. From this data only material based on DPA70-15 uptakes into the cells.

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A NEW SIMULTANEOUS SYNTHESIS OF PORPHYRIN COMPLEXES WITH CENTRAL CATIONS OF DIFFERENT VALENCE

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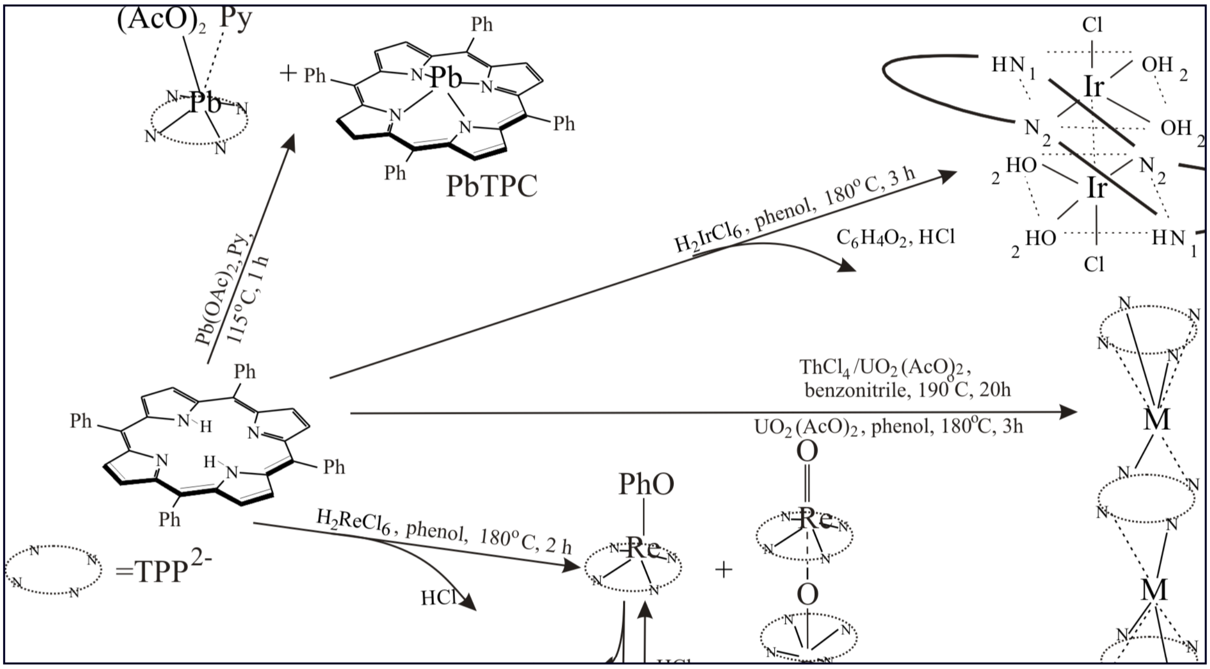
Complex formation between zero-valent metal carbonyls and porphyrins is the classical approach of metalloporphyrins (MPs) synthesis. Since the first preparation of MP carbonyl complex by Tsutsui and his co-workers [1], innumerable examples of compounds of cobalt, vanadium, iron, nickel, chromium, molybdenum, ruthenium, osmium, rhodium, iridium, rhenium and technetium in low oxidation state with CO as axial ligand have been synthesized [2]. MP carbonyl complexes are of suitable starting materials for investigations in the noble metal porphyrin field because of possibility to synthesize the compounds with different coordination sphere by oxidation and ligand-exchange reactions.

When metal compounds containing metal in the oxidation state higher than two are used in complexation with porphyrins, the metal cation, the porphyrin, or solvent can be involved in redox reactions. The latter may facilitate formation of complex with reduced macrocycle/metal or mixtures of two complex species. In order to obtain porphyrin complexes of one metal in different oxidation states, a one-pot synthesis by reductive coordination of p/3d-4d metal in stable oxidation state, can been used.
Simultaneous generation of tetraphenylporphyrin complexes of Pb^{II} and Pb^{IV} from $Pb(OAc)_2$, U^{III} and U^{IV} from $U^{VI}O_2(AcO)_2$, Ir^{I} and Ir^{III} from $(H_3O)_2Ir^{IV}Cl_6$, Re^{III} and Re^{V} from $H_2Re^{IV}Cl_6$ in the appropriate conditions according to scheme, is presented.



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[2]. In *Porphyrin Handbook*. V. 3. Kadish, K. M.; Smith, K. M.; Guilard, R., Ed. Academic Press, San Diego, San Francisco, New York, Boston, London, Sydney, Tokyo, 2000.

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INNER- AND OUTER SPHERE HYDROPHOSPHORYLATION OF 2,6-DIBENZYLIDENECYCLOHEXAN-1-ONE AND 3,5-BIS(BENZYLIDENE)-PIPYRIDINE-4-ONES

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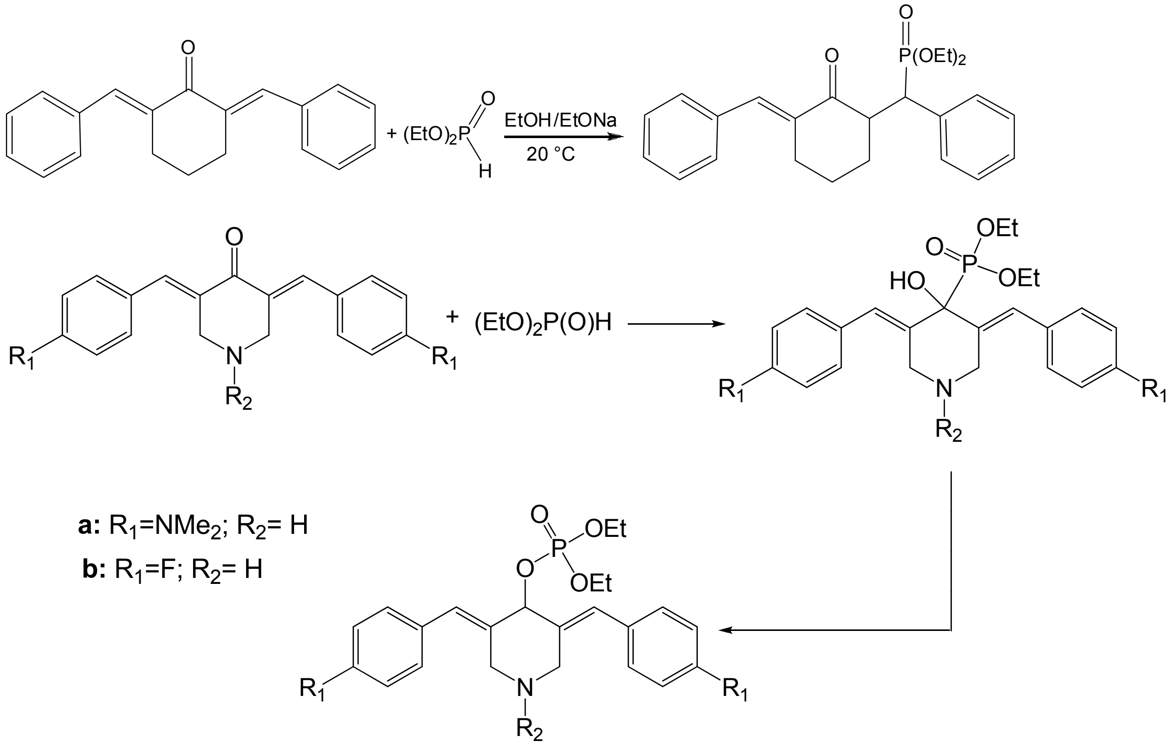
Firstly we have studied the hydrophosphorylation of the non-coordinated functionalized conjugated dienones. Previously it was considered that 3,5-bis(benzylidene)pipyridine-4-ones are inert towards dialkyl(H)phosphonates in various conditions. We've managed to find the conditions allowing to obtain the products of 3,5-bis(4-(dimethylamino)benzylidene)-pipyridine-4-one and 3,5-bis(4-fluorbenzylidene)-pipyridine-4-one.



Also we have studied the inner-sphere hydrophosphorylation of 2,6-dibenzylidenecyclohexane-1-one 3,5-bis(benzylidene)pipyridine-4-ones coordinated with carbonyltungsten and carbonyltriazacyclohexanetungsten cores.

The strong bonding of dienones with the metals' core observed both for (dienone)$W(CO)_4$ and (dienone)W(tach)(CO) via the comparison of spectral signatures and the results of quantum-chemical calculations makes an obstacle for the addition reaction towards the C=C bonds of the dienone. The inner-sphere hydrophosphorylation occurs according with the Abramov's reaction route with subsequent hydroxyphosphonate-phosphate rearrangements in the presence of the strong base.

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University

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COORDINATION POLYMERS BASED ON CUCURBIT[N]URILS

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The use of cucurbit[6]uril as a polydentate ligand was efficient for the isolation of kinetically labile alkali and alkaline earth metal complexes from aqueous solutions. Complexes with molecular and chain structures are known. The design of highly organized organic-inorganic supramolecular architectures by selfassembly of several organic and inorganic building blocks is a topical task in chemistry.

The chain coordination polymers $[\{Li(H_2O)_3\}_2(CB[6])]Cl_2\cdot 6H_2O$ and $[Na_3(\mu\text{-}H_2O)_4(H_2O)_4(CNPy@CB[6])]Cl_3$□$8H_2O$ were prepared by heating of a mixture of metal chloride, cucurbit[6]uril, H_2bdc or CNPy, and water. According to X-ray diffraction data, binding of cations with CB[6] occurs through coordination of the oxygen atoms of the cucurbit[n]uril portals to metal atoms. Both complexes of the above composition isolated to the solid phase as supramolecular compounds with CB[6] were structurally characterized for the first time.

The crystal structure of $[\{Li(H_2O)_3\}_2(CB[6])]Cl_2\cdot 6H_2O$ is composed of alternating $[\{Li(H_2O)_3\}_2(CB[6])]^{2+}{}_\infty$ polymeric chains, solvent water molecules, and chloride anions.

The crystal structure of $[Na_3(\mu\text{-}H_2O)_4(H_2O)_4(CNPy@CB[6])]Cl_3\cdot 8H_2O$ is composed of alternating $[Na_3(\mu\text{-}H_2O)_4(H_2O)_4(CNPy@CB[6])]^{3+}{}_\infty$ polymeric chains, solvent water molecules, and chloride anions. The polymeric chain consists of alternating CB[6] molecules linked through carbonyl groups to the centrosymmetric linear trinuclear aqua complex cations $[Na_3(\mu\text{-}H_2O)_4(H_2O)_4]^{3+}$.

Thus, the possibility of using the supramolecular approach for isolation of coordination polymers based on CB[6] from an aqueous solution has been shown.

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EFFECT OF THE J_2 COORDINATION IN THE OKM-2 PHOTOPOLYMERIZATION

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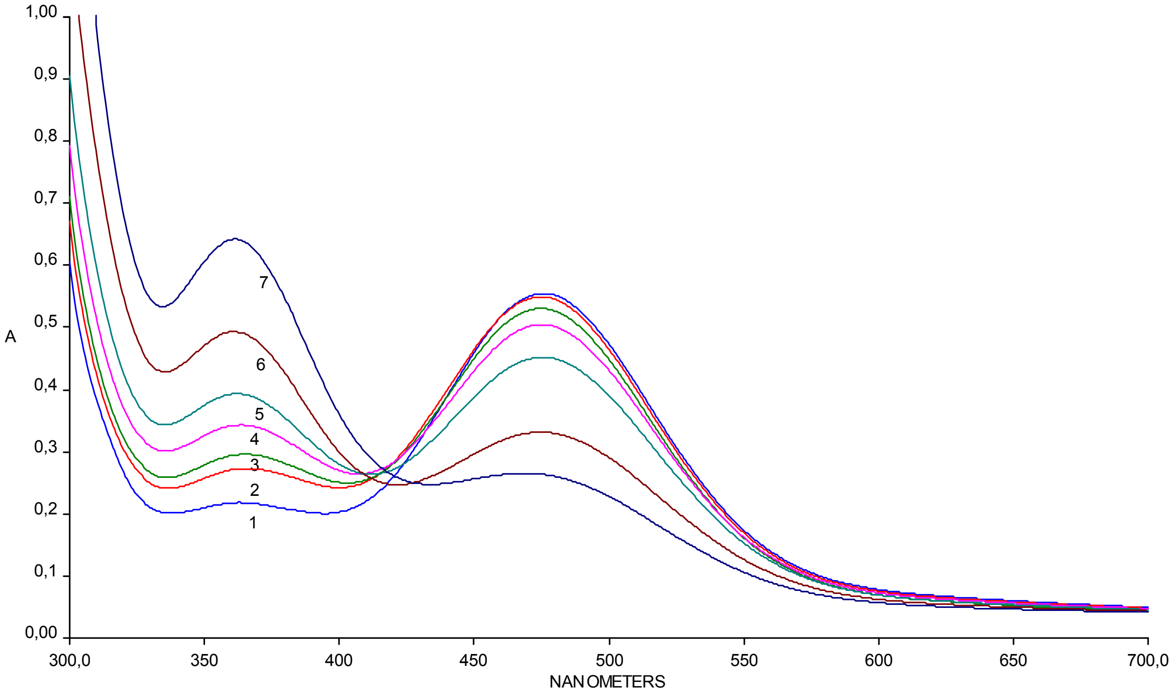
Transparency of the optical systems using polymer compositions is one of the most important properties of such systems. Polymer OKM-2 may have optical defects. The reason of the defects is not optimal condition for obtaining polymers. We used initial DMFAF system (irradiation in near UV-region (360 nm) for photopolymerization OKM-2. As well known, molecules of J_2 coordinates with alkenes [1] and CT-band is obtained in these regions. We investigated the dynamic changes of the spectra depending from the time of the irradiation in the near UV and visible regions. The results are shown in the fig.



It was shown that CT-band (360 nm) is increases at the first stage of irradiation (to 30 sec) and intensity of the iodine band (470 nm) is decreases. But in the cases more irradiation (to 45 sec) CT-band is stable and then is decreases. The absorption band of the DMFAF is compensated in the second canal of the spectrometer. The results of the measurement: the first stage is CT-complex formation, the second stage is the polymerization process. The CT-complex is regulator of the chain growing.

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Acknowledgements -

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CATALYTIC SYSTEMS BASED ON COMPLEXES OF D-ELEMENTS FOR THE OXIDATION REACTIONS OF ALIPHATIC THIOLS IN BIOLOGICAL OBJECTS

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The oxidation process associated with the transformation of endogenous thiols (cystein (Cys), 2-aminoethanethiole (2-aet), glutathione (GSH), etc.), as regulators of the Ox-Red or signal process in living organisms, is schematically represented by the reaction:

$$2R\text{-}SH - 2\bar{e} \rightleftarrows R\text{-}S\text{-}S\text{-}R + 2H^+ \qquad (1)$$

The aforementioned oxidation processes appear to be signal processes and are carried out by endogenous oxidizers, such as Reactive oxygen species (ROS: H_2O_2 etc.). Also, they can be catalyzed by enzymes, including metal-containing ones.

The experimental research of a trace amount of $[Pd_2(\mu\text{-}OH)_2(NH_3)_2]^{2+}$ and $[Pd_2(\mu\text{-}OH)_2(dipy)_2]^{2+}$ coordination complexes (10^{-7} – 10^{-9} M) in oxidation reactions of GSH to GSSG showed increase of catalytic efficiency and biological activity in compare with the analogous reactions involving *cis*-$[Pt(NH_3)_2Cl_2]$. The studies of biological activity of the drugs developed on the basis of the specified complexes were conducted on the A431 line cells of an epidermoid carcinoma of the human and cells of an acute myeloid leukemia of HL-60. Similar drugs are used for chemotherapy support as modulators of system of internal protection of an organism. The initial active centers of proposed catalysts for the reaction (1) are $\{L_2M(\mu\text{-}OH)_2ML_2\}^{2+}$ and $\{L_2M(\mu\text{-}OH)_2M'(\mu\text{-}OH)_2ML_2\}^{2+}$ ($M = Pd^{II}$; $M' = Cu^{II}$; L = ammine) polynuclear species. As the main reactions the following are considered:

$$[L_2M(\mu\text{-}OH)_2ML_2]^{2+} + 2RSH \rightleftarrows [L_2M(\mu\text{-}SR)_2ML_2]^{2+} + 2H_2O \qquad (2)$$

$$[L_2M(\mu\text{-}SR)_2ML_2]^{2+} + H_2O_2 \rightleftarrows \{[M_2(\mu\text{-}SR)_2(OH)_2L_4]^{2+}\} \qquad (3)$$

$$\{[M_2(\mu\text{-}SR)_2(OH)_2L_4]^{2+}\} \rightleftarrows [L_2M(\mu\text{-}OH)_2ML_2]^{2+} + RSSR \qquad (4)$$

Equations (2) and (4) represent the reaction stages, where catalyst $[L_2M(\mu\text{-}OH)_2M'L_2]^{2+}$ is consumed and regenerated again. Reaction (3) appears to be the main stage on which the formation of an intermediate $\{[M_2(\mu\text{-}SR)_2(OH)_2L_4]^{2+}\}$, capable to intramolecular Ox-Red process (4), is possible.

Modeling, carried out by the quantum-chemical DFT method (M06, PBE0/Def2-TZVP) showed that the suggested catalysts keep a steady spatial complementarity at all stages of the process. Their main and interrelated functions consist of spatial approach of RS^- anions in an inner sphere of bridge coordination complexes, which is necessary for its disulfide (-S-S-) cross-link and securing complementary n-electron Ox-Red transfer under the transformation of those anions to disulfide R_2S_2. It was experimentally determined that under the combination of Pd^{II} coordination ions with the trace amount of Cu^{II} ions the catalytic activity essentially increases. DFT quantum-chemical modeling showed that Cu^{II} and Pd^{II} ions are able to form a polynuclear active center $\{Pd^{II}(\mu\text{-}OH)_2Cu^{II}(\mu\text{-}OH)_2Pd^{II}\}^{2+}$, that provides the approach of the greater number of mutually oriented thiolate anions, which affects the rate of disulfide formation.

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NEW EXTRACTION SYSTEM FOR SEPARATION OF RARE EARTH ELEMENTS FROM NEUTRAL MEDIA

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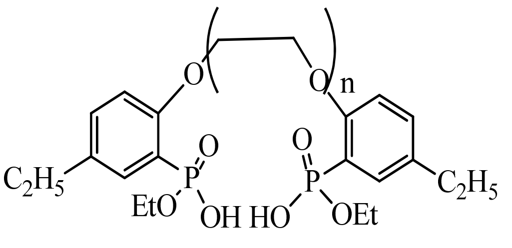
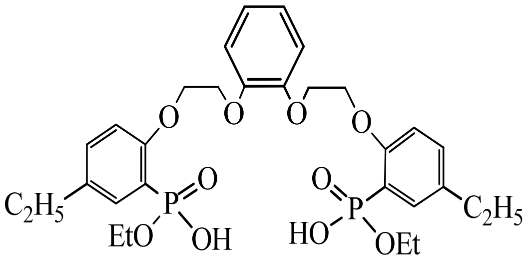
[b]*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Russia*

New extraction systems for separation of REEs on the base of acid phosphoryl-containing podands L^n (n=1-5), L and a 1,1,7-trihydrododecafluoroheptanol were studied. Effective and selective separation of REEs depends on the structural features of podands (length (n) and rigidity of polyester chain) and acidity of the medium.



L^n n=1-5



L

It was found that L^3 is the best extractant of REEs among ligands. Embedding of the benzene fragment in the ethylene glycol chain of the podand L^3 decreases extraction (fig.1).

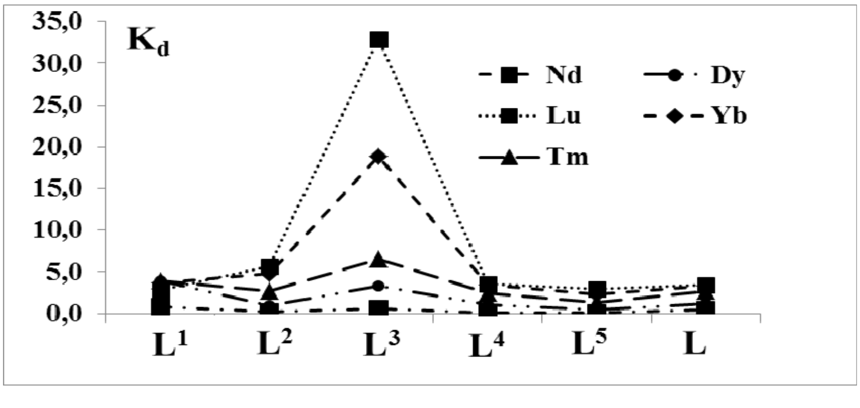


Fig.1 The dependence K_d of length (n) and stiffness of polyester chain

The extraction efficiency was enhanced from the neutral media. The REEs of the yttrium subgroup were found to be extracted much better than that of the cerium subgroup.

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COMPETITIVE HYDROGENATION OF CHLORONITROBENZENES IN THE PRESENCE OF PALLADIUM-PHOSPHORUS NANOPARTICLES

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The report presents the results of an investigation of the nature of catalytically active particles in hydrogenation in systems formed from $Pd(acac)_2$ and P_4 in hydrogen under mild conditions. The reduction of $Pd(acac)_2$ by hydrogen in the presence of white phosphorus leads to the formation of nanoparticles 5-6 nm in diameter. The phase composition of the nanoparticles formed is represented by palladium phosphides and Pd(0) clusters. The ratio between Pd(0) clusters and phosphides, the composition of phosphides, the state of the surface layer and the size of the Pd(0) clusters are determined by the P/Pd ratio [1]. Since the beginning of the 21st century, transition metal phosphides have been postulated as a new potential class of hydroprocessing catalysts [2]. Therefore, both Pd(0) clusters and palladium phosphides can be hydrogenation catalysts. To determine the nature of the catalytically active species under mild conditions, the method of phase trajectories of the competitive hydrogenation of chloronitrobenzene (CNB) isomers is used. The tangent of the slope angle of the tangent to the abscissa axis at each point of the phase trajectory corresponds to differential selectivity [3]. The coincidence of phase trajectories indicates identical active species.

A formal kinetic study showed that the adsorption of o-CNB and hydrogen proceeds on the same active centers of the Pd-P catalyst, and molecular hydrogen participates in the limiting stage. Competitive hydrogenation of o-CNB and m-CNB in the presence of 6 different palladium catalysts (Pd-black, Pd/C, Pd-P nanoparticles (P/Pd = 0.3, 0.7, 1.0)) allowed us to establish the following patterns. The phase trajectories of the competitive hydrogenation of the chloronitrobenzene isomers depended on the P/Pd ratio and the nature of the precursor. The coincidence of the phase trajectories for the Pd-P catalyst (P/Pd = 0.3) and Pd/C indicates that Pd(0) clusters are active in the Pd-P catalyst (P/Pd = 0.3). These data also confirm the model proposed for Pd-P nanoparticles (P/Pd = 0.3) such as core@shell (core - Pd_6P, shell - Pd(0) clusters). The coincidence of the phase trajectories for the three Pd-P catalysts (P/Pd = 0.7, 1.0, precursor $Pd(acac)_2$, P/Pd = 0.3, $PdCl_2$ precursor) containing small palladium clusters and palladium phosphides of different composition in the surface layer again indicates the predominant activity of Pd(0) clusters in comparison with palladium phosphides under the mild conditions. The difference in the phase trajectories of the competitive hydrogenation of the CNB isomers for the Pd-P catalyst (P/Pd = 0.3) from the Pd-P catalysts (at P/Pd = 0.7; 1.0) is associated with a decrease in Pd(0) cluster sizes with increasing P/Pd ratio and the structure-sensitivity of the hydrodehalogenation reaction.

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THE INFLUENCE OF THE COMPOSITION AQUEOUS-ORGANIC SOLVENT ON THE PROCESS OF COMPLEXATION OF THALLIUM(I) WITH 18-CROWN-6-ETHER

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Siberian state aerospace University named after academician
M. F. Reshetnev, Krasnoyarsk, Russia.

The accumulation and study data on the formation of complexes in solutions is an important task of modern chemistry. Prediction of the forms of existence of substances in solution, the ability to manage the processes of their formation and destruction are of great importance for applied Sciences. The importance for them due to the fact that a great many technological processes use the solutions as the environment in which the chemical transformation.

In the present work studied the processes occurring during the complexation of the ions Tl^+ with 18-crown-6-ether under standard conditions. As the medium used is a mixed aqueous-organic solvents based on dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF). The choice of research objects and environments due to the lack of literature data about the properties and stability of complex compounds of thallium (I) with crown-ethers [1].

The complexation process was studied by the method of direct potentiometric titration, using as indicator electrode - thalliumselective electrode, and chlorine-silver electrode as the reference electrode. The measurements were carried out at pH – meters N5170 [2].

The values of logarithms of stability constants (±0.04) crown ether complexes of thallium(I) from a mole fraction of aprotic dipolar solvent is presented in table

Solvent	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
DMSO	2.81	-	2.66	2.58	2.50	-	2.34	2.27
DMF	2.70	2.83	2.95	3.08	3.21	3.33	3.46	3.59

On the basis of the data obtained found that the stability of the studied complexes with the change in the composition of the mixed aqueous-organic solvent varies antisymbatic similar in these two solvents. This difference is due to the specific interactions and different structure of the studied solvents [3], which have different impacts on the values of stability constants for the same complex.

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COMPLEXATION BETWEEN CU(II) AND HYDRAZONES DERIVED FROM PYRIDOXAL 5’-PHOSPHATE AND PYRIDINECARBOXYLIC ACIDS HYDRAZIDES IN AQUEOUS SOLUTIONS AT PHYSIOLOGICAL PH

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Schiff bases formed by pyridoxal/pyridoxal 5’-phosphate (PLP) and pyridinecarboxilic acids hydrazides are of biological relevance. Pyridoxal isonicotinoyl hydrazone (PIH) prevents copper-mediated free radicals formation in presence of ascorbate thus providing antioxidant activity [1]. The mechanism of such action could be related to the PIH capability of Cu^{2+} binding, which, in turn, may prove useful for treatment of Wilson disease, gene-determined disorder of copper metabolism [1]. Therefore, the aim of present work was to determine the stability of complexes of Cu(II) with Schiff bases ligands derived from PLP and pyridinecarboxylic acids under conditions mimicking the physiological ones. Our experimental method of choice was spectrophotometry, an example of primary experimental data indicating the formation of coordination compound is given (Fig.).

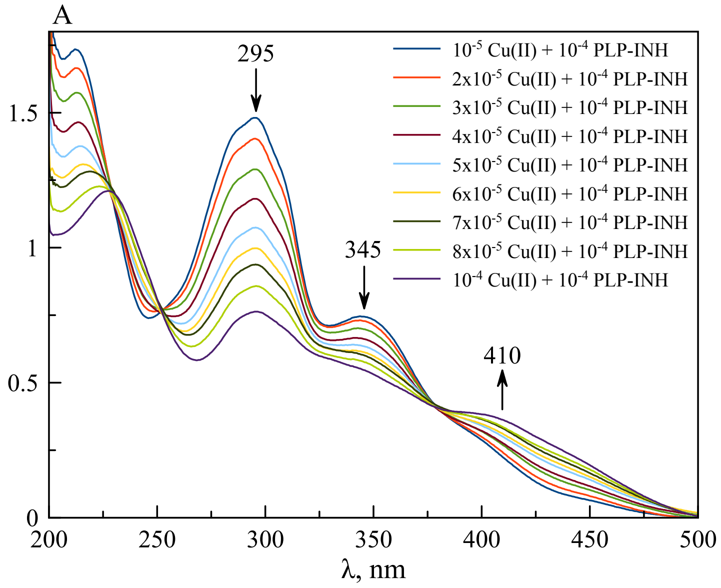

Figure. Complex formation between Cu(II) and PLP-isonicotinoyl hydrazone (INH) in aqueous solution at 6.6. pH. The values in plot description stand for initial molar concentrations.

The Fig. data allow estimating the complexation equilibrium constant (lg K = 4.8±0.5).

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Acknowledgements - *The study was carried out in Research Institute of Thermodynamics and Kinetics of Chemical Processes of Ivanovo State University of Chemistry and Technology with financial support of Russian Foundation of Basic Research (project 16-33-60017) and under grant of Council on grants of the President of the Russian Federation (project 14.Z56.16.5118-MK).*

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SYNTHESIS AND SPECTRAL PROPERTIES OF NOVEL DIBROMO-BIS-1,3-DIKETONE CALIX[4]ARENES

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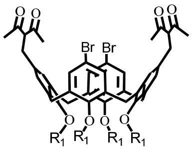
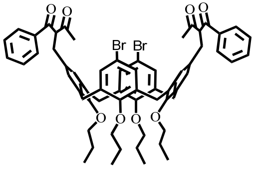
The unique photophysical properties of lanthanide complexes make them promising building blocks in the developing of advanced luminescent materials for bio-medical diagnostics, optoelectronics, OLED’s and solar energy conversion. It has been well demonstrated that 1,3-diketones are ideal candidates for the sensitization of visible and near infrared (NIR) luminescence emitted by lanthanide ions due to the significant antenna effect. The substituent’s effect is well known tool in design of both complexing ability and photophysical properties of ligands. Calix[4]arene backbone provides convenient basis for embedding various substituents in order to guide the properties of the ligand.

The antenna effect of a ligand is greatly affected by an efficacy of intersystem crossing. The introduction of halogen atoms into molecules can induce a strong spin–orbit coupling, which facilitates the intersystem crossing, well known as heavy-atom effect.



1 $R_1 = H$
2 $R_1 = C_3H_7$



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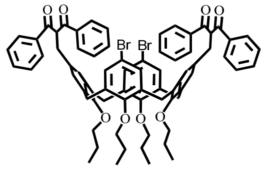

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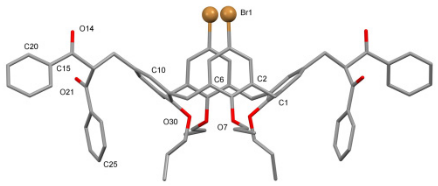
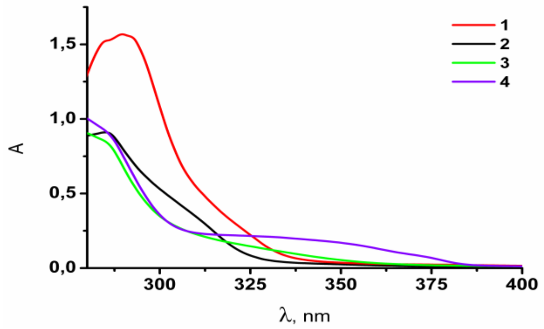
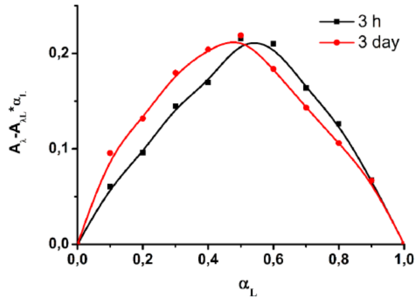




UV-Vis spectra for compounds **1**-**4**in DMF (C = 0.1 mM).



The Job plot of DMF solutions at the varied time of solution storage, L_2:Tb:TEA (1:1:4)

The synthesis and characterization of the upper rim dibromo-substituted bis-1,3-diketone calix[4]arenes with hydroxy and propyloxy groups at the lower rim as ligands for Gd^{3+} and Tb^{3+} complexes were investigated. NMR and X-Ray analysis reveals that all synthesized calix[4]arenes adopt *cone* conformation of macrocyclic framework. The UV-Vis spectral data and quantum-chemical calculations indicate that the dibromo-substitution does not affect the 1:1 complex formation with the lanthanide ions arisen from their coordination via two 1,3-diketonate groups incorporated at the upper rim of the calix[4]arene. The measurements of Tb^{3+}-centered luminescence indicate the better antenna effect (~1.7) of dibromo-substituted bis-1,3-diketonate calix[4]arenes against its non-substituted counterpart.

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SYNTHESIS AND STUDY Co(II) AND Ni(II) COMPLEXES OF N-SALICYLOIL-N′-MALEOIL-HYDRAZINE

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Compounds based on hydrazides of carboxylic acids and their complexes with metal ions have biological activity and are used in various fields of medicine and engineering. Hydrazides are used as medicines for the treatment of tuberculosis [1-2], have anticancer [3], antimalarial [4], and antimicrobial [5] activity.

In this study, the previously unknown unsymmetrical potentially tetradentate three anionic ligand -N-salicyloil-N'-maleoil hydrazine and its Co(II) and Ni(II) complexes were synthesized. These compounds were investigated by various physicochemical and spectroscopic methods. The molecular structure of Co (II) and Ni (II) complexes was determined by diffraction of the X-ray diffraction pattern of single crystals (Figure 1).

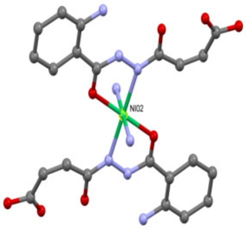

*Fig.*1 The structure of Ni(II) complex o f N-salicyloil-N’-maleoil hydrazine

The present study revealed that the Co(II) and Ni(II) ions give complexes of the ML_2*X_2 composition, where X is a dimethylformamide molecule. When these complexes are formed, the ligand acts as a monoanionic bidentate and binds to the metal ion through the nitrogen of amide and the oxygen of carbonyl groups of the salicylic residue in the enol form. The enol form is confirmed by the length of the C=N bond of 1.195Å. Square planar geometry around metal is completed to an octahedron by coordinating the metal ion with two solvent molecules (DMF). It is noteworthy that in these compounds the carboxyl group does not participate in coordination.

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OPTICAL, SORPTION AND SELECTIVE PROPERTIES OF CAMPHOR SABSTITUTED TETRAPYRAZINOPORPHYRAZINES

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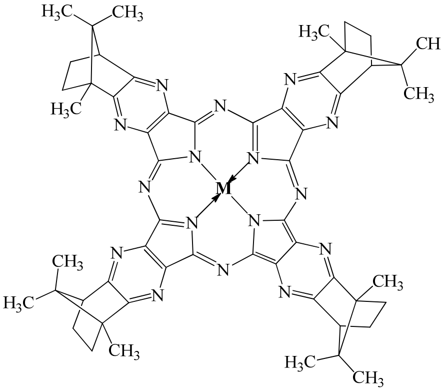
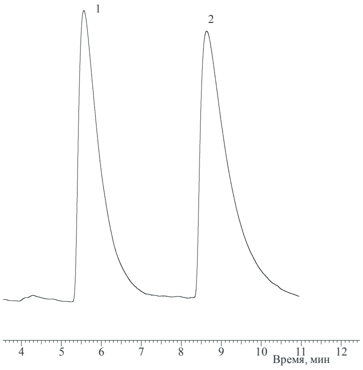
The synthesis of the complexes of Cu(II), Ni(II), Pd(II), Sn(II), Hg(II) of 1’,7’,7’-trimethylbicyclo[2.2.1]heptano-[2’,3’-b]-2,3-pyrazinoporphyrazine for new materials for variety of potential applications is described. Metalic complexes were synthesized by the template cyclotetramerization of dicarbonitrile with metal chlorides at temperature 150 ºC for 10 min. The products were purificated by chromatography on silica gel. Complexes of Pd(II), Sn(II) and Hg(II) were synthesized first of all. The chemical structures of the complexes of Cu(II), Ni(II), Pd(II), Sn(II), Hg(II) of 1’,7’,7’-trimethylbicyclo[2.2.1]heptano-[2’,3’-b]-2,3-pyrazinoporphyrazine were characterized by proton nuclear magnetic resonance and mass spectrometry. Optical properties of the synthesized complexes were studied. The electronic absorption spectra of the complexes in their chloroform, DMF, acetic and sulfuric acids solutions were obtained. In organic solvents the typical B band (Soret band, around 400 nm) and Q band (in 600-700 nm region) of phthalocyanines were identified. Complexes of Pd(II), Sn(II) and Hg(II) in their sulfuric acid solutions are non-stable. Emission properties of the synthesized complexes of Pd(II) and Hg(II) in their chloroform and DMF solutions were analysed. Hg(II)-porphyrazine has very intensive fluorescence. The solution has blue color and red fluorescence in common condition.



M = Cu, Ni, Pd, Sn, Hg



Separation of *3,4-/3,5*-lutidines. 10% nikel phthalocyanine on Chromaton, 140 ºC, column length 1 m

The modified adsorbents for gas chromatography were prepared by using complexes Cu(II), Ni(II), Pd(II) of camfor sabstituted tetrapyrasinoporphyrazine. The thermal stability of phthalocyanines and modified adsorbents were analyzed by thermogravimetric analysis method. The sorption from the gas phase of same organic compounds by the complex of Cu(II), Ni(II), Pd(II) of camfor sabstituted tetrapyrasinoporphyrazine has been studied by gas chromatography method. Strong polar of methylpyridines and dimethylpyridines isomers, low polar xylenes and alcohols isomers was used as sorbates. Specific retention volume and separation parameters of the sorbates were calculated. Sorption and selective properties of the adsorbents based on complexes of Cu(II), Ni(II), Pd(II) of the camfor sabstituted tetrapyrasinoporphyrazine were analyzed.

Acknowledgements – the given study was supported by the Russian Science Foundation (Grant no. 14-23-00204 p). The study was conducted using the resources of the Center for Collective Use of scientific equipment of ISUCT

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STABILITY OF BISARENECHROMIUM ISOXAZOLINO[4',5':1,2]- AND N'-BENZOYL-7'-AZAINDOLIZIDINO[1',2':1,2][60]FULLERIDES

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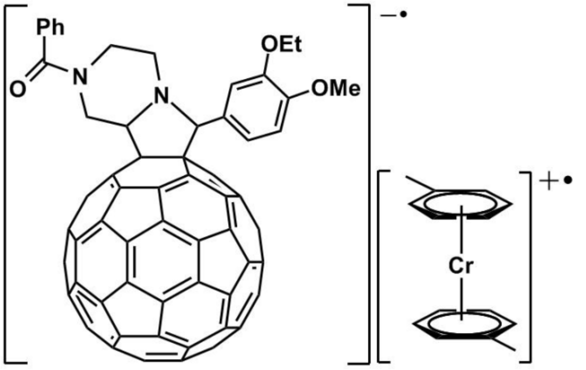
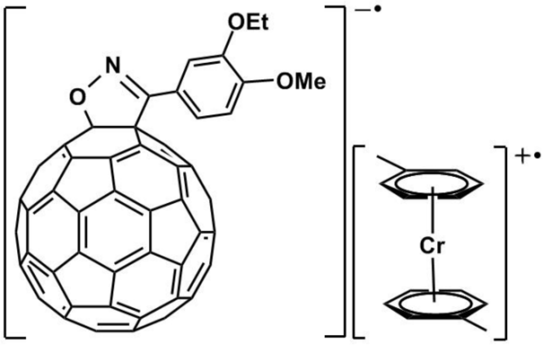
Bis(toluene)chromium reacts with N'-benzoyl-7'-aza-3'-(3-ethoxy-4-methoxyphenyl)indolizidino[1',2':1,2][60]fullerene (**1a**) and 3'-(3-ethoxy-4-methoxyphenyl)isoxazolino[4',5':1,2][60]fullerene (**1b**) in toluene at 293 K to form ion-radical salts - bis(toluene)chromium N'-benzoyl-7'-aza-3'-(3-ethoxy-4-methoxyphenyl)indolizidino[1',2':1,2][60]fulleride (**2a**) and bis(toluene)chromium 3'-(3-ethoxy-4-methoxyphenyl)isoxazolino[4',5':1,2][60]fulleride (**2b**) as a brown precipitates. Fullerides **2a** and **2b** are insoluble in hexane, sparingly soluble in PhMe, soluble in THF. Fulleride **2a** is stable at 293K but is decomposed above 393 K in THF solution (in an evacuated and sealed ampoule). Fulleride **2b** is stable at 293K but is decomposed above 373 K in THF solution (in an evacuated and sealed ampoule) losing 3'-(3-ethoxy-4-methoxyphenyl)isoxazolino moiety to form simple bis(toluene)chromium fulleride.



2a



2b

Thus, anion-radicals of N'-benzoyl-7'-aza-3'-(3-ethoxy-4-methoxyphenyl)indolizidino[1',2':1,2][60]fullerene is more stable than 3'-(3-ethoxy-4-methoxyphenyl)isoxazolino[4',5':1,2][60]fullerene anion-radicals. Fullerene **1a** has been obtained by heating of C_{60} with N-benzoylpiperazine and 3-ethoxy-4-methoxybenzaldehyde (molar ratio close to 1:7:18 correspondingly) in *ortho*-dichlorobenzene at 498 K in an evacuated and sealed ampoule. After solvent evaporation in vacuo, the residue was washed by hexane, acetone, dried in vacuo and dissolved in toluene. Column chromatography over silica gel with toluene as eluent gave first unreacted [60]fullerene and then (with toluene/acetone 36:1 as eluent) fullerene **1a** in 35% isolated yield as amorphous brown solid. Fullerene **1a** is insoluble in hexane, soluble in $CHCl_3$ and THF. The UV/vis spectra of **1a** in decaline at 290 K show absorption bands at 432 nm typical for 1,2 [60]fullerene derivatives. All reactions were carried out under an inert atmosphere.

Acknowledgements - This work was supported by RFBR (№16-03-01109, 15-53-52008, 18-53-52012).

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COMPLEXATION OF COBALT(II) RHODANIDE WITH N,N´,N´´,N´´´-TETRAKIS(DIPHENYLPHOSPHORYLMETHYL)-1,4,7,10-TETRAAZACYCLODODECANE

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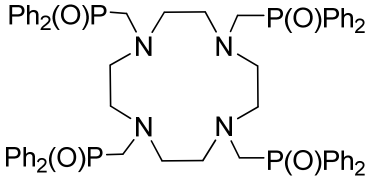
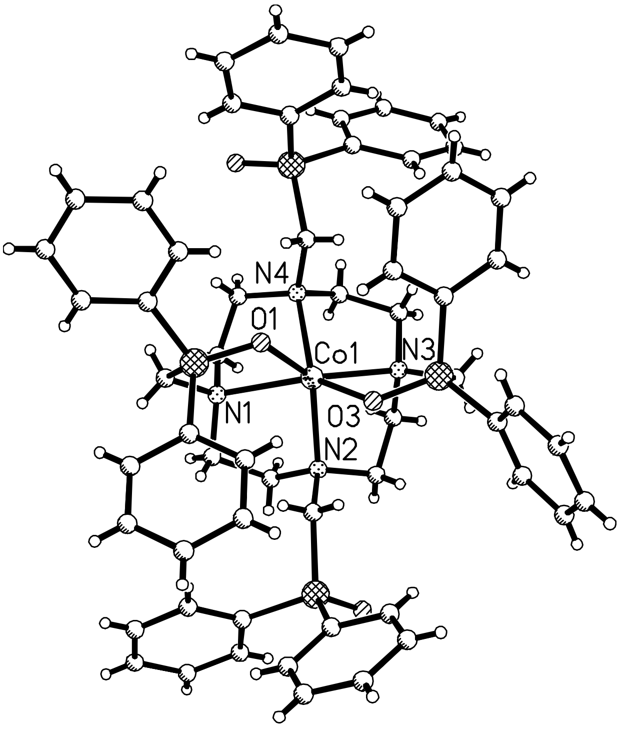
In the crystal structure of complex $[Co(DOTMPPh_2)](ClO_4)$ studied earlier, Co atom is coordinated by four nitrogen atoms of the macrocycle and oxygen atoms of four phosphoryl groups in the shape of a twisted Archimedean antiprism. In an attempt to obtain complex cation of the same unusual coordination with the rhodanide anion, it was found that an acetonitrile solution contains complexes of the Co: $DOTMPPh_2$ = 1:1 and 2:1 compositions. The stability constants of the cobalt(II) rhodanide complexes with $DOTMPPh_2$ in acetonitrile were estimated from UV–vis spectrophotometric data: $\log \beta_1 = 4.85 \pm 0.09$ ($M^{2+} + L = M^{2+}L$), $\log \beta_2 = 8.16 \pm 0.30$ ($2M^{2+} + L = M_2^{2+}L$). The IR, UV-vis, and ESR spectra of 2:1 complex in solid state and solution were studied. The X-ray diffraction study revealed that crystals grown from acetonitrile and ethanol solutions have the $[Co(DOTMPPh_2][Co(NCS)_4]\cdot 2CH_3CN$ and $[Co(DOTMPPh_2][Co(NCS)_4]\cdot 2EtOH\cdot 2H_2O$ compositions. Solvent does not affect the coordination sphere of cobalt. In the $[Co(DOTMPPh_2]^{2+}$ complex cation, the polyhedron of the cobalt atom is a distorted trigonal prism formed by four nitrogen atoms and oxygen atoms of only two phosphoryl groups. In the $[Co(NCS)_4]^{2-}$ complex anion, Co atom is tetrahedrally coordinated by four N atoms of NCS^- anions.



DOTMPPh₂



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SYNTHESIS AND X-RAY STRUCTURE OF THE VINYL-TERMINATED IRON(II) BORON, ANTIMONY-CAPPED MACROBICYCLIC PRECURSORS AND THEIR HYBRID PHTHALOCYANINOCLATHROCHELATE DERIVATIVES

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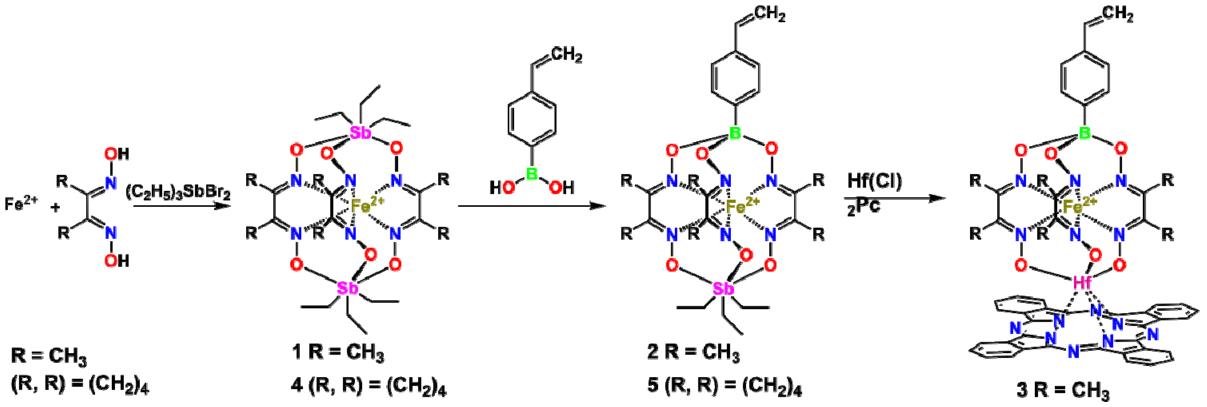
Cage metal complexes (clathrochelates) with terminal reactive, donor or biologically relevant groups are prospective chemically robust, three-dimensional molecular platforms and building blocks for the design of new types of (photo)electronic devices, modern functional materials and prodrugs [1]. Novel boron, antimony-capped macrobicyclic iron(II) tris-dioximates with labile triethylantimony cross-linking group were prepared by transmetallation of their bis-triethylantimony-capped clathrochelate precursors **1** and **4** with 4-vinylphenylboronic acid. The obtained B, Sb-capped complex **2** undergoes a transmetallation with hafnium(IV) phthalocyaninate as a Lewis acid by Scheme, thus giving a binuclear hybrid HfPc-cross-linked cage complex **3**.



Scheme

The compounds obtained were characterized using UV-Vis, MALDI-TOF MS, IR and multinuclear 1D and 2D NMR spectra, as well as by single crystal X-ray diffraction.

[1] Y.Z. Voloshin, I.G. Belaya, R. Krämer. Cage metal complexes: clathrochelates revisited. Heidelberg: Springer; 2017

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FORMATION OF 15-METALLACROWNS-5 WITH GLYCINEHYDROXIMATE LIGANDS IN WATER SOLUTIONS

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Metallacrowns are self-assembling polynuclear macrocyclic compounds which reveal various attractive properties. They are efficient catalysts, superordinary molecular magnets, "building blocks" in supramolecular design and selective agents of cations and anions [1]. Water-soluble lanthanide 15-metallacrowns-5 based on aminohydroxamic acids can be directly obtained with one-pot synthesis (Fig. 1) [2]. Self-assembly processes of such metallacrowns have not been investigated by computational methods so far. In the present work DFT calculations at the B3LYP/DGDZVP level with PCM approach have been carried out to explain the metallacrown formation in water solution. Modeling of various kinds of possible metallacrown precursors predicts thermodynamic preference of copper species with NNCuNN coordination. However in presence of lanthanide ion the NNCuOO chelating mode is more stable. Moreover, the "guest" cation does not suggest formation of linear or ramified oligomeric chains with NNCuOO units leading into five-membered macrocyclic structure. This explains experimental failures concerning detection and isolation of a metallacrown ring bearing no ion. In addition, changes in electronic structures of copper species on binding with the core metal have been revealed by analysis of the deformation electron density.

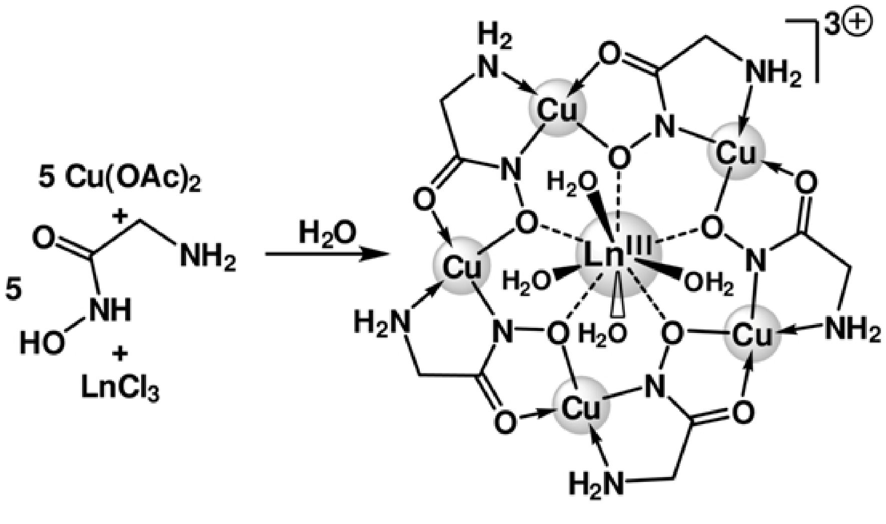

Fig.1. Synthesis of a 15-metallacrown-5.

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SYNTHESIS, CRYSTAL STRUCTURE, PROPERTIES AND BIOLOGICAL ACTIVITY OF HEXAFLUOROSILICATES WITH HETEROCYCLIC CATIONS

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In recent years, several research groups demonstrated the possible usage of "onium" hexafluorosilicates as new perspective caries preventive and hyposensitive agents in the practice of dentistry [1-3]. In present communication synthesis, structural characteristics, properties and potential pharmaceutical application of "onium" hexafluorosilicates with heterocyclic cations will be discussed.

The crystalline salts with the composition $(L^{1-4}H)_2SiF_6$ (L^1 = 2-pyridineacetic acid, **I**; L^2 = 3-pyridineacetic acid, **II**; L^3 = 4-pyridineacetic acid, **III**; L^4 = 2-amino-4,6-dihydroxypyrimidine, **IV**) were obtained by the interaction of hexafluorosilicic acid (45 %) with methanol solution of corresponding "onium" chlorides $(L^{1-3}H)Cl$ (**I** – **III**) or free base L^4 (**IV**). The complexes **I** – **IV** were characterized by elemental analysis, ^1H, ^{19}F NMR, IR, mass-spectrometry, thermogravimetric analysis, solubility data and X-ray crystallography. In crystal structures **I** – **IV** anion SiF_6^{2-} occupying position on inversion centers in the centrosymmetric $P2_1/n$ (**I**), $P2_1/c$ (**II**), and I2/a (**III, IV**) space groups. The inter-ionic interactions of the NH···F and OH···F types released in the structures of salts **I** – **III** (NH···F and NH···O type in the case of **IV**), and for the anion SiF_6^{2-} the symmetry deviation from the ideal octahedral one is dictated by its closest environment and an involvement of all or part of the fluoroligands in H-bonds of different strength. Hexafluorosilicate anion in the structures has the geometry of the distorted octahedron with the Si–F distances running from 1.6479(18) till 1.6984(12) Å. The solubility data of **I** – **III** in water (25 ºC) are 0.82, 1,02 and 0,58 mol. %, respectively. The pyridinium hexafluorosilicates revealed a tendency toward solubility decrease with increase the number of strong and medium H-bonds ($D\cdots A \leq 3{,}2$ Å) [3, 4]. The ^{19}F NMR spectra of compounds **I** – **IV** in D_2O have one sharp and additional broad resonance peaks. We assigned these peaks as SiF_6^{2-} anion ($\delta_F = -132.90 \div -133.00$ ppm) and the hydrolysis intermediate $[SiF_5(H_2O)]^-$ ($\delta_F = -132.33$ ppm). In dilute water solutions ($1\cdot10^{-4}$ M), salts **I** – **IV** underwent practically quantitative hydrolysis with formation of fluoride-ions and soluble form of silicon dioxide, which catalyzed the process of formation of calcium phosphate sediment from saliva [1].

All hexafluorosilicates reduce the depth and the number of dental caries of animals (Wistar rats), and provide efficiency of caries prevention up to 45 %. Salts **III** and **IV** show the highest caries prevention efficiency, exceeding the same index for NaF in 5 times. The data of biochemical tests showed almost complete absence of toxic effects in a given dosing, with the exception of **IV** (hepatotoxic compound).

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THE ROLE OF SECONDARY BONDING AND STERIC EFFECTS ON SUPRAMOLECULAR ASSEMBLY OF LEAD(II) COORDINATION COMPOUNDS

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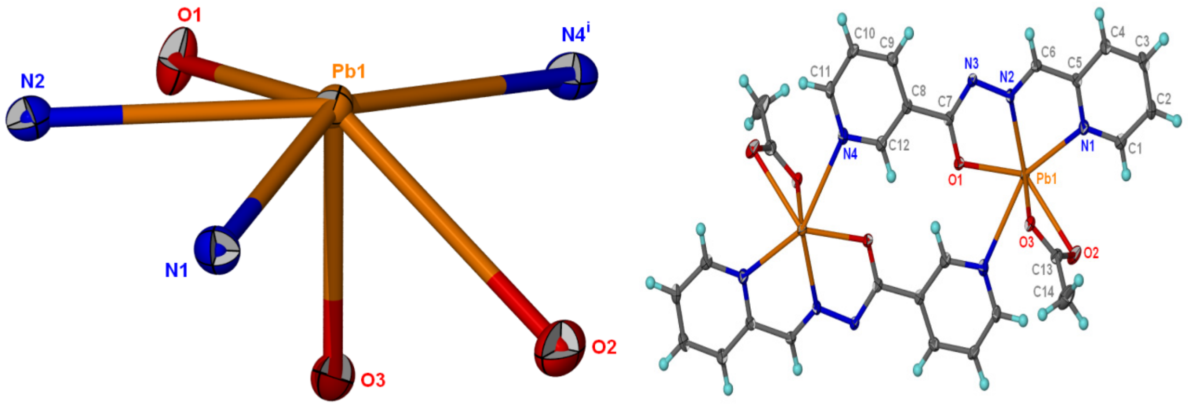
Apart from the widely used hydrogen bonding interactions for the construction/modification of MOFS, other specific noncovalent interactions like σ–hole interactions, especially halogen bonds, are becoming prominent players [1-3].The strongest σ–hole interactions occur in systems where a heavy atom of groups IV to VII is covalently bonded to electronegative ones [4]. Taking advantage of this understanding, herein we report the synthesis and X-ray characterization of four new Pb(II) complexes with (iso)nicotinohydrazide-based ligands and different anions (azide, nitrate, acetate and iodine) as coligands. The nature of the tetrel bonds in all four structures was studied by DFT calculations, which showed the presence of the σ–hole at the Pb atom and the considerable strength of these interactions. In these MOFs, Pb···S and Pb···N noncovalent tetrel bonds interconnect the covalently bonded units into supramolecular assemblies. A combined DFT study and a statistical survey of the Cambridge Structural Database (CSD) revealed that tetrel bonds with hemidirectionally coordinated lead occur with high probability and with predictable geometries, thus playing an important role in the solid-state chemistry of lead.



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NEW COPPER(II) COMPLEX POTENTIALLY HAVING ANTICANCER ACTIVITY

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The first of the metal-containing cytostatic agents used in cancer chemotherapy is cisplatin (cis-[$Pt(NH_3)_2Cl_2$]). Series of more advanced compounds based on platinum of malignant tumors are used in modern therapy, but almost all of them have cisplatin-like structural motif and mechanism of action: when they enter the zone of the pharmacological target - the nucleus of the cell - they covalently intercalate into DNA, thereby blocking its further transcription and replication, which leads to programmed cell death (apoptosis). All these compounds, however, have very high neuro-, nephro- and ototoxicity, as well as low selectivity to tumor cells, induce vomiting, diarrhea, etc. [1].

Nowadays a class of copper complexes having a different mechanism of toxic effect is found and lacking a significant part of the side effects of platinum compounds. These complexes catalyze the formation of reactive oxygen species (ROS), that permeabilizes the mitochondrial membrane in turn, with cytochrome-c activating the caspase cascade, which leads to apoptosis, into the cytosol of the cell [2]. At present times, preparations of the type [Cu(N∩N)(Gly)]NO_3 and [Cu(N∩N)(acac)]NO_3 (N∩N - aromatic nitrogen-containing ligands: 4,7-dimethyl-1,10-phenanthroline or 4,4-dimethyl-2,2-dipyridyl, Gly = L-glycine, acac-acetylacetone) undergo the two stage of clinical trials [3].

In the present work, new aminate complex of copper (II) with potential activity against tumor cells has been synthesized and characterized: [Cu(phen)(L-Met)(H_2O)]Cl. Complex was obtained by the interaction of [Cu(phen)Cl_2] (phen = 1,10-phenanthroline) and L-methionine (L-Met) in aqueous solution. The synthesized complex was described by X-ray diffraction and element analysis, UV and IR spectroscopy. The mononuclear complex [Cu(phen)(L-Met)(H_2O)]Cl·2.5H_2O crystallizes in a rhombic syngony with sp. gr. $P2_12_12_1$ with the parameters of the unit cell a = 22.6837(6), b = 21.1684(5), c = 12.4647(4) Å, V = 5985.27 $Å^3$, Z = 4, R = 0.060.

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ENCAPSULATION OF IODOBENZOIC ACIDS INTO DIMERS OF β-GLYCYRRHIZIC ACID

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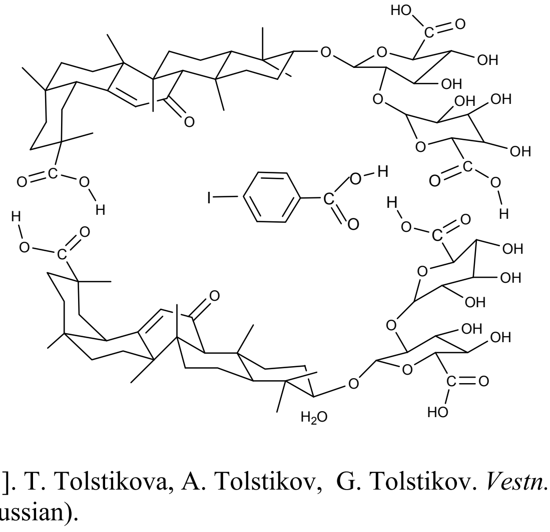
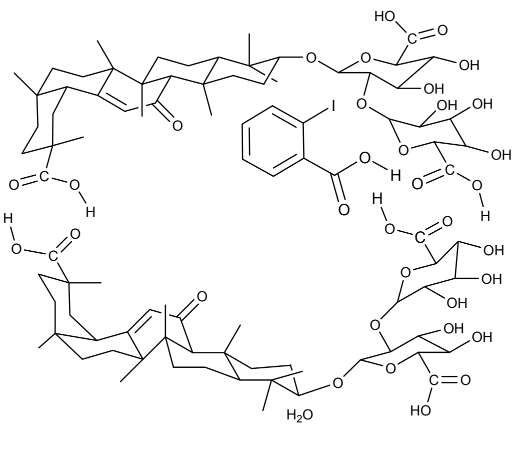
The synthesis of nontoxic iodine-containing compounds is an urgent task, as the effect of the development of rapid resistance of pathogenic flora to antibiotics is observed. In this paper iodine-containing compound [**p-BAI@2GA**] based on interaction the 4-iodobenzoic acids (**p-BAI**) with β-glycyrrhizic acid, triterpene glycoside – 20β-carboxy-11-oxo-30-norolean-12-ene-3β-yl-2-O-β-D-glucopyranuronosyl-α-uronic acid D-glucopyranoside (**GA**), have been prepared and characterized by the elemental analysis, UV-VIS, IR- and NMR-spectral methods. The complex of 2-iodobenzoic acid (**o-BAI**) with β-glycyrrhizic acid [**o-BAI@2GA**] was presented previously. Glycyrrhizic acid is known as a matrix, a "host"-molecule, for the formation of supramolecular complexes [1].

There in [2] it was shown that **GA** forms dimers "head-to-head" in solutions. The «guest»-molecule can be included in the cavity of this dimer. According to the results of the study, it was found that a more compact molecule **o-BAI** interacts with **GA** mainly through the glucuronic acids residues in carbohydrate part of **GA**. When the [**p-BAI @ 2GA]** complex is formed, the coordination of the molecules is also mainly due to the interaction between the carboxyl groups of the **p-BAI** and the glucuronic fragment of the **GA** molecules. But the iodine atom **p-BAI** is presumably coordinated on the conjugate system and to the carboxyl group in the triterpene part of the **GA** molecule.

The proposed structures can be represented as follows:





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IR, UV and NMR spectra were recorded on equipment at the Center for the Collective Use “Chemistry” of the Ufa Institute of Chemistry of the Russian Academy of Sciences.

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THE TRIS-O-BENZOSEMIQUINONATO CHROMIUM COMPLEXES

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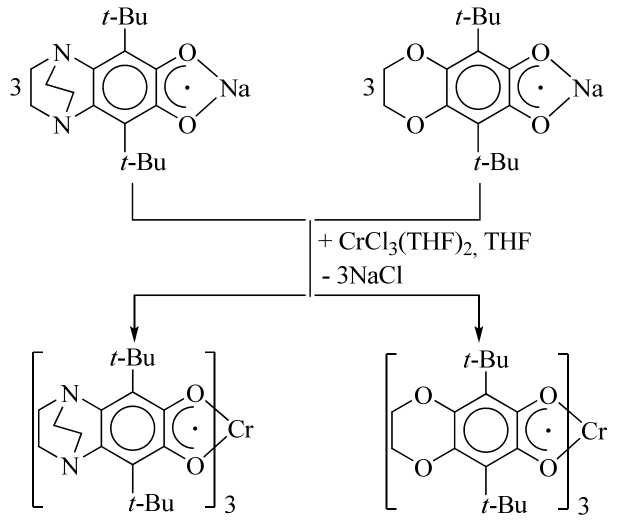
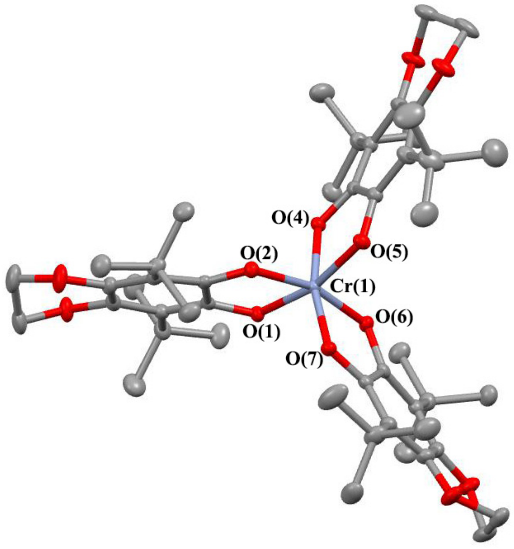
The investigation of magnetic exchange interaction between radical centers in molecule of metal complexes is an interesting and perspective field of coordination chemistry. In particular, it applies to create a magneto-structural correlations because the character and the value of magnetic exchange interactions strongly depend from the geometry of coordination polyhedron. Moreover, we can control the last one via the introduction of different substituents into the ligand. The previously described tris-3,6-di-*tert*-butyl-*o*-benzosemiquinonato chromium compound has the slightly distorted octahedral geometry and is diamagnetic [1]. However, it was found recently that the presence of N,N'-piperazino- and O,O'-ethane-1,2-diolato- heterocycles in 4,5-positions of sterically hindered semiquinones leads to interligand C…H and O…H interactions which results in trigonal prismatic (or close to it) molecular geometry in corresponding tris-*o*-semiquinonato cobalt complexes [2], while the tris-3,6-di-*tert*-buthyl-*o*-benzosemiquinonato cobalt compound is octahedral [3]. We suppose that the use of *o*-benzoquinones containing N,N'-piperazino- and O,O'-ethane-1,2-diolato- heterocycles can lead to trigonal-prismatic chromium complexes with another magnetic properties. Chromium compounds were synthesized by the exchange reaction of three equivalents of sodium *o*-semiquinolate with one equivalent of $CrCl_3(THF)_2$ in THF solution.





The complexes obtained have heavily distorted octahedral geometry in accordance with X-Ray diffraction analysis. With such a geometry of coordination center, the antiferromagnetic exchange interaction between radical ligands and unpaired electrons of d-orbitals of chromium-d^3 atom is realized. The complexes obtained are diamagnetic as the result.

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FORMING OF SUPRAMOLECULAR SALTS BASED ON THE HYDROXYCARBOXYLATOGERMANIC ACIDS AND NITROGEN-CONTAINING ORGANIC MOLECULES

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The modern stage of development of supramolecular chemistry is characterized by the appearance of a significant number of publications devoted to the study of various chemical systems, which self-organize due to non-covalent, in particular, hydrogen bonds.

As building blocks of such supramolecular architectures, in aqueous solution we have established stable hydroxycarboxylatogermanate acids (GeHoca) (biscitrate -$H_2[Ge(HCit)_2]$, tartrate-$H_2[Ge_2(\mu\text{-}Tart)_2(OH)_2]$, xylarate-$H_2[Ge(H_2Xylar)_2]$ nitrogen-containing organic molecules (L= nicotinic acid, nicotinamide, isonicotinic acid hydrazide, diphenylguanidine, diantipyrylmethane, cytosine, imidazole, 1,10-phenanthroline, 2,2'-bipyridine). From all systems which contained these molecular components, products with the same molar ratio GeHoca:L=1:2 and composition $(HL)_2[GeHoca]\cdot nH_2O$ were obtained. It was established, that they are ionic associates, cations of which are monoprotonated forms of HL^+ (independently from the number of atoms capable for protonation in L molecules) and complex hydroxycarboxylatogermanate anions with the same structure as in the starting acid [1-5].

In the monomeric complex anions the coordination polyhedron of the Ge atom is a distorted octahedron formed by six O atoms of two tridentate chelating ligands. In the dimeric anion $[Ge_2(\mu\text{-}Tart)_2(OH)_2]^{2-}$ the metal atoms are bound to two completely deprotonated ligands $Tart^{4-}$. The coordination of each Ge atom is completed to trigonalbipyramidal by the O atom of the hydroxy ligand in the axial position.

There was carried out the analysis of the obtained data and it was revealed that the type of crystal structure (stratified, three-dimensional net) of the studied supramolecular salts determines the steric and topological features of building blocks, their ability to electrostatic interaction and the formation of hydrogen bonds with the participation of crystallization water.

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FEATURES OF COMPLEX FORMATION OF SOME β-DIKETONES WITH IONS OF LANTHANIDES IN LANGMUIR MONOLAYERS

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Currently, we pay significant attention to the preparation of Langmuir-Blodgett films based on amphiphilic β-diketones and their complex compounds (CC) with lanthanide ions, since similar ordered molecular assemblies containing cations of rare-earth elements possess unique optical and magnetic properties and can be widely used in the field of thin-film luminescent and sensory systems, light-transforming coatings, molecular electronics devices, etc. The study of structural transformations in Langmuir monolayers that occur as a result of changes in the ion composition of the water subphase is necessary to understand the basic principles of the interaction of metal cations with 2D ordered molecular structures at the phase interface. Thereby, we studied the complex formation of ordered molecular Langmuir assemblies on the basis of a series of synthesized β-diketones (octodecane-2,4-dione, hexadecylacetoacetate) with Eu^{3+} and Tb^{3+} ions. To do this, an analysis of the change in the limiting surface area of molecule in the molecular layer from the concentration of lanthanide ions in the subphase was made. An increase in the limiting surface area of the molecule in the monolayer and its compressibility with an increase in the concentration of lanthanide ions in the subphase is revealed, which is obviously the result of complex formation processes taking place in the film. It is assumed that the formation of a complex compound of composition 1:1, 1:2 and 1:3 in a monolayer occurs in the same plane at the interface. First, an increase in the concentration of lanthanide ions in the subphase leads to the formation of LnL_3 complexes (in this case, the coordination sphere is expanded to the characteristic coordination numbers 8, 9 by water molecules). This leads to a strong disordering of the molecular layer of the ligand due to the complex geometry of the lanthanide ion coordination sphere of the resulting CC, as a result of which the limiting surface area of the monolayer of β-diketonates increases. Further changes are associated with the formation of $[LnL_2]^+$ and $[LnL]_2^+$ complexes.

To confirm the described processes, we proposed a model describing the process of molecular organization in the formation of Langmuir films (LF). The calculation was carried out by molecular mechanics using the MM+ force field. In the modeling of the LF, we considered superclusters consisting of 25 ligand molecules and a variable number (from 125 to 400) of water molecules of the aqueous phase. In this case, the molecules of β-diketones were located on a sublayer of water molecules of different area, but of constant thickness about 10Å. Varying the number of water molecules in the sublayer with a constant thickness of the sublayer allowed us to simulate the effects of compression of the molecular layer, as well as calculate the local minima of the formation energy for studied molecular layer, the value of the limiting surface area of amphiphylic molecule, the surface pressure and microstructural parameters. The proposed approach was previously tested using the example of calculations of the parameters of LF of stearic acid and stearate complexes with Gd(III).

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SYNTHESIS AND CRYSTAL STUCTURES OF TWO NEW HEXABROMOTECHNETATES WITH METHYLIMIDAZOLIUM AND ETHYLIMIDAZOLIUM CATIONS

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Two new hexabromotechnetates with methyl- and ethylimidazolium cations have been synthesized in form of single crystals and the structures of these compounds have been determined (Bruker KAPPA APEX II area-detector diffractometer).

The first compound was hexabromotechnetate of methylimidazolium $[(CH_3)(Im)]_2[TcBr_6]$ (**I**) with chemical formula weight 743.69. It forms red plate orthorhombic crystals, sp. gr. $P2_12_12$ with parameters at 100(2) K being a = 7.8599(6), b = 16.0412(13), c = 7.2519(6) Å, Z = 2, $R1$ = 0.0359.

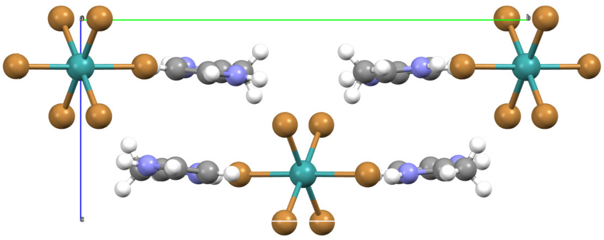

Fig.1. Structure of $[(CH_3)(Im)]_2[TcBr_6]$ (**I**)

The structure is composed of 5 atom types (C, N, H, Tc, Br) all in general positions. The configuration of the $TcBr_6^{2-}$ is slightly distorted octahedron. Tc–Br distances are typical for this type of bonds: 2.4978(12) - 2.5060(12) - 2.5190(7) Å. The structure is packed in layers parallel to (001) plane.

The second compound was hexabromotechnetate of ethylimidazolium $[(C_2H_5)(Im)]_2[TcBr_6]$ (**II**). It forms red monoclinic crystals, sp. gr. $P2_1/n$, with parameters being a = 7.9083(19), b = 13.088(4), c = 10.176(2) Å, β = 107.329(8)°, Z = 2, $R1$ = 0.0347. Tc–Br distances in practically ideal centrosymmetric octahedron are 2.5058(6), 2.5059(6) and 2.5063(7) Å.

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AGOSTIC INTERACTION UNDER THE COORDINATION OF THE CYCLIC β,β'-TRICARBONYL COMPOUNDS WITH METALS IN OXIDATION STATES

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It is known that one of the reasons for the implementation of the three-center two-electron connection, M…H−C (agostic interaction) becomes the desire of transition metal to achieve the 18 electron configuration. However, perhaps this type of interaction is selected, and for some alkali metals in the study of their complexation with 2-(diphenylacetyl)indandione-1,3 (H**L**), which is a typical representative of β,β'-tricarbonyl compounds.

Analysis of the structural data revealed for metals in the oxidation state +I, with increasing ionic radii in the row Li − Na − K − Rb − Cs in addition to the formation of different types of coordination polyhedron with the expected η^2(O,O) coordination $\mathbf{L}^-$ increases the tendency for additional coordination of the carbon atoms of the phenyl groups, acyl fragments $\mathbf{L}^-$. If in case Li is difficult to say about any interaction (the shortest Li-C = 4.67Å), while for other compounds discovered contacts, hardening with increasing ionic radius of the central metal atom (Na-C = 3.21Å; K-C = 3.47Å; Rb-C = 3.45Å; Cs-C = 3.46Å). At the same time, increases the involvement in additional interactions of the carbon atoms of the phenyl groups $\mathbf{L}^-$ from 1-2 (Na, K) [1,2] till on 3-6 (Rb, Cs) [3,4].

Somewhat different is the coordinate in the case of the transition element Ag with H**L**. Ag**L** was recorded for an extremely short distance of Ag-C is equal to 2.49Å, but geometrically overlap is implemented rather for only one of the C atoms of the phenyl ring of the acyl fragments of the ligand [5]. In this case, it is appropriate to talk about the classic example of the implementation of agostic interaction. However, for the alkali metals it is confidently possible to tell only about the additional coordination in the case of Rb and Cs, which is implemented as favorable geometric orientation of the ligand (phenolic groups of acyl fragments $\mathbf{L}^-$), 18 electronic configuration and the distance M-C is comparable to the sum of the van der Waals radii.

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SUPRAMOLECULAR COMPLEXES FORMED IN "β-CYCLODEXTRIN – AMINOACID – LANTHANIDE ION" SYSTEMS

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Constantly increasing interest in cyclodextrin inclusion complexes last few decades is mostly due to their ability to rather easily form numerous inclusion compounds with the great variety of the "guests". Moreover, cyclodextrins possess important practical properties: nontoxicity, biodegradability, and relative cheapness. The use of cyclodextrin complexes makes it possible to improve bioaccessibility, to decrease toxicity, and to facilitate the penetration through biological barriers.

Previously [1, 2], binary inclusion complexes of some bioactive ligands with β- cyclodextrin (CD) were investigated. As the further development of this work, a more complex system: β-CD – amino acid – lanthanide ion was studied. Such systems could be very useful as spectral labels, making possible to track the transport of drug substance in biological systems [3].

In the present work the Pr^{3+} – tryptophan – β-CD and Pr^{3+} – phenylalanine – β-CD systems were studied by ^{1}H NMR spectroscopy in water solution. Preliminary study was carried out for the tryptophan – β-CD and phenylalanine – β-CD systems. Both cases show the same pattern in chemical shifts changes: signals of the protons, disposed at the inner space of β-cyclodextrin cavity, are shifting into the strong field while the signals of aromatic protons (in case of phenylalanine) or indole protons (for tryptophan) shifting in a weak field.

The ternary systems were obtained as follows. The different quantity of praseodymium chloride solution was added to the β-CD – amino acid system making successive series with different Pr^{3+} to aminoacid – β-CD ratio. The volumes and concentrations for each point in serie were calculated to compensate dilution effect. pH value was held constant through the serie. With the successive change of praseodymium chloride to aminoacid – β- CD ratio we observe broadening and shifting the signals of the amino acid α and β protons to the low field. At the same time, the addition of Pr^{3+} practically does not affect to the β- CD protons.

There are at least two scenarios for complex formation scheme. First one – aminoacid leaves the β-CD cavity and coordinates with lanthanide ion forming conventional aminoacid – metal ion complex. Second scenario – the aminoacid coordinates with lanthanide ion being encapsulated in the β-CD cavity. ROESY spectra of Pr – Trp – β-CD and Pr – Trp – β-CD systems in solution exhibits cross-peaks between 3 and 5 protons of β-CD and phenyl (for PhA) or indole (for Trp) protons. Together with the chemical shifts changes patterns it allows to conclude that the second scheme is implemented in water solution.

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Cu^{II}-MEDIATED ACTIVATION OF A CYANO GROUP IN ARYLHYDRAZONE OF MALONONITRILE

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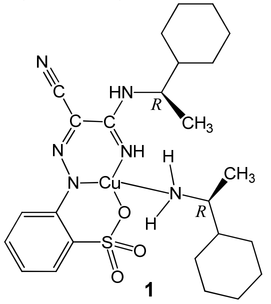
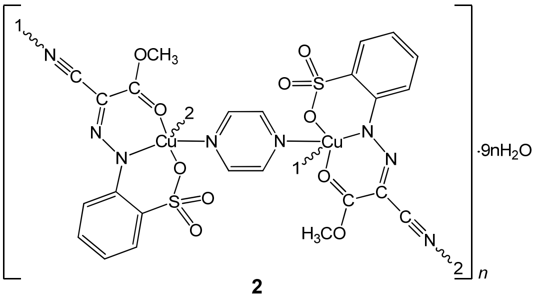
Metal-assisted specific nucleophilic attacks to the cyano moiety(s) of arylhydrazones of malononitrile lead to a variety of amidine, carboxamide and iminoester containing multinuclear coordination compounds, depending on the nucleophiles and conditions used [1-3]. (*R*)-1-Cyclohexylethylamine (*R*-cy) and pyrazine (py) were applied in the template synthesis of the Cu^{II} complexes [Cu(L^a)(*R*-cy)] (**1**) and [{(CuL^b)$_2$(py)}·9H$_2$O]$_n$ (**2**), where L^a are L^b are the ligands derived from nucleophilic attack of *R*-cy or water/methanol on a cyano group of 2-(2-(dicyanomethylene)hydrazinyl)benzenesulfonic acid, respectively, giving the corresponding ligands, *i.e.,* (*R,Z*)-2-(2-(1-cyano-2-((1-cyclohexylethyl)amino)-2-iminoethylidene)hydrazinyl)benzenesulfonate (L^a) or (*Z*)-2-(2-(1-cyano-2-methoxy-2-oxoethylidene)hydrazinyl)benzenesulfonate (L^b).



1



2

The use of other types of reagents, such as isocyanides, aminoalcohols, mercaptans, etc., is in progress in our laboratories. Moreover, for the synthesis of the other enantiomer of **1**, *R*-cy will be replaced by (*S*)-1-cyclohexylethylamine (*S*-Cy). The obtained complexes are being tested as catalysts for the asymmetric Henry reaction between nitroalkanes and aldehydes.

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LANTHANIDE COMPLEXES WITH ARYLHYDRAZONE OF BARBITURIC ACID

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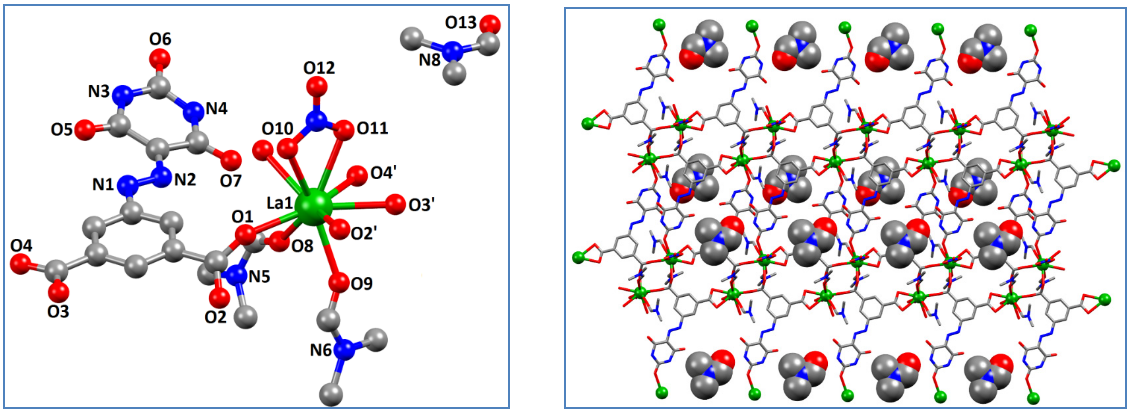
Recently, we have reported the pH dependent synthesis of Zn(II) and Cd(II) coordination polymers based on dicarboxylfunctionalized arylhydrazone of barbituric acid ligand and its application in the Knoevenagel condensation reaction [1]. Now we extended our work to lanthanide metal systems and test their catalytic activity in the cyanosilylation of aldehydes. Thus, five new isostructural Ln-MOFs were synthesized by using solvothermal reaction conditions. The solvothermal reactions of 5-[2-{2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene}hydrazinyl]isophthalic acid (H_5L) with different lanthanide salts in the presence of DMF and water at 75°C leads to the formation of the isostructural 2D frameworks $[Ln(1\kappa OO',2\kappa O'',3\kappa O''',4\kappa O''''\text{-}\mu 4\text{-}L)(NO_3)(DMF)_2]_n\cdot n(DMF)$ {Ln= La^{3+} (**1**), Ce^{3+} (**2**), Nd^{3+} (**3**), Sm^{3+} (**4**), Dy^{3+} (**5**); L = 5-[2-{2,4,6-trioxotetrahydropyrimidin-5(2H)-ylidene}hydrazinyl]isophthalate; DMF = N,N'-dimethyl formamide} (Figure 1). These complexes exhibit excellent heterogeneous catalytic activities towards the cyanosilylation of aldehydes under solvent-free conditions. These catalysts can be recycled at least up to five cycles without losing activity.



A **B**

Figure 1. (**A**) The molecular structure of Ln-frameworks (Ln = La^{3+}, Ce^{3+}, Nd^{3+}, Sm^{3+} and Dy^{3+}) with partial labeling scheme. (**B**) Two dimensional packing diagram of Ln-frameworks.

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THE ROLE OF LIGAND ENVIRONMENT OF NON-TRANSITION AND TRANSITION METAL COMPLEXES IN THE RADICAL POLYMERIZATION OF VINYL MONOMERS

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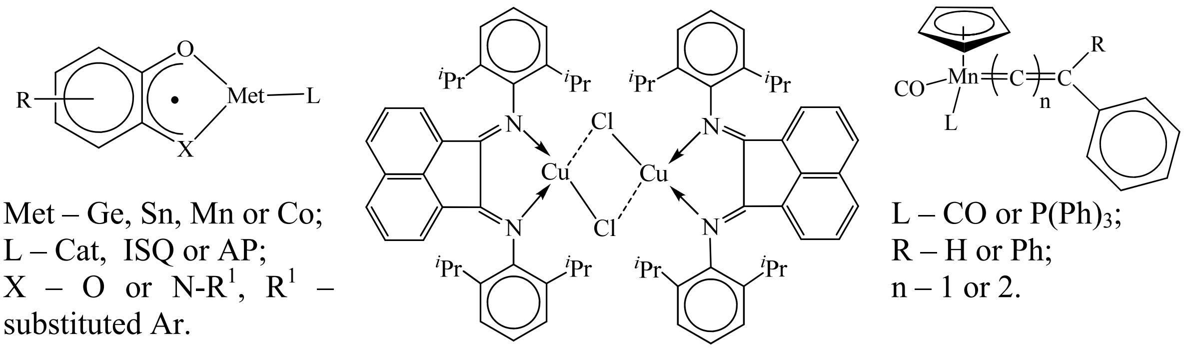
In last decades a wide range of metallocomplexes was offered for polymerization processes, allowing for the facile synthesis of specific macromolecular architectures with excellent control over the chemical and physical properties. The efficiency of metal-based catalytic systems may be finely tuned by changing ligand environment. A use of redox-active ligands, which can dramatically change reactivity of metal center, is a very promising way to tune catalyst activity in polymerization processes.

In our work different complexes of non-transition (Ge, Sn) and transition (Mn, Co, Cu) metals with redox-active ligands (scheme) in the radical polymerization of acrylonitrile (AN), methyl methacrylate (MMA), styrene (St) and vinyl acetate (VA) were investigated.



Met – Ge, Sn, Mn or Co;
L – Cat, ISQ or AP;
X – O or N-R^1, R^1 – substituted Ar.

L – CO or $P(Ph)_3$;
R – H or Ph;
n – 1 or 2.

Scheme

Investigation of vinyl monomers polymerization in the presence of Co and Cu complexes with redox-active ligands showed their ability to regulate kinetic and molecular weight parameters of polymers synthesized using alkyl halides or AIBN as a radical source. The presence of iminobenzosemiquinone ligand in Co complex structure allows minimizing catalytic chain transfer to cobalt center during MMA polymerization. It was established that the ligand environment of manganese complexes plays a key role in the polymerization mechanism. The manganese complex with iminobenzoquinone ligands acts as an inhibitor of polymerization vinyl monomers. The complexes of Mn with redox-active vinylidene and allenylidene ligands were capable to spontaneously initiate the polymerization of vinyl monomers. The presence of redox-active quinone-based ligands in complexes of non-transitional elements of 14-th group allowed these compounds to participate in reversible termination of propagating polymer chain. In this case ligand acts as a redox-active center responsible for regulating of polymerization contrary to transition metal complexes where regulating ability is determined by metal atom. Mono- and bis-catecholate complexes of non-transition metals are capable to accept carbon-centered radicals and act as regulators of MMA and St polymerization.

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EPR STUDY OF PALLADIUM COMPLEXES WITH IMINONITROXIDE LIGAND

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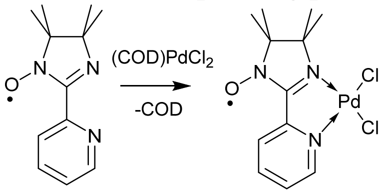
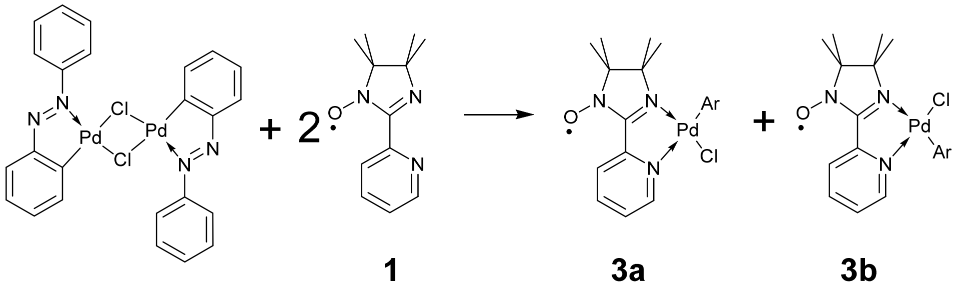
Complexes of palladium with iminonitroxide ligand (ImNitrox) **2** and **3** may be easily achieved by reaction of the ligand **1** with corresponding palladium precursor.



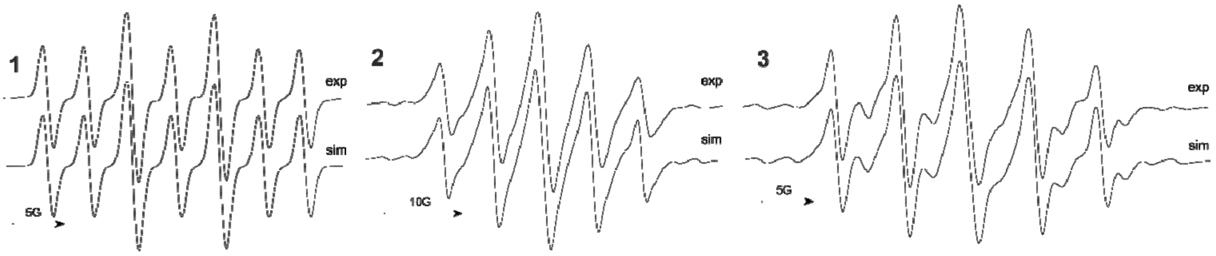
1 **2**

Complex **3** forms as a mixture of two geometry isomers **3a** and **3b** with approximate ratio 1:4.



1 **3a** **3b**

Coordination of ImNitrox fragment on the metal leads to sufficient spin density redistribution in imidazole ring. Initially inequivalent nitrogens in **1** (a_{N1}=4.2G, a_{N2}=8.6G) become almost equivalent (a_{N1}=6.5G, a_{N2}=7.1G for **2**, a_{N1}=6.1G, a_{N2}=7.0G for **3a**, a_{N1}=6.5G, a_{N2}=7.1G for **3b**). Relatively large splitting on palladium (a_{Pd}=3.1G for **2**, a_{Pd}=4.5G for **3a**, a_{Pd}=3.1G for **3b**) with simultaneously increasing of g-factor value from 2.0059 to 2.0085 - 2.00106 is observed too.



EPR spectra of **1** - **3** (toluene, r.t.).

Temperature dependence of the spectrum of **3** is absent. This fact means that there are no interconversion of the isomers of **3a** and **3b**.
The coordination of ImNitrox ligand to palladium is relatively weak. So, the interaction of **2** and **3** with various substrates (AsEt$_3$, PPh$_3$, NEt$_3$, pyridine) leads to decomposition of the complexes with liberation of **1** back.

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SYNTHESIS AND KINETICS OF COMPLEXATION OF NITRO-SUBSTITUTED 5,15-DIPHENYLTETRAMETHYLTETRAETHYLPORPHYRIN WITH MANGANESE ACETATE IN ORGANIC SOLVENTS

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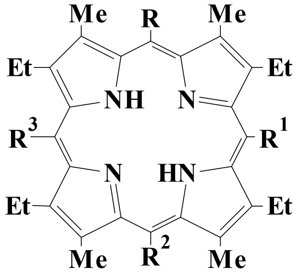
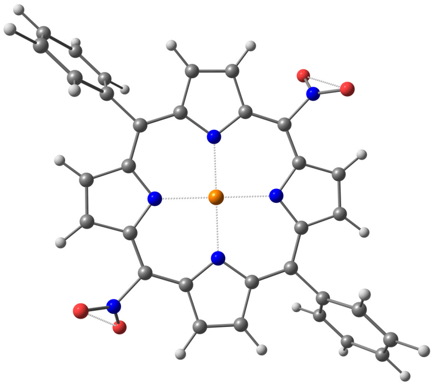
Synthesis of 5,15-diphenyltetramethyltetraethylporphyrin and its nitro-substituted ones was carried out. The nitro groups in the 5,15-diphenyltetramethyltetraethylporphyrin are in the *meso*-positions of the tetrapyrrole macrocycle and (or) the para positions of the phenyl rings (Fig. 1).



I: R=R^2 =Ph, R^1 =R^3 = H
II: R=R^2 = Ph, R^1 =R^3 = NO_2
III: R= Ph, R^2 =4-NO_2Ph, R^1 =R^3 = NO_2
VI: R=R^2 = 4-NO_2Ph, R^1 =R^3 =NO_2

Fig. 1

The resulting porphyrins are characterized by ESP, ^{1}H NMR spectra and IR spectra, their structure is determined by quantum chemical calculations by the DTF method. The purity and individuality of the synthesized compounds is proved by TLC and elemental analysis data.



Reactions of complexation of nitrosubstituted 5,15-diphenyltetramethyltetraethylporphyrin with manganese acetate in pyridine and acetic acid were studied. It has been established that the rate of reactions of formation of manganese complexes in pyridine with the introduction of nitro groups in 5,15-diphenyltetramethyltetraethylporphyrin increases as the degree of deformation of the tetrapyrrole macrocycle increases and the strength of its N-H bonds decreases. In an acetic acid, the effect of macrocycle deformation leads to a decrease in the reaction rate. This is due to the specific solvation of the reaction center of porphyrin by acetic acid molecules.

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COMPLEX FORMATION IN THE SYSTEM Zn^{2+}-PYRIDOXINE-WATER IN THE PRESENCE OF SURFACTANT

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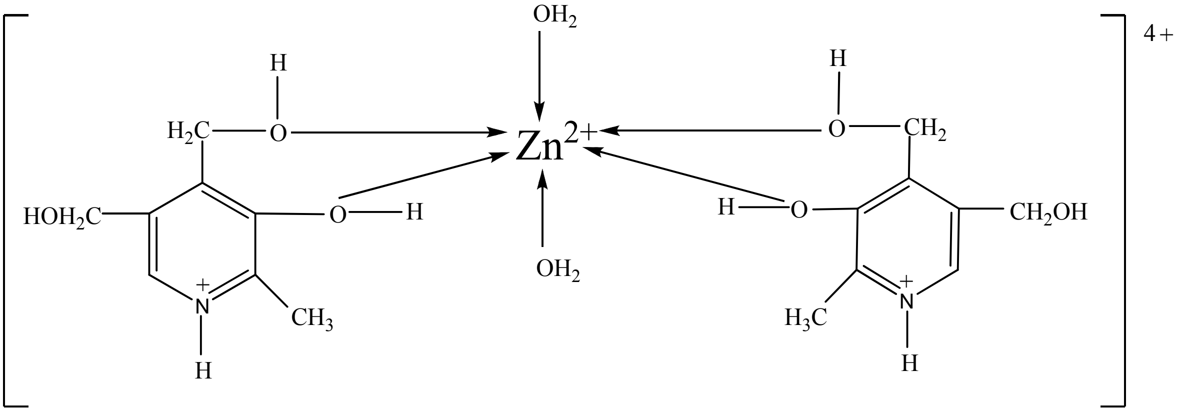
Solutions of surfactants are the unique environment for many chemical processes. They influence on complex formation, on the composition and stability of the complex [1,2].

Complex formation in the system Zn^{2+}-pyridoxine-surfactant in aqueous environment is studied. Studies are carried out by UV-spectroscopy method in the presence of anionic surfactant sodium pentadecylsulfonate (SPDS). The composition and stability of complex are obtained by methods of isomolar series and molar ratios, studies are conducted for premicellar solutions of SPDS. At the first step of studies the effect of Zn^{2+} ions and pyridoxine on critical micelle concentration (cmc) of SPDS in aqueous solutions has been studied. It was observed that cmc of SPDS decreases in the presence of Zn^{2+} ions (cmc of SPDS in aqueous solutions in the absence of Zn^{2+} is $1.62\cdot10^{-3}$ mol/l and at $[Zn^{2+}]=0.35\cdot10^{-4}$ mol/l is $0.12\cdot10^{-3}$ mol/l). Under influence of pyridoxine cmc of SPDS increases (at [pyridoxine]=$1.0\cdot10^{-2}$ mol/l cmc of SPDS in aqueous solutions is $2.39\cdot10^{-3}$ mol/l).

It is shown experimentally that in the formed complex the ration of Zn^{2+}:pyridoxine is 1:2. Complex also contains 2 water molecules. The structural formula of the complex may be represented as (at pH <5):



The studies have shown that SPDS practically has no effect on the composition of the inner sphere of the complex: it means that the interactions between Zn^{2+} and pyridoxine are stronger than between Zn^{2+} and SPDS. But the presence of PDS^- anion in the inner sphere of the complex has effect on the stability of the complex: in the absence of SPDS lgβ=5.5 and in the absence of SPDS lgβ=5.2.

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METAL-CONTAINING IONIC LIQUIDS AS A PRECURSOR FOR CHEMICAL METALLIZATION

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Significant interest in ionic liquids (IL) has recently stimulated research in the field of compounds related to low-temperature ILs, which have a melting point above 100 ° C and belong to the so-called class of "hard" ionic liquids. As a rule, these compounds contain a complex anion of a transition metal.

Metal-containing ionic liquids represent a promising subclass of charged ILs that combine IL properties with magnetic, photophysical, optical, or catalytic properties. Ionic liquids containing palladium, platinum, iron, ruthenium and other transition metals are used as catalysts or catalytic precursors.

In the present work, studies have been carried out on the synthesis, investigation of the properties and catalytic activity of ammonium tetrachloropalladates and pyridinium, which, along with imidazolium ionic liquids, are of theoretical as well as practical interest. Tetrachloropalladates of ammonium and pyridinium of general formula R_2PdCl_4 where R: $C_{10}H_{21}NC_5H_5$; $C_{16}H_{33}NC_5H_5$; $(CH_3)_2C_{10}H_{21}NCH_2CH_2OH$; $(CH_3)_2C_{12}H_{25}NCH_2C_6H_5$ were obtained by two methods: solid phase synthesis-the interaction of $PdCl_2$ with an alkyl halide, and metathesis between quaternary ammonium or pyridinium salts and sodium tetrachloropalladate in alcohol solution.

The compounds are dark red crystalline salts with metallic luster. The composition and structure are confirmed by elemental analysis data, visible spectroscopy, UV, IR, and NMR spectroscopy. Their colloidal and chemical properties, thermal stability, and the ability to use these ionic liquids as a new catalytic precursor in the chemical metallization of dielectric materials (glass fibers (d = 7-10 μm, fiberglass, aerosil, etc.) were studied. In spite of the fact that the complex Anion, $PdCl_4^{2-}$ is less catalytically active, more accurately less able to form catalytically active particles, however, in a chemical metallization solution directly or in the process of preliminary acceleration, by treating the plant Sodium hypophosphite thinner, catalytic active palladium nanoparticles are formed, which allows to carry out metallization without a stage of sensitization and thereby simplify the technological process as a whole. Chemical metallization using ionic liquids-complex palladium salts as precursors was carried out using the example of chemical nickel plating as the most common method for obtaining metallic coatings. When ionic liquids were applied to the surface of products, the method of heterogenization of palladium complexes was used. The conducted studies have shown that the use of ammonium and pyridinium tetrachloropalladate in chemical metallization as precursors of surface activation makes it possible to simplify the technological process of depositing metallic coatings as a whole.

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SYNTHESIS AND PROPERTIES OF MESOIONIC CARBENES BASED ON CYMANTRENYL-1,2,3-TRIAZOLIUM SALTS

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Currently chemistry of 1,2,3-triazolium salts and 1,2,3-triazol-5-ylidenes, so-called mesoionic carbenes, is being intensely developed. These compounds are widely used in metal complex and organic catalysis, as biologically active compounds, also chemosensers and ionic liquids.[1,2] 1,2,3-Triazolium salt derivatives are synthetically available compounds due to well-developed variations of the 'click-reaction' of metal-catalyzed 1,3-cycloaddition of azides to acetylenes and subsequent alkylation of the resulting 1,2,3-triazoles[1,2].

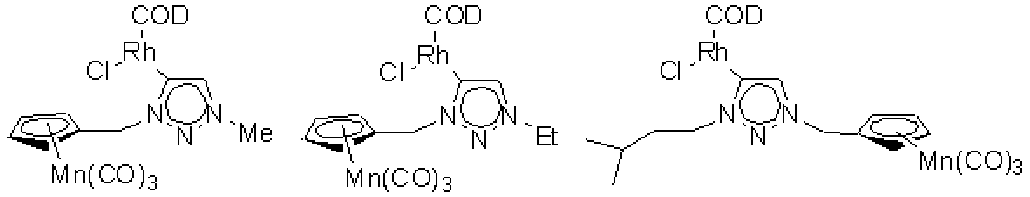

Рис. 1. Rhodium complexes with mesoinic carbenes as ligand.

In this work we obtained a series of 1,2,3-triazolium salts containing the cymantrenyl group in the 1N or 3N heterocycle position. Rhodium complexes with mesoinic carbenes as ligand were obtained by the metallation of these salts with Ag_2O and subsequent transmetalation (Fig 1). The structure of new 1,2,3-triazolium salts and mesoionic complexes was proved by NMR, mass and IR spectroscopy and X-ray studies. NMR ^{1}H investigation of these rhodium complexes in solution at different temperatures showed that hindered rotation of fragments relative to one an other in molecules was observed, which led to the appearance of two sets of signals from two rotation isomers. The degree of the hindered rotation depended on the nature of the substituents at both 1N and 3N heterocycle positions. Rhodium complexes were tested as catalysts in the hydroformilation of terminal double bond. It turned out that the decrease in the internal rotation rate of the complex led to reduction of its catalytic activity.

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SINGLE SOURCE SYNTHESIS OF $Sr_6Co_5O_{15}$·Co_3O_4 COMPOSITE: CHARACTERIZATION OF THE OXIDE PRODUCT AND ITS PRECURSOR

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Cobalt perovskite oxides and their derivatives are intensively studied because of their complex electronic and magnetic properties, that are very attractive for many technological applications. Physical properties of such systems depend strongly on the oxygen deficiency and can be modified by choosing appropriate preparation conditions [1]. The development of novel production methods are thus of particular interest. Herein, we present the synthesis of strontium cobaltite nanopowder from coordination molecular precursor Co-Sr-2,3-PDC (**1**) [2] by a thermal decomposition method as well as structural, magnetic and transport characterization of the composite obtained. Compound **1** exhibits a 2D coordination polymer structure, where the ligands link Co(II) and Sr(II) ions in the molar ratio 1:1; the shortest cobalt-cobalt distance is 6.42 Å. The TGA thermal analysis proves that complex **1** undergoes a controlled thermal decomposition to give a Co-Sr mixed metal oxide residue **2**, which after cooling in air was determined by PXRD as $Sr_6Co_5O_{15}$·Co_3O_4 (CPDC Nr 01-086-0614, and Nr 00-042-1467). The chemical composition and surface morphology analyzed by SEM microscopy and ED X-ray, suggest the formation of crystallite mixture of $Sr_6Co_5O_{15}$·Co_3O_4 with well-defined crystalline particles evently distributed in the range 1-3 μm. Variable temperature magnetic measurements of **1** and **2** have been performed in the range 5 – 330 K. The magnetic studies of polycrystalline sample **1** show the dominant paramagnetic behavior of high-spin (S = 3/2) Co(II) ions (fig.1). While for sample **2**, magnetometry results demonstrate the presence of a major compound $Sr_6Co_5O_{15}$ (fig.2) with a small inclusions of $SrCoO_{2.75}$, probably, remaining as an insignificant part of the intermediate phase. The electrical conductivity (σ) of **2** have been investigated in the temperature range 75 – 330 K. It shows semiconducting-like behavior with values of σ in the range ~10^{-6} – 10^{-1} $\Omega^{-1}cm^{-1}$, that is in good agreement with the expectation for 2H-hexagonal $Sr_6Co_5O_{15}$ [3]. In the high temperature range (200 – 330 K) an activation energy of the material (E_a) was estimated at E_a ~ 0.23 eV.

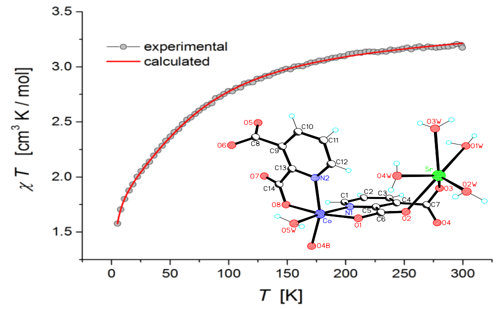

Fig. 1 Plot of χT *versus* T for complex **1**, measured at 50 Oe (*symbols*) and simulation for mononuclear model (*solid line*).

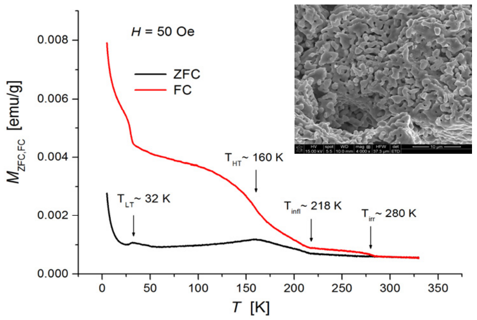

Fig. 2 Temperature dependences of ZFC-FC magnetization measured at 50 Oe and SEM micrograph (*in situ*) of the oxide sample **2**.

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A METHOD FOR OBTAINING COMPLEX-FORMING SORBENT

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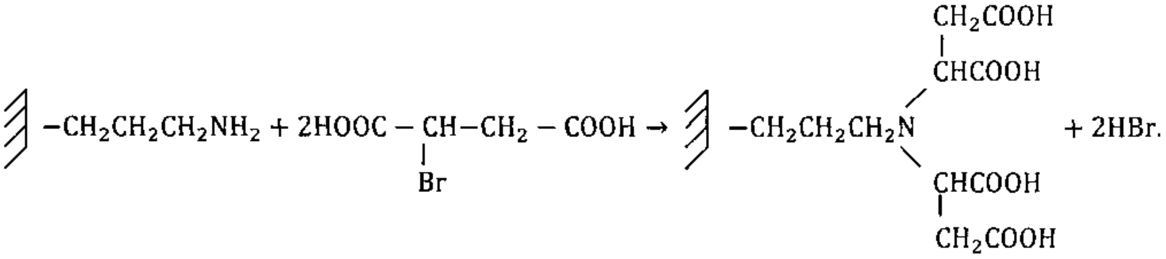
A method for the preparation of a complex-forming sorbent consisting of styrene-divinylbenzene copolymers and an active sorption layer, which is an immobilized complexon, is proposed. Sorbent is effective for the extraction and separation of metals.
Our task was to increase the sorption capacity in relation to metals. This is achieved by the fact that the method for synthesizing a complexing sorbent comprises a base of styrene copolymers and an active sorption layer. As an active sorbing component, iminodisuccinic acid (IDS) is used [1].

To synthesize the sorbent, two molecules of bromacidic acid are grafted onto the amino groups on the activated surface of the matrix to form a crosslinked five-adentate ligand, an iminodisuccinic acid (IDS). This process is easily carried out in connection with the fact that in halogen acids the halogen atom is extremely prone to exchange reactions [2]. The sorption capacity of the resulting complexing sorbent is SC = 3,0 mmol/g.

The effectiveness of the proposed solution is determined by the fact that in the fixed ligand (L) IDS, due to high hydrolytic and oxidation-reduction stability, complexes with metals (Me) are formed in neutral and acid media, the structure of the IDS and its high dentacy equal to 5 (four carboxyl and one Amine groupings), provide in strictly acidic and neutral media the formation of strictly stoichiometric complexes with the ratio Me:L = 1: 1.

he styrene-divinylbenzene copolymer (ST-DVB) was used as a starting material for the synthesis of the complexing sorbent. To fix two acidic fragments of succinic acid, two molecules of bromo-acidic acid were attached to the amino groups:



$$-CH_2CH_2CH_2NH_2 + 2HOOC-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_2-COOH \rightarrow -CH_2CH_2CH_2N\begin{matrix} CH_2COOH \\ | \\ CHCOOH \\ / \\ \\ \backslash \\ CHCOOH \\ | \\ CH_2COOH \end{matrix} + 2HBr.$$

The invention provides an increase in the sorption capacity of the product with respect to metals to 3 mmol / g. Sorbent is effective for the extraction and separation of metals.

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[2] A. Chichibabin, *Basic principles of organic chemistry*, **1953**, *1*, 482.

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OXALIC ACID ELECTROLYTE FOR COPPER-TIN ALLOY PRECIPITATION

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A method of precipitating a copper-tin alloy is proposed, which makes it possible to eliminate the partial oxidation of tin (in comparison with the electrolyte according to RU 2487967 C1, published on July 20, 2013) by introducing a stronger complexing agent-ecologically ethylenediamine succinic acid (EDDS) [1,2].

The proposed oxalate electrolyte for the deposition of the copper-tin alloy [3] consists of the following components, mol/l: copper sulfate five-way - (8-10) · 10^{-2}; Tin sulfate - (1-5) · 10^{-2}; Ammonium oxalate - (3-4) · 10^{-1}; Sodium acetate - (1.81-2.00) · 10^{-1}; Gelatin - (1-5) · 10^{-6}; Vanillin - (1-5) · 10^{-3}; Ethylenediamine succinic acid - (5-100) · 10^{-5}.

Such a composition makes it possible to ensure a uniform supply of copper and tin precipitated metals in the process of electrolysis from the corresponding stable copper and tin complexes with EDDYAK to produce high-quality mirror-bright coatings firmly adherent to the substrate while eliminating environmental contamination.

Table. Dependence of the change in the concentration of tin on the concentration of ethylenediamine succinic acid.

Concentration of additive, mol/l	0	1	5	10	14
0	0.02	0.02	0.06	0.09	0.1
5·10-5	0	0.012	0.035	0.038	0.038
2,5·10-4	0	0.005	0.0076	0.0076	0.0075
5·10-4	0	0.002	0	0	0.002
1·10-3	0	0	0	0	0

Ethylenediaminedisuccinic acid in the aqueous solution of these components provides for the formation of coordination compounds, where copper-tin ions act as complexing ions, and the ligand is ecologically safe ethylenediamine-succinic acid, which prevents the hydrolysis of salts and, thus, prevents even partial oxidation of the metal salts included in the electrolyte (For example, $\text{Ig}\beta_{\text{CuEDDS}} = 18.46$) [4].

This composition can be used for deposition of protective-decorative, corrosion-resistant coatings, as well as as a sublayer.

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ADVANCES IN PHTHALOCYANINE COMPLEXES SYNTHESIS

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It was done by author a comparative analysis of works including own ones, which have been published thus far in the field of metal phthalocyanine (MPc) synthesis. The main conclusions from that are represented here. Template synthesis from dinitrile, phthalimide, phthalic anhydride, the acid itself (with urea) in the presence of a metal in one form or another is the most acceptable. The use of diimino-*iso*-indoline does presence of urea is not mandatory. The synthesis always passes independent from initial precursor across the phthalic acid *o*-dinitrile formation. The last stage is the grouping the imino-*iso*-indolenine dipolar ions which then close in a cycle. The reaction conditions, intermediates and mechanisms are different depending on the template or the substituents in benzene ring of precursor. The reaction passes in the melt as the sintering of dry reagents or in the high boiling solvent namely nitrobenzene, *o*-dichlorobenzene, trichlorobenzene, ethylene glycol, and quinoline. Template synthesis together with metal ion substitution in Li_2Pc in alcohol solution of the corresponding metal salt is the classical methods of MPc synthesis. Among these, synthesis: 1. of polymeric MPcs with linear or 2D structure on 3*d*-metal ion templates, 2. of 1: 1 complexes of lanthanides, (X)LnPc from Li_2Pc and corresponding lanthanide salt in boiling DMSO, and 3. of MPcs of double and triple structure with optimal yields in one procedure based on the reaction of *o*-phthalodinitrile with a rare-earth metal chloride in 6: 1 mole ratio at 563 K during 1 hour were provided by author of this work.

Advanced chemistry of MPcs as materials of science and engineering stimulates a growing interest in optimization of their synthesis. Attempts to decrease the temperature and time, to find one-stage reactions, to increase the yield of complexes, to use the reaction mixture activations and other were realized in many works recently published. *The use of microwave radiation* in the template synthesis has made it possible to shorten the synthesis time from several hours to several minutes in the cases of 1: 1, homoleptic double decker and even heteroleptic double decker complexes. The synthesis can be carried out both dry and reflux method. Advantages of the MPc *electrosynthesis* over the chemical methods are considerably lower temperature (273–373 against 443–523 K), often, high yields, an one-stage procedure, and a possibility to prepare complexes inaccessible in other template syntheses. Sacrificial metal anodes or dissolved metal salts and phthalodinitrile as precursors in protic solvents were used for the obtaining of MPcs. Electrosynthesis using 1,3-diiminoisoindoline is possible in aprotic solvents. There are two ways for the *production of MPcs on a solid carrier* by the template method namely synthesis by a reaction an elemental metal and 1,2-dicyanobenzene with following vacuum deposition on a solid or a synthesis, for example in zeolite, from metal ions and 1,2-dicyanobenzene. The *in situ metalation of phthalocyanine monolayers* on Cu(100), Ag(111), Au(111)), MoS_2, and graphite under ultrahigh vacuum conditions as a new method of MPcs synthesis was developed. The reaction proceeds rapidly at room temperature resulting metalation of the phthalocyanine in high degrees. The first example of *an oxidative dissolution of a metal by adsorbed macrocyclic ligand* under UHV was demonstrated on an example of porphyrin and Zn pre-deposited on an Ag(111) surface.

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SYNTHESIS AND ACID-BASE CHARACTERISTICS OF L-FORMS OF N-(CARBOXYMETHYL)ASPARTIC ACID

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Natural amino acids exhibit optical activity, i.e. are in the form as D- and L-isomers, the vast majority of them belong to L-series. It is known that in the human body are digested and are involved in biochemical processes only L-isomers amino acids [1].

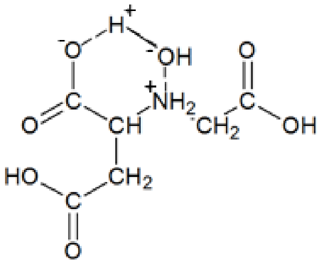
It is interesting to study chemical properties demanded by the nature of the L-isomers of N-(carboxymethyl)aspartic acid (L-CMA) in comparison with chemical properties of the racemate. This was carried out the synthesis of L - CMA by heating in a water bath solution containing L-aspartic acid, chloroacetic acid, and lithium hydroxide. The solution was then cooled and acidified using was acidified with HCl to a pH of 2-2.5 for precipitation.

Table. The negative logarithms of the concentration and speed of acid dissociation constants of D,L- CMA, L- CMA I=0,1 (KNO_3), T=25°C.

	pk_1	pk_2	pk_3
D,L- CMA [2]	2.58±0.04	3.85±0.06	9.65±0.04
L- CMA	3.32±0.02	4.40±0.03	10.42±0.03

The table shows the logarithms of the concentration step acid dissociation constants L-CMA and D,L- CMA.

It should be noted the high basic nitrogen atom of L- CMA (pK_4 = 10.42), which can probably be explained by the fact that the separation of the betaine hydrogen from the amino group of L-isomer in the titration, you must first break the loop formed by the ionized α-carboxyl group and a protonated amine group with a water molecule, included in this cycle by hydrogen bonds:



The CMA is an environmentally friendly chelating agent, derivatives of succinic acid possessing biologically active properties. Complexes metals can be used as microelement fertilizer, as catalysts of reactions of a metabolism, as stabilizers unusual oxidation states of metals, as a vehicle of physiologically important molecules, atoms and cations through the membranes of cells, and the L-isomer has found application as a sorbent for dissymmetrical splitting racemates method legendable chromatography [3].

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ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF BORON DIFLUORIDE NAPHTHALOYL- AND ANTHRACENOYLACETONATES

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[c] *Institute of Chemistry FEB RAS, Vladivostok, RUSSIA.*

Boron difluoride β-diketonates possess intensive luminescence within the whole visible and near IR range. Establishing correlations between spectral characteristics of boron complexes and their electron structure paves the way to targeted synthesis of new luminophores. The most confident information regarding electron structure of chelates one can obtain using simultaneously UV photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS) and quantum chemistry. Comparing ionization energies from photoelectron spectra with Kohn-Sham energies enables one to reveal peculiarities of electronic structure of the studied systems. We demonstrated in [1] that calculations of electronic structure of boron β-diketonates at DFT and TDDFT level correlate well with experimental results obtained by photoelectron and optical spectroscopy. This allows interpreting confidently photoelectron and optical spectra and analyzing electron effects of substitution.

The work investigates electronic structure and optical properties of boron difluoride naphthaloyl- (I) and antracenoylacetonates (II) using UPS, XPS, absorption spectroscopy, luminescence spectroscopy as well as DFT and TDDFT calculations. The absorption spectra were registered using a Shimadzu-UV2550 spectrometer (Japan). The luminescence and excitation spectra were registered on a Shimadzu-RF5301 (Japan) spectrometer. UPS spectra in vapor phase were obtained on a modified electronic spectrometer ES-3201 with hemispherical electrostatic analyzer using monochromatic irradiation source He I (hν = 21.2 eV). XPS spectra molecular crystals were recorded on a high-vacuum photoelectron spectrometer (Omicron, Germany) with hemispherical electrostatic analyzer using monochromatic irradiation source MgKα (hν = 1253.6 eV). DFT and TDDFT calculations were conducted via the Firefly 8.1.1. G quantum-chemical software package using the basis set TZVP and hybrid B3LYP functional.

Substituent's influence on electronic structure and optical properties has been analyzed. Despite of compound I, energy and type of excited state transitions of the complex and anthracene substituent of compound II are observed to correlate. While a bathochromic shift of luminescence band and decrease of relative luminescence quantum yield are indicated. Quantum yield decreases with the reduction of C-C bond order between chelate cycle and substituent along with contraction of the excited state lifetime. UV and X-ray photoelectron spectra structure is in good agreement with Kohn-Sham orbital energies.

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o-QUINONEMETHIDE IN SYNTHESIS OF NEW REDOX-ACTIVE LIGAND AND COMPLEXES BASED THEM

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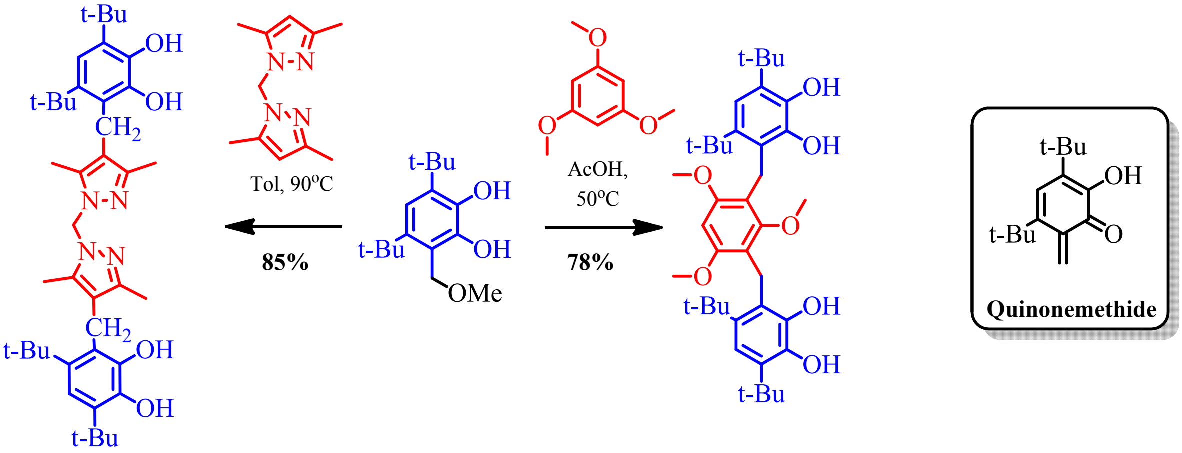
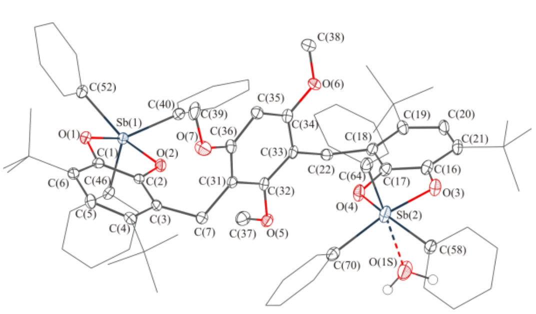
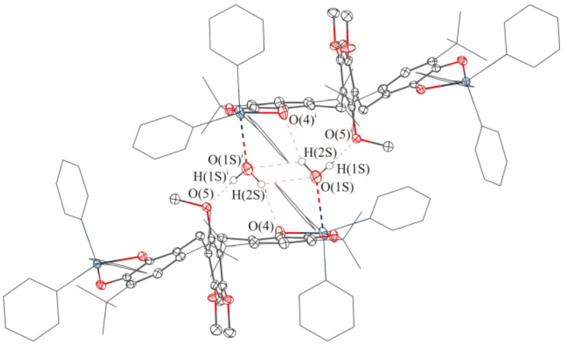
Sterically shielded catechols and its oxidative form o-quinones are of interest as redox-active ligand in coordination chemistry. Also sterically unshielded bis- and oligomeric catechols are well known ligands for synthesis of supramolecular complexes. The synthesis of oligomeric sterically shielded catechols are difficult task. In this thesis we report new syntetical methods (via o-quinonemethide intermediate) for synthesis of oligomeric sterically shielded catechols, its o-quinones and complexes based them.

Earlier we reported the synthesis of 3,5-di-tert-butyl-6-methoxymethylcatechol. This catechol can be used as precursor of sterically hindered o-quinonemethide and thus can be used as alkylating agent. Reactions 3,5-di-tert-butyl-6-methoxymethylcatechol with activated aromatic compounds lead to new sterically hindered mono, bis and oligomeric catechols.



Oxidation of them leads to new o-quinones, which are used as redox-active ligand in synthesis of new complexes (Cu, Ni, Sb etc.).





Acknowledgements - The works were financially supported by Grant of President of Russian Federation (MK-1951.2017.3)

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IMPROVEMENT OF SOLUBILITY OF 1,2,4-THIADIAZOLE DERIVATIVE VIA COMPLEX FORMATION WITH VARIOUS EXCIPIENTS

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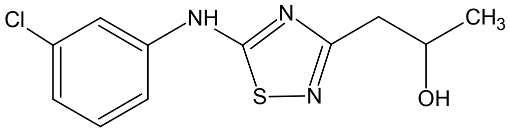
The 1,2,4-thiadiazole derivatives synthesized at the Institute of Physiologically Active Substances of the Russian Academy of Sciences (Chernogolovka, Moscow region) are considered as potential neuroprotective agents. It is known that only the drug in soluble form will be available for the adsorption process, therefore, solubility is one of the main properties controlling the bioavailability of pharmaceutically active substances. One of the ways proposed for the improvement of drug solubility can be complex formation with cyclodextrins and polymers, which are widely used in pharmacy as excipients.



Structural formula of 1-[5-(3-chloro-phenylamino)-1,2,4-thiadiazol-3-yl]-propan-2-ol

The aim of this work was to reveal the increase of the aqueous solubility of 1,2,4-thiadiazole derivative via its molecular complex formation with different cyclodextrins and polymers. Binding of 1,2,4-thiadiazole derivative with β- and hydroxypropyl-β-cyclodextrins as well as with polymers (polyethylene-polypropylene glycol (Kolliphor P407), polyvinylpyrrolidone (PVP), polyethylene glycol (PEG)) was studied by means of ^{1}H NMR and UV-spectroscopy in buffer solutions (pH 1.2 and 7.4) simulating the biological fluids of the living organism. It is shown that 1:1 complex formation of 1,2,4-thiadiazole derivative with cyclodextrins is realized via the inclusion of hydrophobic fragment of the guest molecule into host cavity. Interactions of 1,2,4-thiadiazole derivative with the polymers under consideration are governed by the van der Waals forces and H-bonding. Compared to polymers, cyclodextrins exhibit a higher complexing activity and their solubilizing effect towards the 1,2,4-thiadiazole derivative is more pronounced. The increase in solubility of thiadiazole in the presence of polymers occurs in the following order Kolliphor P407 > PVP ≥ PEG. It has been established that the acidity of the medium has an insignificant effect on the complexation processes in the systems under consideration.

Acknowledgements This work was supported by Russian Science Foundation (grant №15-13-10017).

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HALOGEN BONDED CHAINS OF BINUCLEAR COPPER(II) ISOCYANIDE COMPLEX LINKED BY MOLECULAR IODINE

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Co-crystal of binuclear isocyanide complex of copper(II) and molecular iodine $[\{Cu(CNXyl)_2I\}_2O]\bullet I_2$ (Figure 1, LEFT) was obtained in the reaction of copper(I) complex $[Cu(CNXyl)_3Br]$ and iodoform in the light. In the binuclear complex, two metal atoms are bridged through an oxygen atom (chemical occupancy for oxygen atom is ½). Complexes form independent chains connected through molecular iodine via I•••I–I•••I weak halogen bonding interactions (Figure 1, RIGHT).

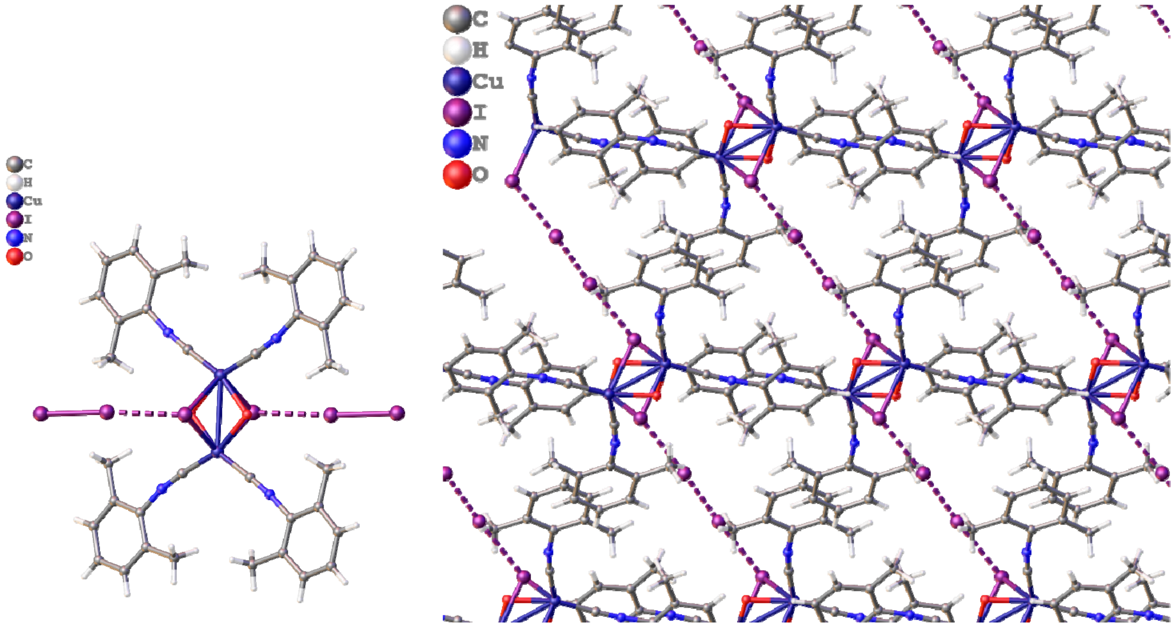

Figure 1. LEFT: crystal structure of $[\{Cu(CNXyl)_2I\}_2O]\bullet I_2$; RIGHT: packing of the halogen bonded chains in the co-crystal. Contacts shorter the sum of Bondi’s van der Waals radii are represented by dashed lines.

Short contacts $d(I\bullet\bullet\bullet I)$ = 3.278 Å are less than $R_{vdW}(I) + R_{vdW}(I)$ = 3.96 Å, meanwhile $d(I–I)$ = 2.774 Å is slightly elongated than in free iodine (2.67 Å) [1]; ∠(I–I•••I) = 176.78° and ∠(I•••I–Cu) = 105.93°). Hence, the I•••I weak interactions represent type II of halogen bonding, where electrophilic region of one halogen atom is interacting with the nucleophilic region of the other [2].

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SPIN CROSSOVER IN A PROTOTYPICAL IRON(II) COMPLEX WITH 4-AMINO-1,2,4-TRIAZOLE: A REINVESTIGATION

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The spin crossover phenomenon is a spin state switching between the low spin state (LS) and the high spin state (HS). For potential applications it is desirable to synthesize complexes showing wide, abrupt, symmetric and reproducible thermal hysteresis loops near room temperature. One of the most exciting examples of such complexes is the 1D polymeric complex $Fe(ATrz)_3(NO_3)_2{\cdot}H_2O$ (ATrz = 4-amino-1,2,4-triazole) [1].

Magnetic properties of $Fe(ATrz)_3(NO_3)_2{\cdot}H_2O$ were reinvestigated to gain an insight into the impact of water molecules on the spin transition [2]. Variations in the outerspheric water molecule content in the complex induce dramatic changes in its spin crossover regimes. Under vacuum the complex loses water molecules and shows a wide (*ca.* 30 K) and reproducible hysteresis loop, $T_c\uparrow = 337 - 345$ K, $T_c\downarrow = 316 - 313$ K. In sealed ampoules the complex $Fe(ATrz)_3(NO_3)_2{\cdot}H_2O$ shows a narrow hysteresis (*ca.* 1 – 4 K), $T_c\uparrow = 326 - 329$ K, $T_c\downarrow = 326 - 324$ K. After adsorption of water the complex $Fe(ATrz)_3(NO_3)_2{\cdot}nH_2O$ (n = 1.25 – 1.6) demonstrates a narrow two-step spin transition. For the system $Fe(ATrz)_3(NO_3)_2{\cdot}nH_2O$ (n = 3.6 – 16.6) wide hysteresis (*ca.* 5 – 20 K) re-appears near room temperature ($T_c\uparrow = 319 - 321$ K, $T_c\downarrow = 300 - 315$ K). Importantly, a possibility of switching between these spin crossover regimes has successfully been tested by adding or removing water [2].

Kinetics of the LS → HS and the HS → LS spin transitions within hysteresis loop have been studied for the first time for 1D polynuclear iron(II)-triazole complexes [2]. To our surprise, for anhydrous complex and for the complex containing *ca.* one water molecule per formula unit, kinetics appeared to be decelerating and not sigmoidal. In fact, this behavior is typical for non-cooperative systems and not for the systems demonstrating highly cooperative spin crossover behaviour with sigmoidal kinetics of the transition. Moreover, kinetics (and cooperativity) appeared to be strongly sensitive to the presence of extra-amounts of water in the system. High water content switches the decelerating (non-cooperative) HS → LS kinetics to sigmoidal. Thus, the presence or absence of water molecules can affect cooperative interactions between Fe^{2+} ions in 1D polynuclear iron(II) complexes with 1,2,4-triazoles. Thermodynamic parameters of spin transition are also strongly dependent on water content.

Our results provide the first experimental evidence that water produces dramatic changes in the spin crossover behaviour of the prototypical 1D polymeric complex $Fe(ATrz)_3(NO_3)_2{\cdot}H_2O$ (ATrz = 4-amino-1,2,4-triazole).

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IRON(II) COMPLEXES WITH *N,N,N*-TRIDENTATE PYRIMIDINE-BASED LIGANDS: IMPACT OF SUBSTITUENTS ON SPIN CROSSOVER

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The spin crossover phenomenon in iron(II) complexes has attracted attention due to its fundamental importance and prospects for applications. One of the challenges in this field is synthesizing complexes exhibiting wide, abrupt, symmetric and reproducible hysteresis loops.

Iron(II) complexes with 2,6-bis(pyrazolyl)pyridines/pyrazines are one of the flexible groups of spin crossover compounds [1]. We began studying spin crossover properties of their analogs, *i.e.*, iron(II) complexes with 2,6-bis(1*H*-pyrazol-1-yl)pyrimidines. However, these ligands appeared to feature rather weak ligand field favoring the high spin state either low temperature spin crossover [2].

To enhance the ligand field and to promote relative stabilization of the low spin state we replaced one of the pyrazol-1-yl groups by the pyridin-2-yl group and synthesized a series of new hybrid ligands, 2-(pyridin-2-yl)-4-(1*H*-pyrazol-1-yl)pyrimidines. Magnetic properties of iron(II) complexes with these ligands were studied both in solid state and in solutions.

Depending on the substituents in the ligand core, iron(II) complexes with 2-(pyridin-2-yl)-4-(1*H*-pyrazol-1-yl)pyrimidines can show spin crossover at various temperatures. The amino group in the 6 position of the pyrimidine ring stabilizes the high spin state and favours low temperature spin transitions (due to π-donating effect) whereas the methyl groups both in the 6-position of the pyrimidine ring and in the 3 and 5 positions of the pyrazolyl groups shift the spin transition to higher temperatures (due to σ-donating effect). Importantly, some complexes show thermal hysteresis loops, *e.g.* an anhydrous mononuclear complex $[FeL_2](BF_4)_2$ ($\mathbf{1^A}$, L = 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(pyridin-2-yl)-6-methylpyrimidine) shows an exceptionally wide thermal hysteresis loop spanning up to 145 K [3–6]. Isothermal and non-isothermal kinetic measurements allowed us for the first time to estimate kinetic parameters of cooperative spin transition with hysteresis and to get the first experimental evidence that wide thermal hysteresis loops are associated with high activation barriers [4–6].

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VARIABILITY OF CRYSTAL STRUCTURES OF ACTINIDE(VI) CHROMATE COMPLEXES

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Three actinide(VI) chromate complexes with AnO_2:CrO_4 ratio 1:2 have been synthesized in form of single crystals, their structures have been determined at 100 K (Bruker KAPPA APEX II area detector diffractometer).

Crystal data: **$Li_2[NpO_2(CrO_4)_2]\cdot5H_2O$ (I):** a = 10.0817(3), b = 10.9190(3), c = 11.6790(3) Å, β = 102.168(2)°, sp. gr. $P2_1/n$, Z = 4, $R1$ = 0.0360; **$K_2[PuO_2(CrO_4)_2]\cdot2.5H_2O$ (II):** a = 18.0637(14), b = 7.6452(6), c = 19.808(2) Å, β = 116.276(4)°, sp. gr. Cc, Z = 8, $R1$ = 0.0384; **$Rb_2[(NpO_2)(CrO_4)_2]\cdot2H_2O$ (III):** a = 5.9242(1), b = 13.1766(3), c = 7.4966 (2) Å, β = 99.186(1)°, sp. gr. $P2_1/n$, Z = 2, $R1$ = 0.0200.

The structure I contains anionic layers $[NpO_2(CrO_4)_2]_n^{2n-}$, in which NpO_2^{2+} dioxocations are linked by bidentate- and tridentate-bridging chromate anions with formation of a 343^24 net. Coordination polyhedron (CP) of Np atom is a distorted pentagonal bipyramid with two O atoms of bidentate and three O atoms of tridentate chromate anions. Coordination numbers (CN) of Li^+ cations are 5 and 5+1, their CP being distorted trigonal bipyramid and cube.

The structure II contains anionic chains $[PuO_2(CrO_4)_2]_n^{2n-}$, in which PuO_2^{2+} dioxocations are linked by bidentate cyclic-bridging and bidentate-bridging chromate anions. The CP of Pu atoms are distorted pentagonal bipyramids forming paires sharing one equatorial edge due to bridging O atoms of bidentate cyclic-bridging chromate anions. The structure contains two crystallographically independent formula units with similar functions of PuO_2^{2+} dioxocations and chromate anions. A difference can be found in K^+ cations environment with CN 8 and 9.

The structure III contains anionic chains $[NpO_2(CrO_4)_2]_n^{2n-}$, in which NpO_2^{2+} dioxocations are linked by bidentate-bridging chromate anions. The Np atom occupies a special position in inversion centre, its CP being a distorted tetragonal bipyramid. The CN of Rb^+ cation is 10.

All the three compounds with the same AnO_2:CrO_4 ratio contain complex anions with similar composition but different structures. Anionic layers, similar to found in I, make a base of a lot of structures of An(VI) molybdates. Tetragonal bipyramid, found in III as CP for Np atom, is rather uncommon for An(VI) compounds with tetrahedral doubly charged anions.

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COORDINATION COMPOUNDS OF COPPER(II) WITH N-ALKYL, N-PHENYL AND MORPHOLINE-DERIVATIVES OF HYPERBRANCHED POLYESTER POLYOLS

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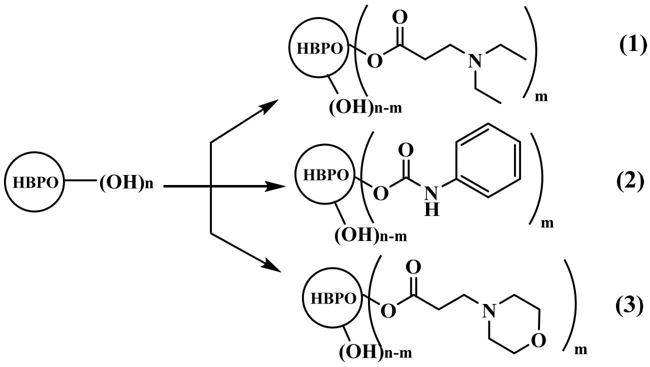
The coordination compounds of d-metals formed by functional derivatives of non-toxic and biodegradable hyperbranched polyetherpolyols (HBPO) are the basis for creating promising bio- and composite materials with the desired practical properties. A number of nitrogen-containing hyperbranched polyesters of the second and third generations containing N-alkyl **(1)**, N-phenyl **(2)** and morpholine-functional **(3)** fragments in terminal positions were synthesized. New polynuclear complexes of copper (II), based on the polydentate ligands obtained, were synthesized and characterized by IR and UV-type spectroscopy.



For ligands **(1)**, complexation with Cu (II) ions have occured due to interaction with nitrogen atoms of amino groups and oxygen atoms of the C = O group of the polyester; in the IR spectrum there were vibration bands of Cu-O at 512 cm^{-1} and Cu-N at 473 cm^{-1}. In the solution of the Cu (II) - **(1)** system, complex forms of the composition M: L - 6:1 (*lgβ* '= 19.4) were formed for the second generation and 13:1 (*lgβ'* = 30.4) for the third generation. The EPR parameters of the complexes corresponded to the presence of two nitrogen atoms of the amino groups and two oxygen atoms of the carbonyl groups in the nearest equatorial copper environment in the presence of tetragonal distortion of the equatorial plane $CuN_2O_2Solv_2$, where Solv was the solvent.

For Cu (II) complexes with ligands **(2)** in the IR spectrum, the C-O-C signal of the morpholine fragment have disappeared at 1114 cm^{-1} with the signal of the ester group of the polymer preserved at 1127 cm^{-1}. There was also a decrease and a shift in the stretching band of the C = O group, that have indicated the participation of these groups in the complexation. In the solution of the Cu (II) - **(2)** system, the complex forms of the composition M: L - 3:1 (*lgβ* '= 9.1), 6:1 (*lgβ'* = 17.7) form with the octahedral geometry of the coordination node and the CuN_2O_2 composition in the equatorial plane for HBPO of the second generation and 1:1 (*lgβ* '= 3.7), 8:1 (*lgβ'* = 18.2), 13:1 (*lgβ* '= 34.6) with tetragonally distorted geometry of the coordination node of the composition (CuN_2O_2) at the equatorial position for HBPO third generation.

For ligands **(3)**, the coordination of Cu (II) ions was carried out by the donor oxygen atoms of the carbonyl moiety and the nitrogen of the phenylcarbamate fragment. In the solution of the Cu (II) - **(3)** system, complex forms of the composition M: L - 5:1 (*lgβ* '= 10.7), 9:1 (*lgβ'* = 16.3) were formed for the second generation

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TRANSITION METALS CARBOXYLATES WITH RING METALCORE

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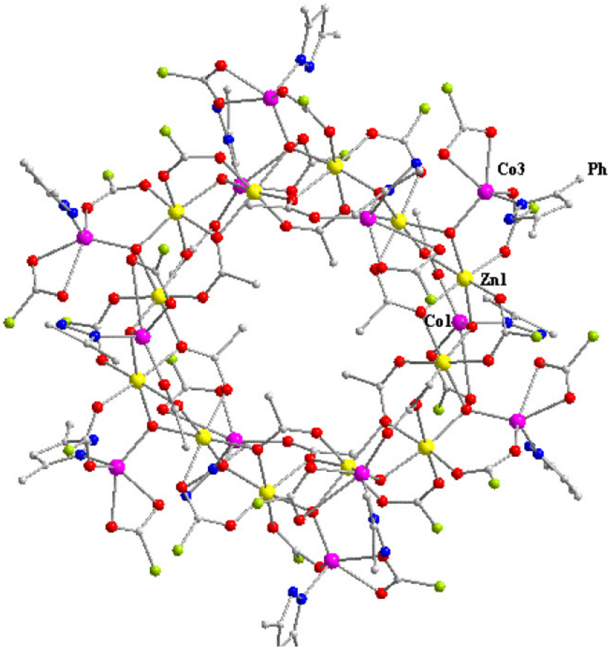
Polynuclear homo- and heterometallic complexes of transition metals are of interest from the point of view of useful magnetic, optical and catalytic properties.

It has been found that mononuclear carboxylates of transition metals (Co, Zn, Ni) with coordinated 3,5-dimethylpyrazole can be initial for the production of polynuclear complexes with a ring metalcore. Thus, the reaction of the complex Co $(Hdmpz)_2(PhCOO)_2$ with aqueous acetates of cobalt, nickel and zinc by boiling in acetonitrile leads to the formation of structures with the metalcore $M_{12}Co_{12}$ (M = Zn, Co, Ni). In the obtained complexes of $Co_{12}M_{12}(\mu\text{-}OOCMe)_{12}(\mu\text{-}OOCPh)_{18}(\mu,\eta^2\text{-}OOCPh)_6(\mu^3\text{-}OH)_{12}(Hdmpz)_{12}$, 24 metal atoms are bound by 12 bridging hydroxy groups and 36 carboxylate anions.



It is possible that the resulting ring complex is the first compound of the homologous series of ring heterocarboxylates of transition metals and the transition to complexes with M24 skeletons results from the deprotonation of bridging water molecules and coordination due to the oxygen atom of the μ-O acetate group.

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THE INFLUENCE OF SOLVENT COMPOSITION ON THE STABILITY OF [AG18C6]$^+$

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The stability constants of complexes between silver(I) ion and 18-crown-6 ether (18C6) in mixed ethanol-dimethyl sulfoxide solvents (EtOH-DMSO; $\chi_{DMSO} = 0.0 \div 1.0$ mol.fr.) as well as the Gibbs transfer energy of Ag^+ ion from EtOH to DMSO ($\Delta_{tr}G^0(Ag^+)_{EtOH\rightarrow DMSO}$) were determined potentiometrically at 298.15 K. Calculations of logK^0 values for the formation of the $[Ag18K6]^+$ complexes were carried out using the HyperQuad software. The value of $\Delta_{tr}G^0(Ag^+)_{EtOH\rightarrow DMSO}$ was calculated by the equation: $\Delta_{tr}G^0(Ag^+)_{EtOH\rightarrow DMSO} = F(E_{(DMSO)} - E_{(EtOH)}) - RT\ln(C_{Ag+(DMSO)}/C_{Ag+(EtOH)})$, where $E_{(DMSO)}$ and $E_{(EtOH)}$ represent the *emf*s of the cell in DMSO and EtOH, respectively (mV), and C_{Ag+} is the concentration of Ag^+ ions ($mol\cdot l^{-1}$).

It was found that the transition from amphoteric EtOH to aprotic DMSO causes a sharp decrease of the complex stability. According to the literature, the low stability of $[Ag18C6]^+$ in many aprotic solvents, especially those with donor numbers above 25, likely results from the increase in the stability of Ag^+ solvate complexes.

The results are discussed following the solvation-thermodynamic approach, which allows one to consider the influence of the solvent on the complexation reaction through the thermodynamic functions of solvation or transfer of the reagents: $\Delta_{tr}G^0_r = \Delta_{tr}G^0(ML)^{z+} - \Delta_{tr}G^0(M)^{z+} - \Delta_{tr}G^0(L)$, where $\Delta_{tr}G^0_r$, $\Delta_{tr}G^0(ML)^{z+}$, $\Delta_{tr}G^0(M)^{z+}$ and $\Delta_{tr}G^0(L)$ are the standard Gibbs energies for the transfer of the reaction, complex particle, metal ion and ligand from the individual solvent to the binary mixture, respectively. In the formation of complexes, the crown significantly shields the central ion from interaction with solvent; based on this, it was concluded in that the solvate state of the complex ion in solution would be determined mainly by the solvate state of ligand [1]. As a result, the solvation-thermodynamic effect of solvent was represented as the sum of two contributions: the differences in the solvation of the complex ion and the ligand and the solvation effect of metal ion.

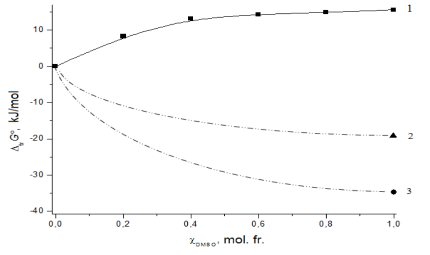

Fig. The ratio of solvation contributions of reagents to change in the Gibbs energy of $[Ag18C6]^+$ formation reaction in the EtOH-DMSO solvents: 1 - $\Delta_{tr}G^0_r$; 2 - $[\Delta_{tr}G^0([Ag18C6]^+) - \Delta_{tr}G^0(18C6)]$; 3 - $\Delta_{tr}G^0(Ag^+)$.

The dynamics of the solvation contributions of the reagents to the stability change $[Ag18C6]^+$ is shown in the figure. The determining factor in the displacement of the complexation equilibrium is the change in the solvate state of the central ion. A similar ratio of the solvation contributions of the reagents to the $\Delta_{tr}G^0$ variation of the complexation of Ag^+ with 18C6 is observed for mixed solvents methanol-dimethylformamide [2] and acetonitrile-dimethyl sulfoxide [3], which is a distinctive feature of the results obtained for water-organic solvents obtained previously.

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PREPARATION AND COORDINATION ABILITIES OF (2,2’,3,3’)-N,N'-(1,2-PHENYLEN)-BIS-(PENT-3-EH-2-IMINE)

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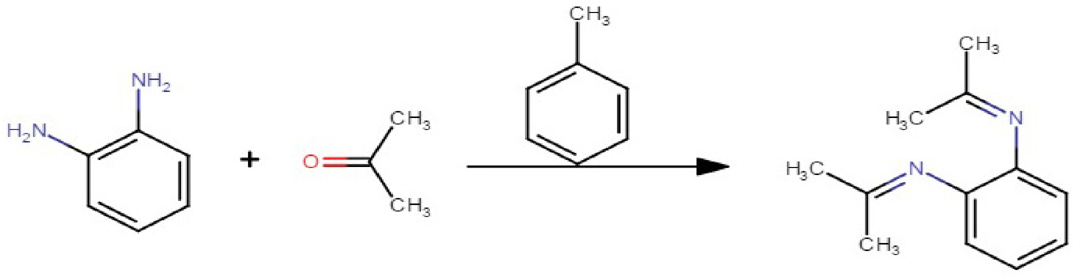
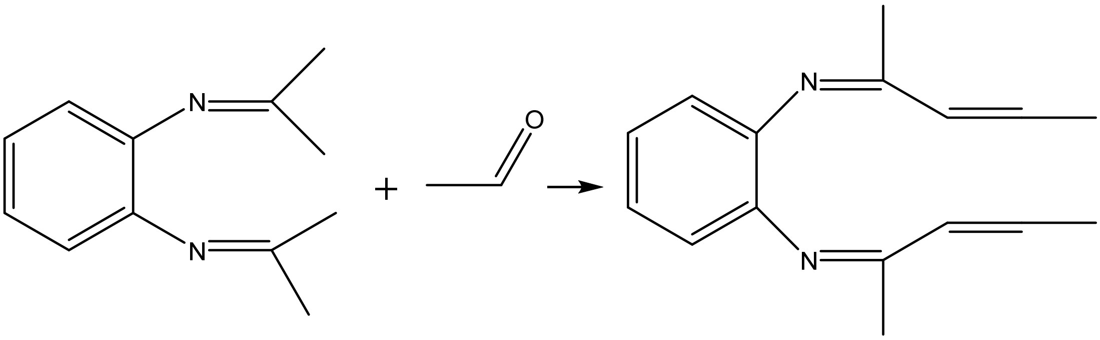
Preparation of the polymetallic coordination compounds having different metals is of great interest because such complexes can act as multifunctional catalysts for chain processes where one metal promote one reaction and the other – the following chemical process. In order to obtain such type of complexes it is necessary to synthesize polydent ligands having “harsh” and “soft” coordination sites for the interaction of complement metal ions.

We have synthesized such kind of ligand - (2,2’,3,3’)-N,N'-(1,2-phenylen)-bis-(pent-3-ен-2-imine) (*bis*-ene-imine) where nitrogen atoms act as harsh Lewis bases and C=C and C=N bonds present soft Lewis bases. The synthesis of *bis*-ene-imine is two-staged. The first stage is the reaction of dimethylketone with o-phenylenediamine producing N,N'-di-iso-propylidene-1,2-benzenediamine, that subsequently reacted with acetic aldehyde with the formation of the desired product.





We have also studied the coordination abilities of title *bis*-ene-imine with hexacarbonyl complexes of chromium group metals as well as its reactivity towards dialkyl(H)phosphonates as well both in free state and in metals’ coordination sphere.

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X-RAY CRYSTAL STRUCTURES, HIRSHFELD SURFACE ANALYSIS, AND DFT CALCULATIONS ON Hg(II) COMPLEXES: EXPLORING THE EFFECT OF WEAK INTERACTION ON THE FINAL STRUCTURE

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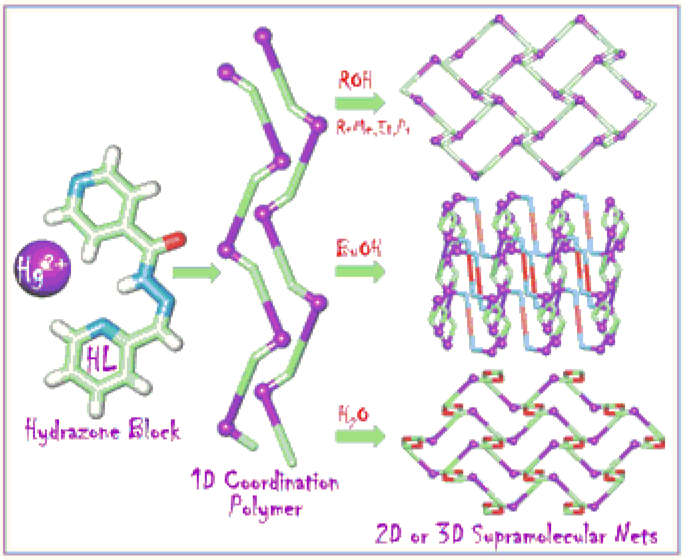
Schiff bases are important systems in asymmetric catalysis [1] and their transition metal complexes can often mimic biological sites; they are therefore of great interest as enzyme models [2]. When growing crystals from solution, the solvent used sometimes plays a role in determining the crystal structure that is obtained [3]. This role can range from influencing the polymorph that is grown to being built in into the crystal structure itself to form a solvate.

In this study, we synthesized a novel mercury complex using Schiff base namely 2-pyridinecarbaldehyde isonicotinoyl hydrazone (HL), described the IR, X-ray crystal structures of this compounds.



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КОМПЛЕКСООБРАЗОВАНИЕ КАДМИЯ(II) С 1-МЕТИЛ-2-МЕРКАПТОИМИДАЗОЛОМ В ВОДНЫХ И ВОДНО-СПИРТОВЫХ РАСТВОРАХ

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В настоящем докладе приведены экспериментальные результаты по исследованию процесса комплексообразования кадмия (II) с 1-метил-2-меркаптоимидазолом в водных и водно-спиртовых растворах. Проведенные исследования показали, что при титровании раствора Cd(II) 1-метил-2-меркаптоимидазолом в водном и водно-спиртовом растворе потенциал кадмиевого электрода уменьшается. Для определения характера комплексообразования Cd(II) с 1-метил-2-меркаптоимидазолом по данным потенциометрического титрования строили график зависимости ΔE от –lg[L], из которой находили количество частиц образующихся в системе Cd(II) – 1-метил-2-меркаптоимидазол-R при 298K, где R- CH_3OH и C_2H_5OH. Установлено, что Cd(II) с 1-метил-2-меркаптоимидазолом как в водных, так и водно-спиртовых растворах реагирует ступенчато. При этом природа растворителя не влияет на количество частиц образующихся в растворе. Общие константы устойчивости комплексов по данным потенциометрического титрования находили методом Ледена (табл. а,б).

Таблица. Общие константы устойчивости 1-метил-2-меркаптоимидазольных комплексов кадмия(II) при 298K в водно – спиртовых растворах

а)

Константы	Концентрация, объемн. %					
	Этанола					
	0	15	35	55	75	96
$\lg\beta_1$	2,59±0,07	3,17±0,02	3,42±0,16	3,59±0,04	3,80±0,09	4,18±0,10
$\lg\beta_2$	4,95±0,14	5,49±0,02	5,77±0,03	5,89±0,08	6,19±0,02	6,53±0,10
$\lg\beta_3$	7,16±0,22	7,49±0,02	7,65±0,02	7,89±0,02	8,00±0,01	8,82±0,06
$\lg\beta_4$	8,65±0,19	8,91±0,06	8,98±0,09	9,16±0,13	9,48±0,04	10,9±0,13

б)

Константы	Концентрация, объемн. %					
	Метанола					
	0	15	35	55	75	96
$\lg\beta_1$	2,59±0,07	2,70±0,13	2,87±0,02	3,13±0,11	3,32±0,08	3,51±0,09
$\lg\beta_2$	4,95±0,14	5,17±0,04	5,24±0,09	5,27±0,03	5,69±0,03	5,77±0,06
$\lg\beta_3$	7,16±0,22	7,21±0,05	7,29±0,06	7,35±0,04	7,83±0,06	7,85±0,03
$\lg\beta_4$	8,65±0,19	8,94±0,05	9,12±0,13	9,13±0,08	9,32±0,13	9,43±0,14

Данные таблиц показывают, что при добавлении к воде органического растворителя устойчивость комплексов Cd(II) с 1-метил-2-меркаптоимидазолом возрастают. Устойчивость монозамешенного комплекса при переходе от воды к 96% - этанолу увеличивается 1,61 раза, а к метанолу 1,35 раза. На устойчивость комплексов оказывает влияние так же и природа растворителя. Для воды устойчивость монозамешенного комплекса составляет 2,59 лог. ед., для 96% - метилового и этилового спирта 3,51 и 4,18 лог. ед. соответственно. Проведенные исследования показали, что увеличение устойчивости комплексов связано с пересолватацией органического лиганда.

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THE CHALCOGEN BOND

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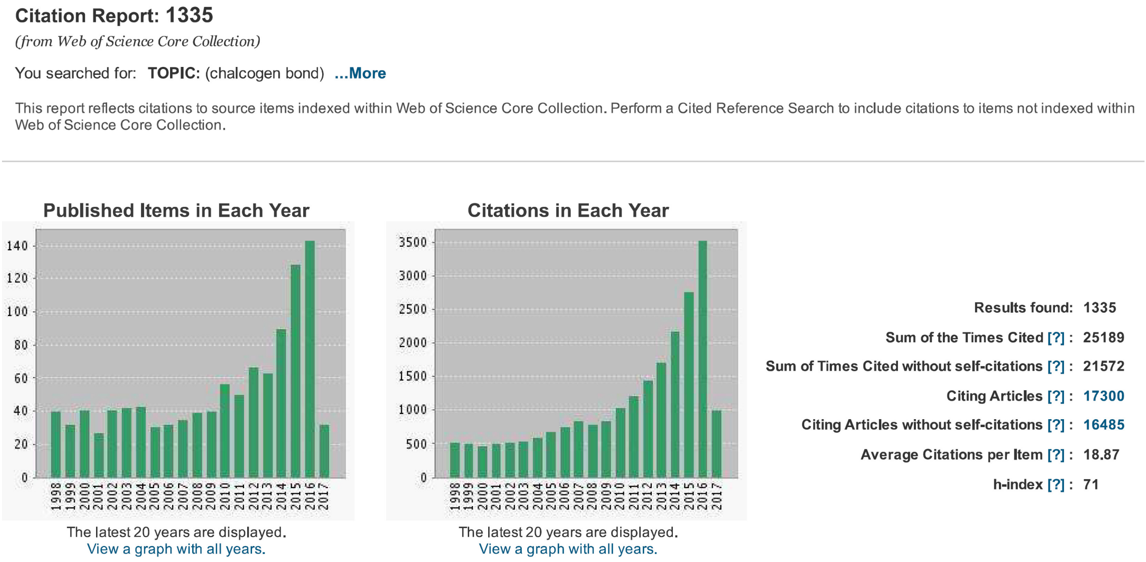
Chalcogen bonding is a novel type of noncovalent interaction in which a covalently bonded chalcogen has one or more region(s) of positive electrostatic potential and acts as an electrophilic species towards a nucleophilic (negative) region(s) in another, or in the same, molecule [1]. As hydrogen and halogen bonds, the chalcogen bonding is also crucial in many specific synthetic transformations, crystal engineering, catalysis, and design of materials involving organic and coordination compounds as synthons/tectons. In fact, the search on the ISI Web of Knowledge demonstrates that over 130 original papers concerning the chalcogen bonding have been published annually over the last two years:



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The field is growing exponentially in the last decade, but, surprisingly, there is no summarized paper (Review) on the use of the chalcogen bonding in synthesis, catalysis and design of materials, relevant topics of modern chemistry. Herein we introduce this perspective Review, which systematizes the existing information on applications of the chalcogen bonding, drawing attention to this new growing field of research.

[1] K.T. Mahmudov, M.N. Kopylovich, M.F.C. Guedes da Silva, A.J.L. Pombeiro, *Coord. Chem. Rev.* **2017**, in press, DOI: 10.1016/j.ccr.2016.09.002.

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PREPARATION OF 1,2-BIS[(2,6-DIISOPROPYLPHENYL)IMINO]ACENAPHTHENE COMPLEXES OF LANTHANIDES BY EXCHANGE REACTIONS

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It is known that diimine derivatives of lanthanides can be synthesized by direct reduction of ytterbium, samarium and europium in THF or DME [1]. However, this method makes it impossible to prepare of rare-earth elements derivatives with a stable bivalent state. Thus, it was interesting to obtain the diimine complexes of lanthanides without coordination solvents.

1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene complexes of ytterbium, lanthanum and lutetium were synthesized by exchange reactions of lanthanide iodides (Yb, La, Lu) with dpp-BIAN and three equivalents of potassium. Heating of these compounds in benzene within 50 h afford to dark green solution of ([(dpp-BIAN)$_2$Yb][K(C$_6$H$_6$)]) or a dark blue solutions of ([(dpp-BIAN)$_2$Ln][K(C$_6$H$_6$)], Ln = La, Lu) as well as a colorless precipitate of potassium iodide.

The molecular structures of obtained complexes were determined by X-ray diffraction analysis (Fig. 1, 2).

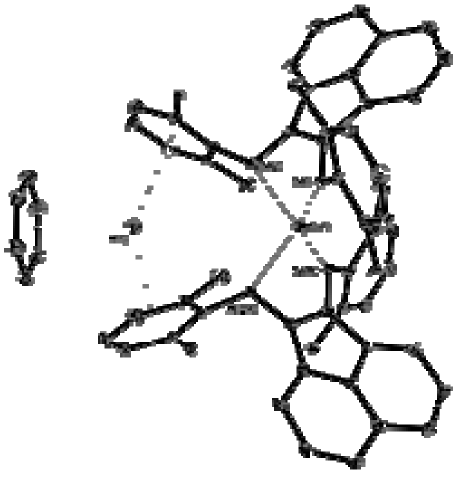

Fig. 1. The structure of the complex [(dpp-BIAN)$_2$Yb][K(C$_6$H$_6$)]

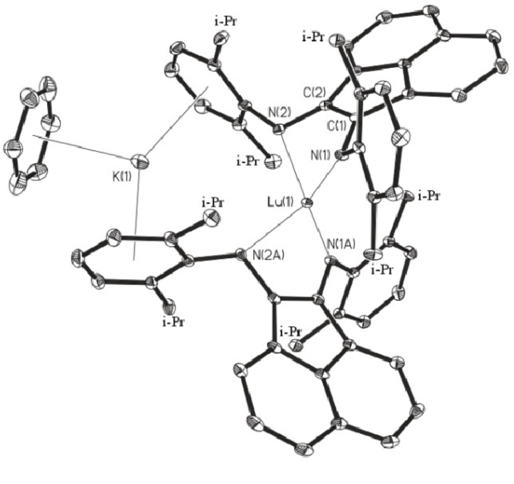

Fig. 2. The structure of the complex [(dpp-BIAN)$_2$Lu][K(C$_6$H$_6$)]

[1] I.L. Fedushkin, O.V. Maslova, E.V. Baranov, A.S. Shavyrin, Inorg. Chem., 2009. 48, 2355-2357.

Acknowledgements - The work was supported by the Russian Foundation for Basic Research and the Ministry of Industry and Innovation of the Nizhny Novgorod Region 15-43-02568.

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October 2-6, 2017, N. Novgorod, Russia

ONE-POT FORMATION OF MONOMERIC AND μ-CARBIDO-BRIDGED DIMERIC RUTHENIUM PHTHALOCYANINATES

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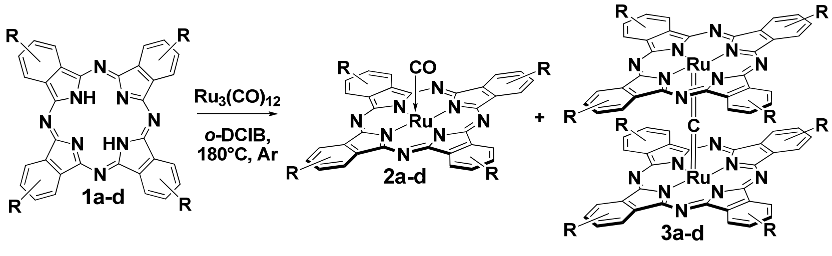
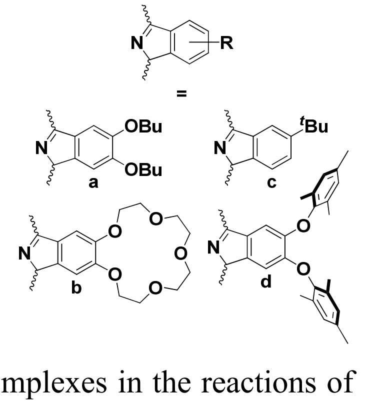
Ruthenium complexes with phthalocyanine ligands (RuPc) can be considered as close analogues of iron porphyrins which constitute active sites of hemoproteins and play crucial roles in the transfer of small molecules and oxidation of organic substrates in Nature. However, the catalytic chemistry of RuPc is much less developed as compared with their iron counterparts. Development of new synthetic approaches to access novel RuPc structures and investigation of their properties are therefore the important tasks.

Although ruthenium phthalocyaninates are commonly synthesized by *template* condensation of phthalonitriles in the presence of the metal source [1], here we report a detailed investigation of the *direct* metalation of the preformed substituted phthalocyanines to broaden the scope of complexes with the required properties.

The interaction between $Ru_3(CO)_{12}$ and various phthalocyanine ligands **1a-d** in *o*-dichlorobenzene at 180°C unexpectedly yielded simultaneously two types of complexes – monomeric carbonyl phthalocyaninatoruthenium(II) **2a-d** and dimeric μ-carbido-bridged bis[(phthalocyaninatoruthenium(IV)] **3a-c**, which have been separated by size-exclusion chromatography and characterized by UV-Vis, NMR, FT-IR, MALDI TOF and HR-ESI MS. The yield of dimeric species gradually decreased upon the increase of bulkiness of the substituents at the Pc periphery. The dimer **3d** with the most bulky mesityloxy-groups could not be obtained under these conditions.





Phthalocyanine	1a	1b	1c	1d
Yield 2, %	62	53	86	73
Yield 3, %	22	13	7	0

Investigation of the catalytic activity of the synthesized complexes in the reactions of carbene transfer are in the progress. Preliminary results indicate their high potential for the catalytic applications in organic synthesis.

[1] T. Rawling and A. M. McDonagh, *Coord. Chem. Rev.*, 2007, **251**, 1128–1157.

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INFLUENCE OF THE COMPLEX OF TETRA-TRIMETHYLTIN(IV) [*MESO*-TETRA (4-CARBOXYPHENYL) PORPHYRIN] AND *MESO*-TETRA (4-CARBOXYPHENYL) PORPHYRIN ON THE ABILITY OF THE BLOOD RBC HEMOLYSATE TO UTILIZE THE SUPEROXIDE ANION IN EXPERIMENTS *IN VITRO*

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Complexes of organotin compounds with porphyrins are potential antitumor drugs [1]. An important role is played by organic ligands, which contribute to enhancement of biological activity and minimization of side effects due to the overall toxicity of the environment. The aim of this work is to study the effect of the tetra-trimethyltin(IV) *meso* tetra (4-carboxyphenyl) porphyrin ($(Me_3Sn)_4TCPP$) and *meso* tetra (4-carboxyphenyl) porphyrin complex on the ability of the blood RBC hemolysate to utilize the superoxide anion radical ($O_2^{\bullet-}$) in model system of adrenaline's autoxidation in alkaline medium. Rate of adrenaline's autoxidation has been assessed spectrophotometrically (λ = 347 nm) by measuring the accumulation of adrenochrome [2].

It has been established that the addition of rat erythrocyte hemolysate leads to a significant decrease in the rate of adrenaline's autooxidation (Fig.), which is explained by the action of the superoxide dismutase enzyme, utilizing $O_2^{\bullet-}$ in the reaction: $2O_2^{\bullet-}+2H^+ \rightarrow O_2+H_2O_2$, the course of a number of other reactions.

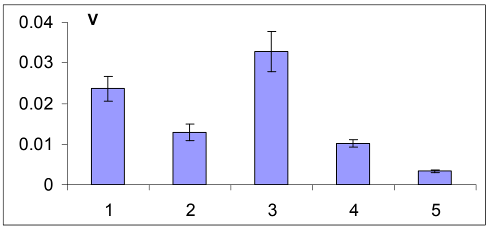

Fig. - Influence of test compounds on the rate of adrenaline's autoxidation (V, units of optical density / minute) without additives-1, also in the presence of hemolysate-2 and: 3 - $(CH_3)_3SnCl$; 4 - $((Me_3Sn)_4TCPP$; 5 - TCPP. Adrenaline concentration = 5.46 mM, test compounds - 0.22 mM; 0.1 M carbonate buffer, (pH 10.65) at 25 °C.

An increase in the oxidation rate of adrenaline in the presence of $(CH_3)_3SnCl$ was found, which indicates the leveling of the ability of hemolyzate of erythrocytes to utilize the $O_2^{\bullet-}$. It has been established that in the presence of the TCPP, $(Me_3Sn)_4TCPP$, the adrenaline oxidation rate is reduced by 77% and 23%, respectively.

Thus, in vitro experiments it was shown that water-soluble meso-phenyl-porphyrin increases the ability of rat blood erythrocytes hemolysate to utilize the superoxide anion radical and thereby improves the adaptive capacity of rodents under oxidative stress conditions. It has also been established that the complexation of trimethyltin chloride with this porphyrin leads to an inversion of the toxicant's prooxidant activity and reduces the likelihood of the compound manifesting side effects.

[1] S. Aydinoglu, T. Biver, S. Figuccia et al., J Inorg Biochem., **2016**, *163*, 311-317.
[2] T. Sirota, Biomed. Khim., **2015**, *61 (1)*, 115.

Acknowledgements - we are grateful to RFBR (17-03-00434) for financial support of this work.

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FIRST ROW TRANSITION METALS MEDIATED AND CATALYZED CYCLOADDTION OF KETONITRONES TO DISUBSTITUTED CYANAMIDES

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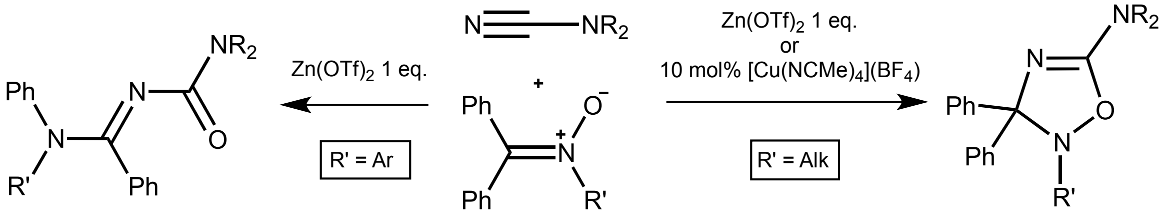
1,3-Dipolar cycloaddition to metal-activated nitrile substrates is a powerful method for preparation of nitrogen heterocycles. Cycloaddition of nitrones $R^1R^2C{=}N^+(O^-)R^3$ to nitriles in platinum(II- and IV) and palladium(II) complexes has been extensively studied for the last two decades [1]. These reactions open up routes to uncomplexed and coordinated 2,3-dihydro-1,2,4-oxadiazoles, which could not be synthesized from nitriles in the absence of metal center. In all studied examples, a cycloaddition product was coordinated to a metal center and additional step of heterocycle decoordination was required for generation of metal-free heterocycles.

In the current work, we turned out our attention to more kinetically labile centers than platinum metals, viz. zinc(II) and copper(I). We studied the reaction of nitrile substrates NCR (R = Alk, Ar, NR_2) with nitrones $R^1R^2C{=}N^+(O^-)R^3$ (R^1 = Ar; R^2 = H, Ar; R^3 = Alk, Ar) in the presence of zinc(II) and copper(I) species, viz. $Zn(OTf)_2$ (1 equiv., CH_2Cl_2, RT, 5h–2d) and $[Cu(NCMe)_4](BF_4)$ (10 mol%, CH_2Cl_2, 45 °C, 1–2d), and determined the scope and limitations of these cycloadditions [2,3]. We found that only the *N*-alkyl ketonitrones $Ar_2C{=}N^+(O^-)Alk$ undergo metal-mediated cycloaddition (Scheme, right), while the *N*-aryl ketonitrones $Ar_2C{=}N^+(O^-)Ar$ gave acyclic products (Scheme, left). Reactivity of the aldonitrones $ArC(H){=}N^+(O^-)Alk$ was insufficient in the attempted reactions and no heterocycles were obtained. Within nitrile substrates only cyanamides $NCNR_2$ can be involved in the cycloaddtion, whereas conventional nitriles NCR (R = Alk, Ar) did not react with any of nitrones under conditions of Cu(I)- or Zn(II)-mediated reactions. Reactions of ketonitrones with cyanamides in the presence of zinc(II) salts required stoichiometric amount of metal-activator (1.0 equiv. of $Zn(OTf)_2$), while copper(I)-involved reactions were performed under catalytic conditions (10 mol% of $[Cu(NCMe)_4](BF_4)$) (Scheme, right).



All studied reactions led to uncomplexed heterocycles in one step and they require relatively cheap metal salts that are certain advantages of these methods. These reactions opened up an easy and convenient way to 5-aminosubstituted 2,3-dihydro-1,2,4-oxadiazoles.

[1] N. A. Bokach, M. L. Kuznetsov, and V. Y. Kukushkin, *Coord. Chem. Rev.*, **2011**, *255*, 2946–2967.
[2] Smirnov, A. S.; Butukhanova, E. S.; Bokach, N. A.; Starova, G. L.; Gurzhiy, V. V.; Kuznetsov, M. L.; Kukushkin, V. Y., *Dalton Transactions* **2014,** *43*, 15798–15811.
[3] A. A. Melekhova, A. S. Smirnov, A. S. Novikov, T. L. Panikorovskiy, N. A. Bokach, V. Yu. Kukushkin, *ACS Omega*, **2017**, *2*, 1380–1391.

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EXPRESS-ANALYSIS OF NITRATE CONTENT BY INDICATOR PAPER

N. Lukyanova, E. Loginova, A. Varlamova, S. Gridchin and V. Nikol’skiy

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Determination of nitrates is an extremely important task for today. Quality food products are currently one of the most important factors for human health. Therefore, we offer careful monitoring of nitrate ions in the food industry.

To solve this problem, we have created an indicator paper for express analysis of nitrate content [1] on the basis of which rapid monitoring of nitrates and nitrites is carried out, for example, in solutions of plant products (juices, beverages). The indicator paper for express analysis of nitrate content consists of the first layer containing N- (carboxymethyl) aspartic acid (CMAC); A second layer containing zinc; A third layer containing reagents for the Griss reaction (where dimethyl-1-naphthylamine hydrochloride is used instead of 1-naphthylamine hydrochloride), sulfanilic acid and a polymer support with a circular hole holder.

The drop of the test solution is applied to the first layer of the test paper, while the CMAC acidifies the reaction medium, and the nitrite ions, in their presence, enter into the nitrosation reaction with the fragment of the secondary amine of the CMAC, thereby eliminating their influence.

In the second layer, the nitrate ions in the acidic medium are reduced to nitrite ions, which in the indicator layer are diazotized with an amine, which reacts with the azo component. The color reaction due to the formation of azo dye is observed in a circular hole on the back of the polymer substrate-holder.

Known in the literature and currently used formulations for impregnating indicator paper usually contain a carcinogenic reagent 1-naphthylamine [2].

We have created a composition for indicator paper, in which α-naphthylamine is replaced by dimethyl α-naphthylamine, which is not a carcinogen, and CMAC is used instead of acid reagents and nitrite ion maskers[1]. This simplifies the device, while maintaining its high sensitivity and selectivity.

Indicator paper is made of two types: to determine the total content of nitrates and nitrites and to determine the content of nitrites. The range of determined concentrations for nitrates is 20-1000 mg / dm^3 (mg / kg), for nitrites - 2.5-800 mg / dm^3 (mg / kg). The shelf life of the paper in a tightly closed container and a dark place for more than two years.

With the help of indicator paper the content of NO_3-ions was found in potatoes - 110 mg / kg, which is below the MPC = 250 mg / kg. Good convergence of results confirms the reliability of measurements with the device we invented.

[1]. A. Varlamova, E. Gyulkhandanyan, V. Nikol’skiy, S. Gridchin, *Patent RF № 169694*, 28.03.2017.
[2]. D. Guseva, E. Loginova, V. Nikol’skiy, *Patent RF № 162596*, 20.06.2016.

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PHOTOLYTIC SYNTHESIS OF NEW OXYGEN-ACTIVE ANTIMONY-CONTAINING POROUS POLYMERS

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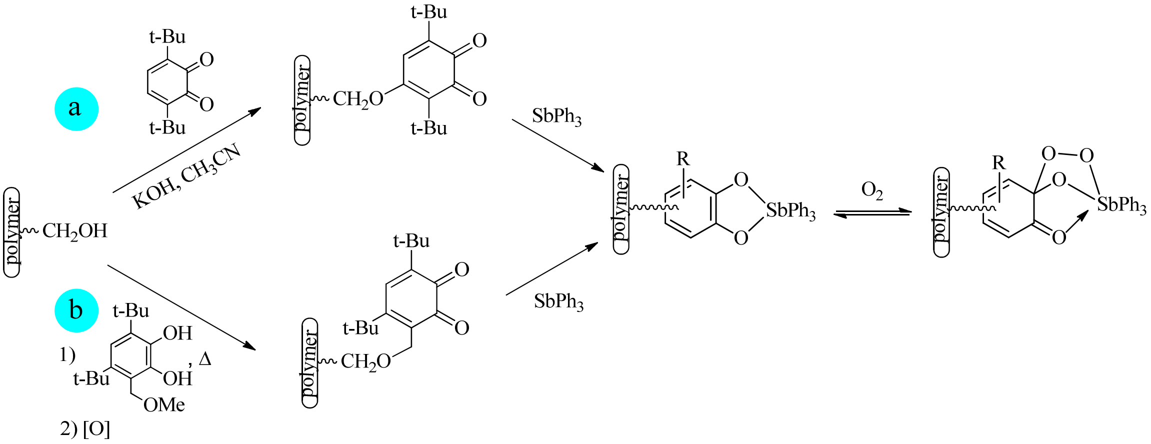
Investigation of materials which can reversible bind of O_2-molecule is very important for development of catalytic oxidation processes and oxygen storage and purification methods. The mechanism of the «classic» dioxygen binding systems (3d-metal compounds) is based on the reversible reaction associated with the change in the oxidation state of the metal center. In recent years the other model systems for a reversible binding of dioxygen – complexes of nontransition metals with redox-active ligands – have been discovered. In such systems the organic redox-active ligand undergoes the oxidation instead of metal fragment. It was found that some of the triphenylantimony(V) catecholate complexes are able to the effective reversible binding of dioxygen. Such type complexes can be easily prepared by the interaction of $SbPh_3$ with *o*-quinones (the oxidative addition reaction). On the basis of this reaction we have developed the porous material capable of the reversible binding of dioxygen with the realization of the conditions of maximal access of O_2 to antimony complex molecules, for example by using polymer matrix with opened and connected porous system.

Polymer matrix was obtained by copolymerization of QM with OCM-2 and MEG in the presence of methanol as the porogenic solvent. Two ways of quinone-containing polymers for preparation of Sb-containing polymers were investigated: alkoxylation of 3,6-di-*tert*-butyl-*o*-benzoquinone (a) and transalkylation of 3,5-di-*tert*-butyl-6-(methoxymethyl)catechol with further oxidation (b).



The reaction with Ph_3Sb to form Sb-containing catechols which are able to reversible binding of oxygen with change in color is typical for. Previously we have shown that this reaction proceeds in copolymer film QM-DMPEG-MEG. O-benzoquinone fragments in the grafted layer also able to form antimony complex by reaction with Ph_3Sb. Convercion antimony catechol complex to spiroendoperoxide on air in the grafted layer up to 46% for 2 hours that is higher in 1,5 order of magnitude compared with this process in copolymer film (60% for 3 days).

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INVESTIGATION OF THERMOCHEMICAL PROPERTIES OF NEW COMPLEXES OF GADOLINIUM WITH SUBSTITUTED THIOPHENOLATES

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The rare earth metals are unique elements which fascinating luminescent properties lead to an outstanding role in light conversion technologies. In the past time, the main attention was focused on the application of lanthanide complexes as electroluminescent materials for organic light emitting diodes (OLED). These materials are a part of the OLED included as nano-sized thin film, commonly obtained by the vapor deposition (MO CVD). For each vapor deposited compound its thermochemical properties should be known.

In the present work we have reported the result of investigation of thermochemical properties of new compounds: 2-(2'-mercaptophenyl)benzoxazole (OSN(H)) (**1**), 2-(2'-mercaptophenyl)benzothiazole (SSN(H)) (**2**), $Gd(SSN)_3$ (**3**) and $Gd_2(OSN)_6$ (**4**). The ligands **1-2** and complexes Gd **3-4** were synthesized according of procedure described in [1]. These compounds **1-4** were characterized by elemental analyses, X-ray diffraction and IR spectroscopy. Mass-spectra of ligands **1-2** were obtained on a Polaris Q mass spectrometer using direct input and mass-spectra of complexes **3-4** were obtained by MALDI-TOF method.

The study of phase transitions of the samples **1-4** in the region of 30-400 ^{o}C was performed using a differential scanning calorimetry (DSC). Within the sensitivity of the method, the substances under investigation are an individual phase. In the above temperature range the sample of compounds **1-2** underwent a phase transition due to melting. For complexes **3-4** at the temperatures 220 and 215 ^{o}C, respectively, a sharp of the peaks and their irreversibility indicate the occurrence of the irreversible phase transformation. This corresponds to the process of decomposition (degradation) of complexes **3-4** at further heating.

The temperature dependence of the vapor pressure of the ligands **1-2** and complexes Gd **3-4** was measured by the Knudsen's effusion method with the registration of the amount of material sublimated in the temperature range 77-200 ^{o}C. Vaporization temperature interval was chose according to the DSC data. The thermodynamic parameters of vaporization process are calculated: for **1** $\Delta_s H=96.3\pm2.1$ kJ/mol, for **2** $\Delta_s H=105.6\pm2.5$ kJ/mol. Unfortunately, we could not get the temperature dependence of the vapor pressure of complexes **3-4** (low volatility).

In additional, according to mass-spectrum, the calculations of thermodynamic parameters were performed for the vapor pressure of sublimation into the monomeric vapor (for ligand **1-2**). The mass-spectrum of complexes **3-4** had the dimer fragments.

[1] V.A. Ilichev, A.V. Rozhkov, R.V. Rumyantcev, G.K. Fukin, I.D. Grishin, A.V. Dmitriev, D.A. Lypenko, E.I. Maltsev, A.N. Yablonskiy, B.A. Andreev, M.N. Bochkarev, *Dalton Transactions*, **2017**, *46*, 3041-3050 DOI: 10.1039/C6DT04519G.

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CATALYSIS BY METAL COMPLEXES IN THE OXIDATION OF MODEL COMPOUNDS OF LIGNIN

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Recently, more and more studies have been devoted to development of environmentally friendly, energy- and resource-saving processes of deep refining of renewable herbal sources to prepare a wide range of products with predefined properties. In this regard, using "green" oxidants (molecular oxygen, ozone, peroxides) is promising. The oxidation processes can be intensified by metal complexes, in particular, polyoxometalates (HPA).

Lignin, a polyfunctional aromatic polymer, is among major components of plants and a promising source for preparation of valuable chemical products.

Mechanism of lignin reactions is usually investigated using model compounds containing the same reactive functional groups as these of lignin. In particular, the following aromatic compounds were used in this study: ferulic acid, vanillin, vanillyl alcohol, representing the guaiacylpropane units of coniferous lignin; sinapic acid, representing the syringylpropane units of hardwood lignin; coumaric and cinnamic acids, representing the *p*–oxyphenylpropane units of lignin of annual plants.

To establish principal regularities of catalytic oxidation of aromatic compounds with peracetic acids, kinetics of the oxidation and the products composition was studied, including effects of the solution pH, the nature and concentration of the substrate, concentrations of the catalyst, oxidant, and temperature. Heteropolyanion, a manganese-containing sodium vanadomolybdophosphate of gross formula $Na_{11}[PMo_6V_5O_{39}Mn(OH)]$ was used as a catalyst [1].

Using NMR ^{31}P installed the formation of catalytically more active intermediates, peroxocomplexes of sodium vanadamolybdophosphate $[HPA(O_2)_n]$.

Analysis of kinetic data indicates parallel realization of both the activation mechanism based on the formation of an intermediate and the cyclic mechanism of catalysis based on regeneration of the reduced catalyst form under the action of peracetic acids.

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PHOSPHINE COMPLEXES OF RUTHENIUM (II) IN CATALYSIS OF CYCLOHEXENE HYDROCARBOMETHOXYLATION

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Alkenes hydrocarboalkoxylation with alcohols and CO in homogeneous catalysis by transition metal compounds opens the way for one-step synthesis of esters of commercial interest. Palladium complexes promoted by free organophosphines and strong protonic acids were now considered as the most active and selective catalysts for hydrocarboalkoxylation. However, palladium catalysts aren't stable. In this connection the question about alternative catalysts of hydrocarboalkoxylation is uncovered. Ruthenium catalysts of these reactions are studied very little. In this work, $Ru(PPh_3)_4Cl_2$, $H_2Ru(CO)(PPh_3)_3$, and $H_2Ru(PPh_3)_4$ were used as catalytic precursors in model reaction of cyclohexene hydrocarbomethoxylation with using of p-toluenesulphonic acid (TsOH) and PPh_3 as promoters which were the most active promoters of palladium catalysts of hydrocarboalkoxylation. The using of hydride ruthenium complexes was of interest to verify the existing information about the hydride mechanism of Ru-catalytic hydrocarboalkoxylation of alkenes [1].

Using autoclave was made of diamagnetic steel. Inside the autoclave, we placed a glass reactor with a special pocket for a thermocouple and open to the autoclave interior. The each experiment was performed at 453 K and the CO pressure of 6.00 MPa with methanol plenty with toluene dilution. The starting concentrations of reaction mass components were (mol/L) $C(C_6H_{10})=0.10$, $C(CH_3OH)=9.87$, $C(Ru)=4.0\cdot10^{-3}$, and $C(TsOH)=4.8\cdot10^{-2}$. In experiment with $H_2Ru(CO)(PPh_3)_3$, besides TsOH addition, the addition of free PPh_3 ($4.0\cdot10^{-3}$ M) was carried in. Thus PPh_3 concentration in reaction mass was identic in all experiments. The promoters concentrations were chosen by the analogy with the optimum composition of palladium catalytic systems in the same reaction. Analysis of the reaction mass samples was performed by gas-liquid chromatography and chromatography-mass spectrometry.

The reaction time was 6 h. The yield of methyl cyclohexanecarboxylate was 4.8 % in the presence of $Ru(PPh_3)_4Cl_2$, 4.9 % in the presence of $H_2Ru(PPh_3)_4$ and 5.0 % in the presence of $H_2Ru(CO)(PPh_3)_3$. 1-Methoxycyclohexane, cyclohexanemethanol and dimethoxymethane were detected in the reaction mass as by-products. These compounds weren't carbonylation products. The summation concentrations of by-products were $1.3\cdot10^{-2}$ M in the presence of $Ru(PPh_3)_4Cl_2$, $1.84\cdot10^{-2}$ M in the presence of $H_2Ru(PPh_3)_4$ and $1.67\cdot10^{-2}$ M in the presence of $H_2Ru(CO)(PPh_3)_3$.

Thus using ruthenium complexes showed the catalytic activity in cyclohexene hydrocarboalkoxylation. The catalytic activity of complexes practically didn't depend on ligands surrounding ruthenium although activity of hydride complexes was a little higher than of $Ru(PPh_3)_4Cl_2$. The formation of ruthenium mohr wasn't observe therefore ruthenium complexes were stable in the reaction conditions.

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COMPLEX FORMATION OF Co(II), Ni(II) AND Cu(II) WITH SALICYLIC ACID HYDRAZIDE IN SOLUTIONS

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The formation of complexes between cobalt(II), nickel(II), copper(II) and salicylic acid hydrazide has been studied by spectrophotometry method and mathematical modeling (programs CPESSP [1] and STALABS [2]) in aqueous solutions with 1.0 mol dm^{-3} KNO_3 as background at 25.0 ^oC. Under the same conditions by means of pH-metric titrimetry three protonation constants of the ligand were determined.

Investigation of complexing processes of cobalt(II) and nickel(II) with salicylic acid hydrazide was carried out over a pH range 0.5–5. In the case of copper(II), the optical density measurements were stopped at pH 3 since the ligand was released from the solution.

In all tree binary systems octahedral complexes with metal:ligand ratios of 1:1, 1:2, and 1:3, including neutral form of hydrazide (LH_2), and of 1:1 with anionic form (LH^-) as well as complexes of type $M(LH_2)(LH)^+$ were found. Formation constants and spectral characteristics of the complexes were determined. The stability of the similar complexes follows the trend Co(II) < Ni(II) < Cu(II) that correlate with the Irving–Williams order. Based on the statistical evaluation of formation constants, it was shown that ligands in the cobalt(II) and nickel(II) *mono*- and *bis*-complexes are bidentately coordinated to the central ion and extra stabilization of *tris*-complexes was revealed.

Specially for the detection of polynuclear complexes, series of solutions with different concentrations of copper(II) and constant concentration of salicylic acid hydrazide have been investigated by spectrophotometry method. The acidity of the solutions was set approximately equal to pH 3, the maximum excess of metal was fourfold. Calculations showed that a significant amount of the Cu_2L_2 complex in which anion ligands (L^{2-}) may serve as a spacers, performing the tridentate function, is formed.

From comparison of stability constants of the complexes studied in the present work and cobalt(II), nickel(II), and copper(II) complexes with benzoic, *para*-methoxybenzoic, and isonicotinic acid hydrazides investigated previously conclusions about factors determining thermodynamic parameters of the hydrazide complexes formation were formulated.

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INTERACTION OF COPPER(II) WITH 1,5-BIS(AMIDOMETHYLSULPHONYL)PENTAN

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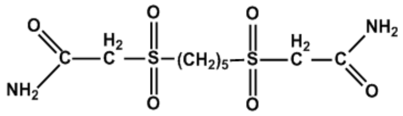
1,5-bis(amidomethylsulfonyl)pentane (**L**) [1] is a new promising antituberculosis substance. In the present contribution its complexes with copper(II) were studied by UV spectrophotometry, pH-potentiometry (T = 25 °C; variable ionic strength) and mathematical modeling (CPESSP program) in water at micellar concentrations of nonionic surfactant Brij-35.



L

It was shown that in the presence of copper(II) the absorbance maximum of substance **L** is red shifted and the absorbance increases. Experimental and additive absorbance spectra are different. Two series of spectrophotometric measurements were performed at constant concentration of copper(II) (C_{Cu2+} $4.8\cdot10^{-5}$, $9.7\cdot10^{-5}$ $mol\cdot L^{-1}$) and various concentrations of substance L (up to tenfold excess, pH 5.70-6.20). The experimental data processing showed that two cationic complexes 1:2 $[Cu\mathbf{L}_2]^{2+}$ (6.36 ± 0.04; 0.30; ε_{220} $0.41\cdot10^3$) and 2:2 $[Cu_2\mathbf{L}_2]^{4+}$ (11.10 ± 0.13; 0.54; ε_{220} $8.23\cdot10^3$) are formed in solution. The data in parentheses present the values of logarithms of apparent equilibria constants, maximum shares of complexes α_{max} and their molar extinction coefficients ε_{220}, $L\cdot mol^{-1}\cdot cm^{-1}$, respectively. The dimeric complex dominates at all concentrations. The share of monomeric complex increases due to the increasing concentration of the substance **L** in the studied system. The formation of monomeric complex can be shown in accordance with the reaction $[Cu_2\mathbf{L}_2]^{4+} + 2\mathbf{L} \rightleftarrows 2[Cu\mathbf{L}_2]^{2+}$, characterized by the apparent equilibrium constant lg K equal to 1.62. Each ligand **L** in the $[Cu\mathbf{L}_2]^{2+}$ complex is bidentate coordinated *via* carbonyl and sulfonyl oxygen atoms and forms six-membered metallacycle. In binuclear complex each ligand is tetradentate coordinated in inner sphere of copper(II) and forms four six-membered metallacycles. Both ligands bind two copper(II) ions forming twenty-membered metallacycle that also contributes to the complex stabilization. Note that a novel antitubercular substance 1,4-bis(amidomethylsulfinyl)butane [1] also forms binuclear complex with copper(II) (12.07 ± 0.06; 0.37). Besides in the 1,4-bis(amidomethylsulfinyl)butane–copper(II) system a mononuclear complex 1:1 (4.21 ± 0.03; 0.65) is formed while the 1:2 (metal:ligand) complex was not found [2].

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SYNTHESIS, PRINCIPLES OF SUPRAMOLECULAR SELF-ORGANISATION (THE ROLE OF SECONDARY INTERACTIONS: Tl···O, Tl···S, Au···S) AND THERMAL BEHAVIOUR OF 3D-POLYMERIC THALLIUM(I) MORPHOLINEDITHIOCARBAMATE AND HETERONUCLEAR DOUBLE COMPLEX OF $([Au\{S_2CN(CH_2)_4O\}_2][TlCl_4])_n$

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Recently, we have discovered the ability of thallium(I) dialkyldithiocarbamates to chemisorptive fixation of gold(III) from solutions (2M HCl), which results in the formation of heteronuclear gold(III)-thallium(III) complexes: $([Au\{S_2CN(CH_3)_2\}_2][TlCl_4])_2$ and $([Au(S_2CNR_2)_2][TlCl_4])_n$ – R = C_2H_5, *iso*-C_4H_9 [1, 2].

In the present study, novel three-dimensional polymeric thallium(I) morpholine dithiocarbamate of $[Tl_2\{S_2CN(CH_2)_4O\}_2]_n$ (compound **I**) and ion-polymeric heteronuclear complex of $([Au\{S_2CN(CH_2)_4O\}_2][TlCl_4])_n$ (**II**) were prepared and characterised using single-crystal X-ray diffraction, ^{13}C CP/MAS NMR and simultaneous thermal analysis.

The basic structural unit of compound I is the binuclear centrosymmetric molecule of $[Tl_2\{S_2CN(CH_2)_4O\}_2]$ comprising two *S,S,S′,S′*-bridging Dtc ligands (the lengths of four inequivalent Tl–S bonds are 3.015, 3.078, 3.104, 3.347 Å), whose geometry can be approximated by a tetragonal bipyramid having four equatorial sulphur atoms and two vertex thallium atoms. In the binuclear molecules, each thallium atom additionally forms two inequivalent secondary Tl···O bonds (3.112 and 3.175 Å) with two nearest neighbours yielding two-dimensional polymeric networks of the dithallium molecules. These polymeric layers, in turn, are combined into a three-dimensional polymeric framework by means of relatively weak secondary interactions of Tl···S (3.687 Å).

The chemisorptive fixation of gold(III) from solutions with a freshly precipitated complex I, which is associated with red-ox process, leads to the formation of a heteronuclear gold(III)-thallium(III) ion-polymeric complex of $([Au\{S_2CN(CH_2)_4O\}_2][TlCl_4])_n$ (compound **II**). This heterogeneous interaction may be represented by the following red-ox reaction:

$$3[Tl_2\{S_2CN(CH_2)_4O\}_2] + 5H[AuCl_4] = 3[Au\{S_2CN(CH_2)_4O\}_2][TlCl_4] + 3TlCl + 2Au + 5HCl$$

The crystal structure of II includes a noncentrosymmetric planar cation $[Au\{S_2CN(CH_2)_4O\}_2]^+$ and two species of tetrahedral $[TlCl_4]^-$ having distorted geometry, one of which is structurally disordered. In gold(III) cation, dithiocarbamate ligands exhibit almost isobidentate coordination: the lengths of the Au–S bonds are in the range 2.330–2.337 Å. Due to the symmetrical secondary Tl···S bonds (3.559 Å), pairs of gold(III) cations make binuclear formations $[Au_2\{S_2CN(CH_2)_4O\}_4]^{2+}$ having an angular structure. In turn, the binuclear cations additionally form the another kind of secondary bonds Tl···S (3.576 Å) to each other, which leads to the construction of cation-cationic polymeric chains $([Au_2\{S_2CN(CH_2)_4O\}_4]^{2+})_n$ of a helical type. Discrete isomeric anions $[TlCl_4]^-$ are localised between the polymeric chains.

The thermal behaviour of I and II was studied using the STA technique. Elemental gold and TlCl (II) and Tl_2S (I) have been identified as final products in thermolysis of the complexes.

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THE INVESTIGATION OF THE KINETICS OF THE INTERACTION BETWEEN THE CALCIUM IONS AND BIOGENIC AMINO ACIDS

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The investigation of the nature of the interaction of calcium ions and amino acids (AA) is one of the most important tasks. It is due to the formation of the pathogenic organomineral aggregates (POA) in the human body under the influence of the factors which are breaching the physiological existence in the norm [1]. At the same time, nowadays there's no complex theory which can explain the kinetics of the interaction of inorganic and organic substituents of POA in the human body.

According to this, the aim of this work was the development of the method of estimation of lability of forming complexes between Ca^{2+} and AA, which are involved in the metabolism.

The object of the research were several AA (isoleucine - Ile, aspartic acid - Asp, arginine - Arg, alanine - Ala, glycine - Gly). From the solutions of the given amino acids (C_{amino} acid = 10^{-2} mole per litre) and $Ca(NO_3)_2$ ($C_{Ca(NO_3)2} = 10^{-3}$моль/л), were selected an aliquots with V=10,0 ml and carried out in the volumetric flask with V=100 ml. Then, from mix were selected 20 ml of process solution, it was acidified to pH = 3 and was titrated by the freshly prepared solution of 0,10M NaOH with the determination of e.m.f. The obtained curves were introduced according to the Gran method (example - fig. 1):

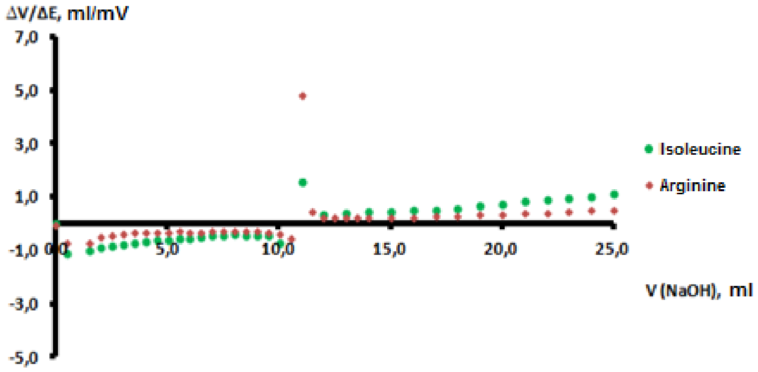

Fig. 1. The curves of potentiometric titration with the Gran method of the mixes of $C_{Ca(NO_3)2} = 10^{-3}$ mole per litre and the amino acid ($C_{amino\ acid} = 10^{-2}$ mole per litre).

For the determination of the lability of all complexes, we suggest semi-quantitative criteria δ:

$$\delta = \frac{\Delta V}{\Delta E}\text{ p. after eq. p.} - \frac{\Delta V}{\Delta E}\text{ p. before eq. p.}$$

After the calculation, according to their lability, complexes of Ca^{2+} with the given amino acids are standing in the following order: δ (Ca^{2+} - Asp) < δ (Ca^{2+} - Ile) < δ (Ca^{2+} - Ala) <δ (Ca^{2+} - Arg) < δ (Ca^{2+} - Gly), so, the most labile complex is with aspartic acid, the most stable - with isoleucine. Lability of the other complexes could be determined at the same way.

[1] Larina T.A., Kuznetsova TA, Koroleva L.Yu, The Scientific proceedings of the research center of pedagogy and psychology, *Scientific notes of Orel State University,* Orel, **2006,** Vol.7, P.135-138.

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QUANTUM-CHEMICAL SIMULATION, SYNTHESIS AND INVESTIGATION OF DIAXIAL COMPLEXES OF PORHYRINATES Sn(IV) WITH ANTIOXIDANT MOLECULES

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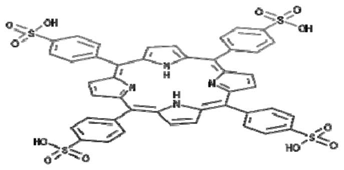
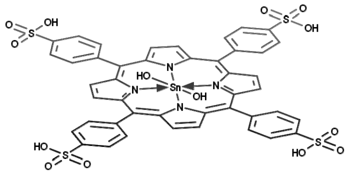
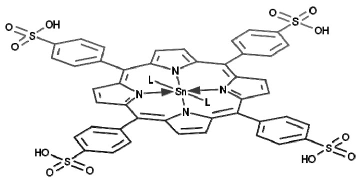
Photodynamic therapy of cancer, creation of fluorescent biomarkers, design of selective transport substance for drugs are important topics in chemistry and material sciences. In this case, porhyrin metallcomplexes, particularly fluorescence metallporhyrins, are interesting and perspective objects.



H_2TPPS_4

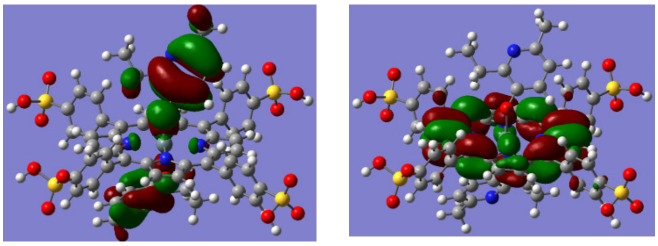


$SnTPPS_4(OH)_2$



$SnTPPS_4$-L_2

The feature of Sn(IV) porhirinates to form hexa-coordinated complexes with two trans-situated ligands of different nature was confirm by quantum-chemical calculations. The geometry was optimized and geometric parameters were studied.



Molecular orbitals of $SnTPPS_4$-L_2:
left – HOMO; right - LUMO

We analyzed molecular orbitals of the optimized structures. On the basis of this analysis differences of complexes quantum yield were interpreted.

Structures of synthesized complexes were confirmed by NMR ^{1}H spectroscopy. Binding of antioxidant molecules by Sn-porhyrinates is indicated by characteristic shifts of porhyrinates and antioxidant protons in complex to strong field area. Especially strong shift is in the case of protons of axial ligands aryl fragments, which are arranged close to porhyrinic macrocycle. Thus, it is established, that Sn(IV)porhyrinates forms with investigated antioxidant molecules stable complexes with 1:2 ratio (porhyrin – drug), which is confirmed by NMR ^{1}H spectroscopy, fluorimetry, mass-spectrometry and quantum-chemical calculations.

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SPIN-CROSSOVER IN IRON(II) COMPLEXES WITH *TRIS*(PYRAZOL-1-YL)METHANE AND CLUSTER ANIONS $[\{W_6(\mu_3\text{–}Hal)_8\}Hal_6]^{2-}$

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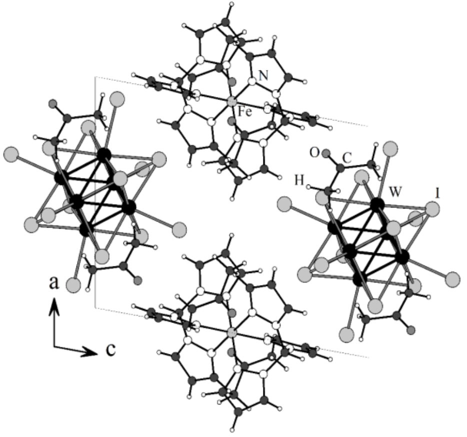
Complex compounds of iron(II), wherein the spin state of the central atom can be affected by environmental conditions such as temperature, pressure, or light of a certain wavelength, are of current interest. Spin-crossover (**SCO**) in the series of complexes having a composition such as $[Fe\{HC(Pz)_3\}_2]A_n$ (where $HC(Pz)_3$ is *tris*(pyrazol-1-yl)methane, A = anion, n = 1, 2) is observed within the temperature range from 270 to 470 K [1].

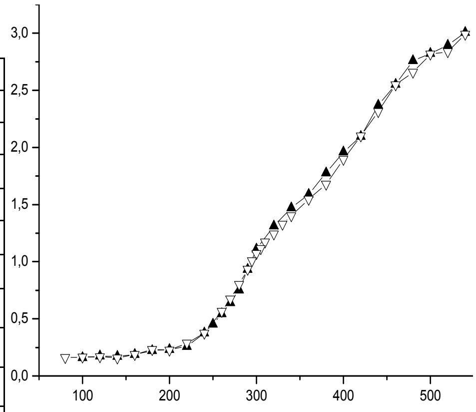
The complexes of Fe(II) with $HC(pz)_3$, containing the outer sphere cluster anions, of the composition $[Fe\{HC(pz)_3\}_2][\{W_6(\mu_3\text{–}Cl)_8\}Cl_6]\cdot 2H_2O$ (**I**), $[Fe\{HC(pz)_3\}_2][\{W_6(\mu_3\text{–}Br)_8\}Br_6]\cdot H_2O$ (**II**) and $[Fe\{HC(pz)_3\}_2][\{W_6(\mu_3\text{–}I)_8\}I_6]\cdot 4C_3H_6O$ (**III**) have been synthesized and investigated by X-ray diffraction analysis, magnetic susceptibility method, IR and duffuse reflectance spectroscopy (DRS). The complex cation $[Fe\{HC(pz)_3\}_2]^{2+}$ has a distorted octahedral coordination polyhedron structure with node FeN_6. According data of DRS, we calculated the values of the splitting parameters of the studied complexes, which prove the manifestation of the spin-crossover in them (Table).



Crystal structure of **III**

Table. The splitting parameters and SCO temperatures

Parameter	Complex		
	I	**II**	**III**
P_{HS}, cm^{-1}	13400	14500	15700
Δ_{HS}, cm^{-1}	11900	12000	11800
B, cm^{-1}	630	630	620
Δ_{LS}, cm^{-1}	20400	20000	19100
Δ_{LS}/Δ_{HS}	1,7	1,7	1,6
$T_{c1}\uparrow$(heated), K	261	340	248
$T_{c1}\downarrow$ (cooled), K	255	325	247
$T_{c2}\uparrow$, K	418	464	290
$T_{c2}\downarrow$, K	411	464	290



Curve $\chi_M T(T)$ of **I**

Investigation of dependence $\chi_M T(T)$ (in sealed ampule) shown that in these complexes SCO $^1A_1 \leftrightarrow {}^5T_2$ with small hysteresis is observed. In **I** – **III** the transition is two-stepwise. The values of the transition temperatures (T_c) are given in Table. SCO in mentioned complexes is accompanied by thermochromism.

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REACTIVITY OF PD(I) AND PD(II) CARBOXYLATES TOWARDS ZWITTERIONIC IMIDAZOLIUM-2-AMIDINATES, A PROMISING CLASS OF ELECTRONEUTRAL, AMIDINATE-TYPE LIGANDS

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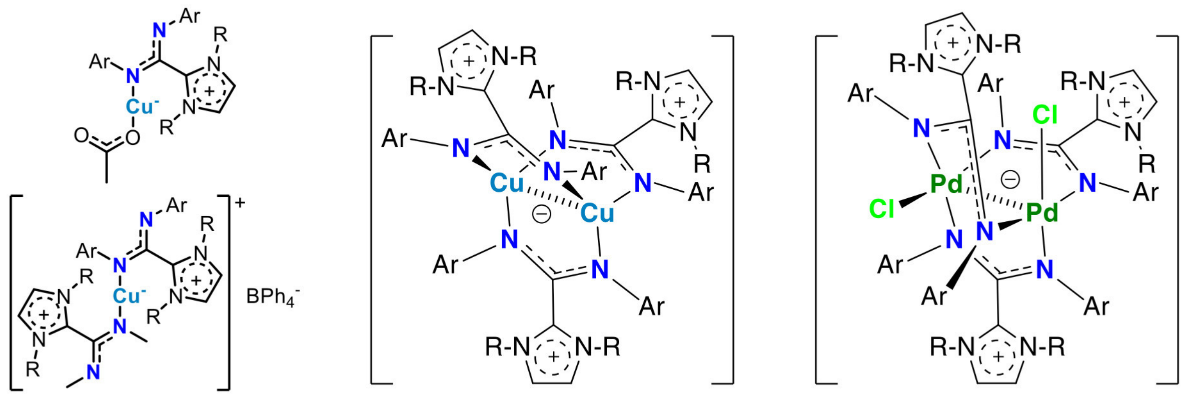
Amidinates is an important class of ligands, which can be considered as the nitrogen analogues of carboxylates: they also usually coordinate in the monodentate, bidentate or bridge modes. Also in the bridging coordination mode, they give rise to a series of appealing multibridged binuclear “paddlewheel” complexes [1]. Very recently first copper(I) complexes containing imidazolium-2-amidinates as ligands (betaine-type adducts of imidazolium-based carbenes and carbodiimides, NHC-CDI) have been reported [2]. Complexes of general formulas [LCu(OAc)], $[Cu_2(\mu\text{-}L)_3](OAc)_2$ and $[CuL_2]^+BPh_4^-$ form depending on substitutes in the ligands and reaction’s conditions (see the figure).



Continuing this work we have studied reactivity of Pd (I) and Pd(II) carboxylates towards IMeCDI$^{p\text{-}Tol}$ (Ar = p-Tol, R = Me) in CH_2Cl_2 or $CHCl_3$ media. We have found that Pd(I) carbonyl carboxylates $Pd_n(CO)_n(R'CO_2)_n$ (R’ = Me, *n* = 4; R’ = ^{tert}Bu, *n* = 6) readily react with the ligand at r.t. but all the products are very unstable and decompose giving Pd black in few minutes. Pd(II) carboxylates $Pd_3(RCO_2)_6$ (R = Me, ^{tert}Bu) react much slower leading to a complex mixture of products. Crystallization from $CDCl_3/CHCl_3$ gave us some crystals of complex of rather unexpected composition $[Pd_2(\mu\text{-}L)_3Cl_2]Cl_2$. A structure of the complex is quite similar to $[Cu_2(\mu\text{-}L)_3](OAc)_2$ but Pd atoms bearing additional terminal chloride groups (see the figure). Outer sphere Cl^- anions are in a pseudo octahedral environment generated by non-conventional Cl···H-C bridges. Each Cl^- form 2 contacts with 2 $CHCl_3$ solvate molecules in trans positions, 2 contacts with imidazolium ring of one Pd_2L_3 molecule and 2 contacts with the ring of neighbouring Pd_2L_3 molecule that results in the assembly of a 3D-network.

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October 2-6, 2017, N. Novgorod, Russia

SUPRAMOLECULAR SELF-ORGANISATION OF CATION-CATIONIC LONG-PERIOD POLYMERIC CHAINS IN THE STRUCTURE OF HETERONUCLEAR GOLD(III)-ZINC(II) COMPOUND OF $([\mathrm{Au}\{\mathrm{S_2CN(C_4H_9)_2}\}_2]_2[\mathrm{ZnCl_4}])_n$

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A novel ion-polymeric heteronuclear complex of $([\mathrm{Au}\{\mathrm{S_2CN(C_4H_9)_2}\}_2]_2[\mathrm{ZnCl_4}])_n$ (**I**) has been synthesized using the chemisorption activity of freshly precipitated binuclear zinc(II) dibutyldithiocarbamate, $[\mathrm{Zn_2}\{\mathrm{S_2CN(C_4H_9)_2}\}_4]$, with respect to a solution of $\mathrm{H[AuCl_4]}$. The crystal structure of I was resolved by means of single-crystal X-ray diffraction analysis. The unit cell of the complex, whose structure involves 13 isomeric gold(III) cations, $[\mathrm{Au}\{\mathrm{S_2CN(C_4H_9)_2}\}_2]^+$ (cations 'A'–'M' comprising gold atoms Au(1)–Au(13), respectively) and 6 isomeric $[\mathrm{ZnCl_4}]^{2-}$ anions, contains 48 formula units of $[\mathrm{Au}\{\mathrm{S_2CN(C_4H_9)_2}\}_2]_2[\mathrm{ZnCl_4}]$. There are pairs of inequivalent Dtc ligands in the coordination sphere of most gold(III) cations, with the exception of centrosymmetric cations 'A' and 'D' having gold atoms Au(1) and Au(4). Therefore, the above compound includes 24 structurally inequivalent Dtc ligands.

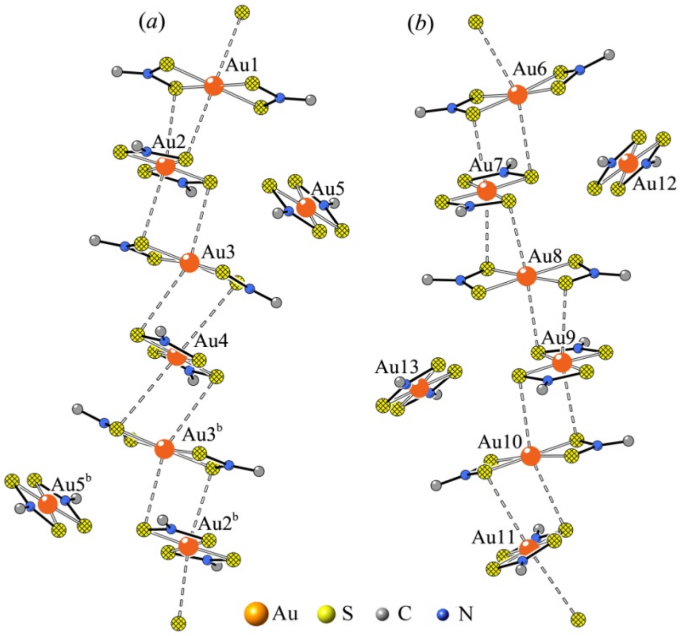

Fig. 1. Complete periods of two independent cation-cationic polymeric chains with concomitant discrete cations (*a*, *b*). Dashed lines show the secondary bonds Au···S. Alkyl groups of dibutyldithiocarbamate ligands are omitted for clarity.

At a supramolecular level, further structural self-organisation of zigzag cation-cationic chains is realised due to pairs of relatively weak non-valence Au···S interactions (*i.e.*, secondary bonds) arising between neighbouring isomeric gold(III) cations. These four ('A'–'D') and six ('F'–'K') cationic conformers, exhibiting various structural functions and unsymmetrically interacting with each other, form two species of zigzag long-period polymeric chains: $(\cdots\mathrm{A}\cdots\mathrm{B}\cdots\mathrm{C}\cdots\mathrm{D}\cdots\mathrm{C}\cdots\mathrm{B}\cdots)_n$ (Fig. 1*a*) and $(\cdots\mathrm{F}\cdots\mathrm{G}\cdots\mathrm{H}\cdots\mathrm{I}\cdots\mathrm{J}\cdots\mathrm{K}\cdots)_n$ (Fig. 1*b*); while the discrete cations E, L, M as well as zinc complex anions of $[\mathrm{ZnCl_4}]^{2-}$ are localised between these cation-cationic chains. The thermal behaviour of crystalline compound I was studied using simultaneous thermal analysis (TG and DSC techniques) taken under an argon atmosphere. Thermal decomposition of I is accompanied by the quantitative reduction of gold(III) to elemental gold and liberation of $\mathrm{ZnCl_2}$ along with its partial transformation to ZnS.

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THERMODYNAMIC AND KINETIC STABILITY OF CERIUM(IV) COMPLEXES WITH A SERIES OF AMINOPOLYACETIC ACIDS

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A potentiometric version of generalized thermodynamic methods for studying complexation ($E_0, \dot{E}_0 - c_L/c_M$, $E_0, \dot{E}_0$–pH integral and integral-differential methods with the initial emf E_0 and $\dot{E}_0 \equiv \partial E/\partial \tau|_{\tau=0}$, s^{-1}) was developed for determining, along with the thermodynamic stability, also the kinetic stability of cerium(IV) complexes (as well as complexes of other metals in unstable oxidation state) toward intramolecular redox decomposition.

The compositions of the complexes, the fact that the ligand in the complex is in the deprotonated form, and the stability constants log β_{1m1} of cerium(IV) complexonates formed in the $Ce^{4+}-L^{m-}-ClO_4^-$ and $Ce^{4+}-L^{m-}-NO_3^-$–systems, where L^{m-} are Gly$^-$, Ida^{2-}, Nta^{3-}, Edta^4, and Hmdta^{4-}–anions, were determined by the above methods and their spectrophotometric analogs at pH in the range 1.3–2.0 in perchlorate and nitrate media at an ionic strength $I = 0.1$ and a temperature of 298.15 K.

It is shown that the cerium(IV) monocomplexonates of the general formula $[CeL]^{4-m}$ (m = 1–4) are formed in all the systems with the values of the logarithms of the stability constants, log β_{1m1} , 13.57 ± 0.05 ($[CeGly]^{3+}$), 14.57 ± 0.06 ($[CeIda]^{2+}$), 16.62 ± 0.14 ($[CeNta]^{+}$), 23.64 ± 0.15 ($[CeEdta]^{2+}$), and 27.54 ± 0.09 ($[CeHmdta]^{0}$) in the nitrate medium, as well as 13.84 ± 0.19 ($[CeGly]^{3+}$), 15.09 ± 0.20 ($[CeIda]^{2+}$), 16.37 ± 0.14 ($[CeNta]^{+}$), 23.66 ± 0.07 ($[CeEdta]^{2+}$), and 27.57 ± 0.09 ($[CeHmdta]^{0}$) in perchlorate medium.

Direct linear correlation was found between log β_{101} of the complexonates and logarithms of the cumulative protonation constants, log B_{m+k} (k = 1–2), of L^{m-} anions, which may be associated with the facts that the complexones in the complexonates $[CeGly]^{3+}$, $[CeIda]^{2+}$, $[CeNta]^{+}$, $[CeEdta]^{0}$, and $[CeHmdta]^{0}$ exhibit the maximal denticity and that log B_{m+k} increases in going from HGly to H_4Hmdta.

The logarithms of the rate constants of intramolecular redox decomposition of the complexonates of the first time order and first concentration order with respect to the complex in perchlorate and nitrate media were determined (for example, the averaged $\log k_{n=1}$ values in the nitrate medium are as follows: – 0.91 ± 0.02 ($[CeGly]^{3+}$), – 0.95 ± 0.02 ($[CeIda]^{2+}$), –1.02 ± 0.02 ($[CeNta]^{+}$), –1.30 ± 0.01 ($[CeEdta]^{2+}$), and –1.43 ± 0.01 for $[CeHmdta]^{0}$).

The quantities log $k_{n=1}$ = 1 and log β_{101} show inverse linear correlation described by the equation log $k_{n=1}$ = log $k^0_{n=1}$ – ρlog β_{101}, which can be considered as manifestation of the linear free energy relationship in coordination chemistry of transition metals.

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FORMATION OF *OCTAKIS*(3,5-DI-*TERT*-BUTYLPHENOXY)PHTHALOCYANINATO) COBALT(II) AND MANGANESE(III) - 4-PICOLINE DONOR-ACCEPTOR COMPLEXES

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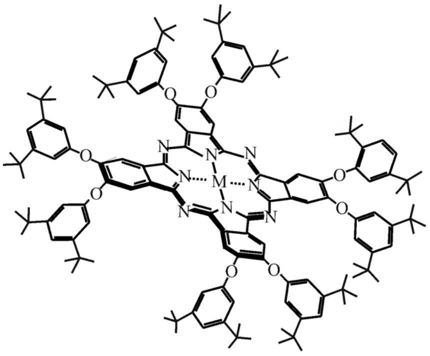
Metal–pyridine complexation has been extensively used in coordination chemistry, especially in a formation of porphyrin-containing architectures [1]. Axial complexation of the pyridyl moieties to metalloporphyrin centers can lead to supramolecular assemblies such as dyads, triads or polyads [2]. In the present work, we represent the studies the bonding of 4-picoline (Pic) with *octakis*(3,5-di-*tert*-butylphenoxy)phthalocyaninato) cobalt(II), CoPc(3,5-^{t}BuPhO)$_8$ (**I**) and manganese(III), (AcO)MnPc(3,5-^{t}BuPhO)$_8$ (**II**).



M = Co, (CH$_3$COO)Mn

I and **II** were synthesized by the methods [3, 4], purified by chromatography and characterized by UV-vis, IR, ^{1}H NMR, mass spectra and elemental analysis. UV-vis (**I**) (toluene), λ_{max} nm (logε): 304 (4.76), 340 (4.72), 607 (4.45), 646 (4.53), 673 (5.17).UV-vis (**II**) (toluene), λ_{max} nm (logε): 407 (4.56), 655 (4.27), 727 (5.03). The reaction of CoPc(3,5-^{t}BuPhO)$_8$ and (AcO)MnPc(3,5-^{t}BuPhO)$_8$ with Pic was studied at 298 K in toluene by spectrophotometry methods. Series of the toluene solutions with a constant concentration of a complex (8 × 10^{-6} M) and different Pic concentrations (from 0 to 6 M) were prepared. Addition of Pic to **I** solution causes gradual decrease in intensity and hypsochromic shift (8 nm) of the *Q*-band at 673 nm. Analogous reaction of **II** with Pic is accompanied by gradual decrease in the intensity of the *Q*-band at 727 nm and hypsochromic shift (9 nm) of the *B*-band at 407 nm. Both complexes bind one Pic molecule each, as followed from the slope of the log*I*-*f*(logC_{Pic}) dependences (tgα=1.02 for **I**; tgα=1.3 for **II**).

$$\mathrm{MPc(3,5\text{-}^tBuPhO)_8 + Pic \xrightleftharpoons{K} (Pic)MPc(3,5\text{-}^tBuPhO)_8}$$

The stability constants of donor–acceptor complexes with Pic (*K*) are (1.01 ± 0.16)×10^4 and (1.50 ± 0.23) L·mol^{-1} for **I** and **II**, respectively. The donor-acceptor type of the (Pic)MPc(3,5-^{t}BuPhO)$_8$ dyads was established by UV-vis, IR and ^{1}H NMR spectroscopy. The influence of the metal nature in the macrocycle on the process of Pic coordination is discussed in the report.

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THE CALCULATIONS OF THE HEATS OF COMBUSTION AND FORMATION OF THE IRON-AMINO ACIDS COMPLEXES

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As is known from the principles of biochemical activity, such amino acids (aa) as alanine (ala), threonine (thr) and asparagine (asp) are able to participate in the complex-formation processes with the carbonate of two valence iron. The heat of formation ($\Delta_f H^o$) of $Fe(aa)_2$ complexes easy calculate through the equation (1), which reflects the formation gas (g), liquid (l) and solid (s) products of combustion ($\Delta_c H^o$) [1].

$$C_aH_bN_cO_dFe\ (s) + nO_2\ (g) \rightarrow xCO_2\ (g) + yH_2O\ (l) + zN_2\ (g) + FeO\ (s) + \Delta_c H^o \quad (1)$$

We calculate the heats of combustion and formation of the given above chelate complexes ($Fe(ala)_2$, **I**), ($Fe(thr)_2$, **II**) and ($Fe(asp)_2$, **III**) with the use of our computer program for the calculation of thermochemical parameters of different metal-organic compounds via equation (2), in which N is the number of valence electrons, g is the number of lone electron pair of heteroatoms, hc are the heat corrections (54.4 kJ mol^{-1}) on two 5-membered cycles around Fe atom [2]. The results are given in Table 1.

$$\Delta_c H^o = 90.3 - 107.7(N\text{-}g) + \Sigma\, hc \quad (2)$$

Table 1. The heat parameters (kJ mol^{-1}, ± 0.5 %) of $Fe(aa)_2$ complexes.

No	Complex, formula, (N-g)	$-\Delta_c H^o$	$-\Delta_f H^o$	$-\Delta_{ws} H^o$	$-\Delta_{aq} H^o$
I	$Fe(ala)_2$, $C_6H_{12}N_2O_4Fe$, 32	3301.7 ± 16.5	789.1 ± 3.9	40.2 ± 0.5	829.3 ± 4.4
II	$Fe(thr)_2$, $C_8H_{16}N_2O_6Fe$, 40	4163.3 ± 20.8	995.0 ± 5.0	58.1 ± 0.5	1053.1 ± 5.5
III	$Fe(asp)_2$, $C_8H_{14}N_4O_6Fe$, 40	4163.3 ± 20.8	995.0 ± 5.0	107.9 ± 0.5	1102.9 ± 5.5

The formation of complexes (I-III) **occur in aqua phase on by this reason was necessary to calculate their $\Delta_{aq} H^o$ values into accordance with equation (3).**

$$\Delta_{aq} H^o = \Delta_f H^o + \Delta_{ws} H^o \quad (3).$$

The molecular mechanic method (MM*X*-PCMOD-1.0 version) was used for the calculation of the heats of water shells ($\Delta_{ws} H^o$) around of complexes. The calculated water shells are large for $Fe(thr)_2$ and $Fe(asp)_2$ complexes (Table 1). It can believe that complexes between iron and threonine and asparagine are more stable.

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BORON OXIDATIVE EXTRACTION AS A METHOD FOR DECABORANE (14) SYNTHESIS

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Boron chemistry is one of the leading branches of modern chemical science and technology. Carborane and metalcarborane derivatives are of interest, which are used to obtain new functional polymers [1] and perspective materials [2]. Some carborane derivatives are known for their pharmacological activity [3]. However the main and only raw compound for carborane obtaining was and is decaboran(14) – $B_{10}H_{14}$, and need in it is growing every year. That fact forced us to develop a new efficient method for decaboran synthesis. Using domestic and foreign works [4, 5] we concluded the most optimal and safe method of decaborane obtaining is two-step synthesis where at the first stage we synthesize undecaborate salt [6] from alkali metals boronhydrydes and haloic alkyls, at the second stage, we oxidize the salt with different oxidizers. The methods described in literature are either laborious at execution which causes raise of product cost price or not efficient enough and non-ecological [7]. That was the reason to find a new method of undecaborate oxidizing. The solution of that problem became ketones and carbonyl compounds as oxidizers. To be noted, that before this unusual reaction was unknown and unlike the common oxidizing methods of $NaB_{11}H_{14}$ [5, 7] it allows to obtain decaborane(14) with high yield.

$$2NaB_{11}H_{14} + 4R'C(O)R'' + H_2SO_4 + 6H_2O \rightarrow 2B_{10}H_{14} + 2H_3BO_3 + 4R'CH(OH)R'' + Na_2SO_4$$

where $R' = H, CH_3, C_2H_5, C_6H_5$
$R'' = H, CH_3, C_2H_5, C_6H_5, CH_2COCH_3$

Developing this direction the optimal technique of sodium undecaborate to decaborane(14) oxidizing reaction using ketones was invented and patented at industrial base of JSC GNIIChTEOS[8].

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MECHANISM OF INTERACTION OF UF_4 WITH QUARTZ MECHANOACTIVATED IN PRESENCE OF SODIUM SALTS ADDITIONS

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During the process of enriching uranium hexafluoride with U^{235} a significant amount of depleted uranium hexafluoride has been formed, which is stored in steel apparatus in open areas, which is potentially dangerous. The problem can be solved by converting DUF_6 to a safer and more convenient form for treatment – DUF_4 or oxides (for example, using mechanically activated quartz) [1]. The temperature of the solid-phase conversion process can be further reduced by using quartz, which is mechanically activated in the presence of so-called stimulating additives (SA), for example 1-3% mass of alkaline elements. The assumption of the increasing of the reactivity of quartz due to the growth of the phase content of metastable β-cristobalite, expressed earlier [1], is unconvincing. The increasing of the α-cristobalite phase content in annealing products at 1200°C has been determined by the ability to stimulate additives to operate as mineralizers. The decreasing of the interaction temperature in the presence of a small amount of stimulating additives in the system can be also related with the ability of SA to catalyze to the solid-phase interaction through the formation of intermediate complex uranium (uranyl) fluorides.

In this paper the results of studying the solid-phase interaction of DUF_4 with quartz mechanoactivated in the presence of two sodium compounds – NaF and Na_2CO_3 have been presented, in an inert atmosphere (dry nitrogen) under conditions of forced removal of the gaseous product of the reaction (details of the experiment are presented in [1]). To provide the mechanism of effect of SA on solid-phase conversion of DUF_4 to uranium dioxide, quartz samples mechanoactivated in the presence of SA up to 20% mass has been used.

Mechanical activation of quartz was carried out in the planetary-ball mill Pulverisette-5 (Fritsch) with using of bowls and balls d = 10 mm from the PSZ (1:20) during 30 min. The efficiency of solid-phase interaction from the results of X-ray Diffraction of products and the loss of mass of the mixture in accordance with the reaction: $UF_4 + SiO_2 \rightarrow UO_2 + SiF_4$ has been evaluated. XRD of reaction products obtained at 400-600°C have showed that the solid-phase reaction in the UF_4-SiO_2(SA) system is initiated with the interaction of UF_4 with SA (reaction products have contained the phase of sodium fluoro uranate $Na_7U_6F_{31}$ and UO_2 already at 400^oC). The progress of process (the increasing of the conversion degree into UO_2) in both systems leads to the same changes: UF_4 passes into $Na_7U_6F_{31}$, which after a subsequent increasing of NaF:UF_4 ratio in the system is converted into Na_2UF_6 (500^oC), then (550^oC) into Na_3UF_7 (Na_2CO_3 as SA) and into $Na_7U_2F_{15}$ (NaF as SA). The product of the reaction at 600^oC is UO_2 and a small amount of NaF.

Obtained results show that the decreasing of the temperature of solid-phase conversion of DUF_4 into uranium dioxide using mechanically activated quartz with a small amount of SA is caused by the formation of sodium fluoro uranates along with Hadwall effect.

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NEODYMIUM HYDROXYCHLORIDE THERMAL DECOMPOSITION

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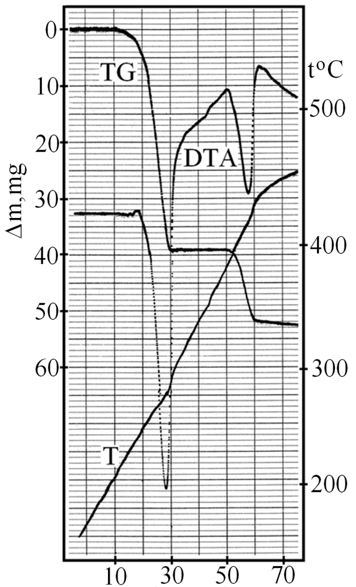
Thermal stability of the rare earth chloride hydrates is of great interest owing to their possible use for the anhydrous salts preparation and production of the rare earth metals. Among these metals neodymium is of especial importance because of its application to produce very strong magnets. Earlier [1, 2] we have reported the first results of the neodymium chloride monohydrate synthesis and thermal behaviour. Now we have obtained the data for a more detailed analysis of the processes of its thermal decomposition. The lowest hydrate was prepared from the hexahydrate, crystallized from acidified water solutions. Special attention was paid to the precise stoichiometric analysis of the latter (± 0.1–0.2 % relative), and standard solutions of Nd were obtained with the same accuracy. Monohydrate was prepared by the controlled isothermal drying of hexahydrate $NdCl_3 \cdot (6.08 \pm 0.04 H_2O)$ through dihydrate $NdCl_3 \cdot 1.95H_2O$ and then to $NdCl_3 \cdot 0.87H_2O$. The Paulik classical derivatograph was used to study the processes of the latter thermal behaviour, and a special pyrex glass ampoule [3] was used to obtain the temperature, at which the vapour pressure of the gas products achieves 1 atm. Two peaks are observed in the figure – the first relates to the decomposition of monohydrate; the second – to the decomposition of neodymium hydroxychloride [4]. Temperatures of these transformations were determined more accurately: 262 ± 2 °C and 396 ± 2 °C. By coprocessing the derivatographic data with the results of chemical analysis and drying, we have obtained the following results for the composition of the substances on each horizontal line in the figure: 1– $NdCl_3 \cdot H_2O$ (97 mass %) with 3 mass % of $Nd(OH)_2Cl$; 2 – $NdCl_3$ (82 mass %) and $Nd(OH)_2Cl$ (18 mass %); 3 – $NdCl_3$ (64 mass %) and NdOCl (36 mass %). The last step in the figure corresponds to the solid-phase reaction of $Nd(OH)_2Cl$ with $NdCl_3$, and we can assume the possibility of an intermediate formation:

$$Nd(OH)_2Cl + NdCl_3 \leftrightarrow 2\ Nd(OH)Cl_2 \leftrightarrow 2\ NdOCl + 2\ HCl\ gas.$$



Derivatogram of $NdCl_3 \cdot 0,87H_2O$
(0.5 g, heating rate 4.5 K/min)

It is interesting that this last step (about 13 mg) does not end in 10 minutes, as is seen in the figure. This process goes on and on, but very slowly – the next 14 mg are lost in 170 min. This phenomenon may indicate the possibility of solid solutions formation in the system Nd – – OH – Cl.

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PRODUCTS OF INTERACTION OF SULFUR DIOXIDE WITH AMINES IN AQUEOUS SOLUTIONS. EFFECT OF AMINES BASICITY AND LIPOPHILICITY ON THE COMPOUNDS COMPOSITION

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Reaction products have been isolated from $SO_2 – L – H_2O – O_2$ systems (L = alkylamines, benzylamines, ethanolamines, aniline, 2,2′-bipyridine and their deravatives). The prepared compounds have been characterized by elemental analysis, X-ray diffraction analysis, X-ray powder diffraction, IR, Raman spectroscopy, ^1H, ^{13}C NMR, and mass spectrometry, thermogravimetry.

The reaction of SO_2 with aqueous solution of aniline ($pK_a = 4.63$) and highly basic ethanolamines ($7.76 \leq pK_a \leq 9.85$), aminoguanidine ($pK_a = 11.04$), benzylamines, and alkylamines ($10.60 \leq pK_a \leq 10.77$) results "onium" salts of sulfur-containing oxyanions according to the equations (1) – (7).

$$SO_2 + H_2O + 2RNH_2 \rightarrow (RNH_3)_2SO_3 \quad (1)$$

$$SO_2 + (RNH_3)_2SO_3 + H_2O \rightarrow 2(RNH_3)HSO_3 \quad (2)$$

$$SO_2 + (RNH_3)_2SO_3 \rightarrow (RNH_3)_2S_2O_5 \quad (3)$$

$$(RNH_3)_2SO_3 + O_2 \rightarrow 2(RNH_3)_2SO_4 \quad (4)$$

$$4(RNH_3)HSO_3 + O_2 \rightarrow 2(RNH_3)_2SO_4 + 2SO_2\uparrow + 2H_2O \quad (5)$$

$$2(RNH_3)_2S_2O_5 + O_2 \rightarrow 2(RNH_3)_2SO_4 + 2SO_2\uparrow \quad (6)$$

$$3(RNH_3)HSO_3 + O_2 \rightarrow (RNH_3)_3SO_4(HSO_4) + SO_2\uparrow + H_2O \quad (7)$$

Van der Waals clathrates $(bipy)_3\cdot(SO_2)\cdot(H_2O)$, $(bipy)_2\cdot(SO_2)\cdot(H_2O)_2$ and $(Bz_3N)_3\cdot(SO_2)$ were obtained with relatively weakly basic 2,2′-bipyridine ($pK_a = 4.34$) and tribenzylamine ($pK_a = 3.64$). Thus, we can conclude salt formation to occur when $pK_a \geq 4.63$ for amine.

"Onium" hydrodisulphates were obtained for alkylmonoamines with the number of C atoms, two or more in the case of $13.24 \leq (pK_a + \log P_{ow})$ in the $SO_2 – L – H_2O – O_2$ reaction system (L – *n*-heptylamine, and *n*-octylamine); $10.42 \leq (pK_a + \log P_{ow}) \leq 11.63$ (L – *n*-butylamine, *t*-butylamine, *n*-propylamine, benzylamine, α-phenylethylamine, N,N-dimethylbenzylamine, or dibenzylamine) – sulphates; $5.81 \leq (pK_a + \log P_{ow}) \leq 10.21$ (L – ethanolamines except for TRIS) – sulphites and hydrosulphites, they have been isolated due to sulphooxidation inhibition. It was found dissociation thermodynamic functions to depend on bases $\log P_{ow}$ for monoethanolammonium, diethanolammonium, and their N-methyl and N-ethyl derivatives. Acid-base dissociation of TRIS and triethanolamine "onium" cations does not correspond to said relationship because TRIS (primary amine), TEA (tertiary amine) act differently on aqueous solutions of SO_2. TRIS having in its molecule the largest number of H- donors and acceptors as compared with other ethanolamines is characterized by the lowest value $(pK_a + \log P_{ow}) = 5.76$ and promotes sulphooxidation of S(IV) → S(VI).

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VAN DER WAALS CLATHRATES $(bipy)_3{\cdot}(SO_2){\cdot}(H_2O)$, $(bipy)_2{\cdot}(SO_2){\cdot}(H_2O)_2$ AND $(Bz_3N)_3{\cdot}(SO_2)$

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Reaction products have been isolated from "sulphur dioxide – 2,2′-bipyridine – water" and "sulphur dioxide – tribenzylamine – water – benzene" systems. Crystallization of 2,2′-bipyridine from aqueous solution containing sulfur(IV) oxide afforded clathrates with the compositions $(bipy)_3{\cdot}(SO_2){\cdot}(H_2O)$ (**1**) and $(bipy)_2{\cdot}(SO_2){\cdot}(H_2O)_2$ (**2**) [1]. X-Ray amorphous guest SO_2 molecules occupy voids in the crystal lattice of 2,2′-bipyridine without distortion of its structure. Van der Waals clathrate with the composition $(Bz_3N)_3{\cdot}(SO_2)$ (**3**) was obtained for tribenzylamine. Only starting Bz_3N was obtained from "sulphur dioxide – tribenzylamine – water – benzene" system. The isolated compounds were characterized by elemental analyses, X-ray diffraction data, and IR, NMR, and mass spectra.

Thus, compounds **1** and **2** are typical lattice clathrates; the crystal structure of bipy includes SO_2 mono- and dihydrates whose interactions with the host lattice involve only van der Waals forces. Unlike previously described $SO_2{\cdot}py$ adduct in which $S\leftarrow N$ interaction was detected, clathrates **1** and **2** are the first representatives of molecular compounds formed by sulfur dioxide hydrates and heterocyclic base.

In contrast to the interactions of SO_2 with aminoethanols in water (where oily onium hydrogen sulfites and crystalline sulfite [2] were isolated) and highly basic dihydric aminoguanidine (crystalline onium sulfite monohydrate was formed [3]), neither dissociation of sulfurous acid ($SO_2{\cdot}H_2O$; $pK_{a1} = 1.86$) nor subsequent protonation of the nitrogen atoms of relatively weakly basic bipyridine ($pK_a = 4.34$) [1] and tribenzylamine ($pK_a = 3.64$) occur in the systems "SO_2 – bipy – H_2O", "SO_2 – Bz_3N – H_2O" and "SO_2 – Bz_3N – H_2O – C_6H_6".

Furthermore, the bipy and Bz_3N crystal lattices don't favor oxidation of SO_2 guest molecules with atmospheric oxygen, which was observed in the systems containing tris(hydroxymethyl)aminomethane, alkylamines, benzylamine, ethylenediamine, morpholine and hexamethylenediamine (mild oxidation product of S(IV) to S(VI), onium sulfates, were isolated and structurally characterized [4]).

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SYNTESIS OF (2,2’)-N,N'-(1,2-PHENYLENE)-BIS-(DIBUTYL-2-ENE)-AMINE AND STUDY OF ITS REACTIONS WITH CHROMIUM GROUP METALS

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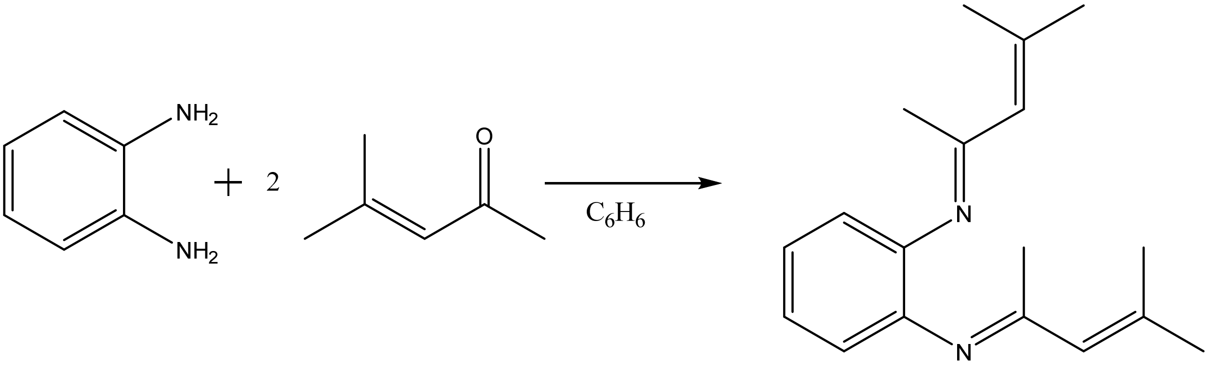
Synthesis of the novel coordination compounds possessing the catalytic activity which contain different metals bound to one macroligand is of great interest because such complexes can act as catalyststhat is possible to promote several catalytic processes. To obtain such type of complexes it is necessary to synthesize polydent ligands having “harsh” and “soft” coordination sites for the interaction of complement metal ions.

We have synthesized such kind of ligand – (2,2’)-N,N'-(1,2-phenylene)-bis-(dibutyl-2-ene)-amine. In this compound nitrogen atoms’ lone orbitals act as harsh Lewis bases and π-electrons of C=C and C=N bonds are soft Lewis bases.

The synthesis of (2,2’)-N,N'-(1,2-phenylene)-bis-(dibutyl-2-ene)-amine proceeds as one-staged process – we have conducted the condensation of o-phenylenediamine with the mesitylene oxide in benzene solution. The purity and the structure of (2,2’)-N,N'-(1,2-phenylene)-bis-(dibutyl-2-ene)-amine was elucidated with the help of NMR ^{1}H, ^{13}C and IR-spectroscopy.



We have also studied the coordination abilities of (2,2’)-N,N'-(1,2-phenylene)-bis-(dibutyl-2-ene)-amine with hexacarbonyl complexes of chromium group metals as well as its reactivity towards dialkyl(H)phosphonates as well both in free state and in metals’ coordination sphere.

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TD DFT STUDY OF THE METAL NATURE INFLUENCE ON THE ELECTRONIC EXCITED STATES IN MIXED SANDWICH COMPLEXES

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Transition metal sandwich compounds appear to reveal in the gas-phase absorption spectra interesting features which arise from electronic transitions originating at the non-bonding metal $a_1(d_{z^2})$ level and terminating at Rydberg MOs [1]. Rydberg excitations provide valuable information on the molecular symmetry, electron density distribution, excitation energies and configuration interactions. Rydberg parameters of the gas-phase sandwich molecules provide, therefore, a powerful instrument to verify the results of quantum chemical calculations.

In this work, the interpretation of the electronic absorption spectra of the cycloheptatrienyl-cyclopentadienyl (Cht-Cp) transition metal sandwith complexes $[(\eta^7\text{-}C_7H_7)M(\eta^5\text{-}C_5H_5)]$ (M = Ti, V, Cr) in the gas phase has been made for the first time. Comparison of experimental data with time-dependent density functional theory (TD DFT) calculations provides new information on the nature and energies of electronic excited states of these compounds. The longest-wavelength valence-shell transition is shifted non-monotonically on going along the 3d row from Ti to V and then to Cr. The calculated transition energies are 1.76, 2.16 and 1.96 eV, respectively. In $(\eta^7\text{-}C_7H_7)Ti(\eta^5\text{-}C_5H_5)$ this excitation corresponds to LMCT, in $(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_5H_5)$ – a mixure of 20% $a_1(3d_z2) \rightarrow e_2(C_7H_7\text{ , }3d)$ and 80% $e_2(3d, C_7H_7) \rightarrow a_1(3d_z2)$, in $(\eta^7\text{-}C_7H_7)Cr(\eta^5\text{-}C_5H_5)$ – pure MLCT. The calculated parameters of electronic excited levels of mixed sandwich complexes were obtained including both valence-shell and Rydberg electronic excitations. The TD DFT results appear to describe correctly the influence of the metal atom and the electronic configuration on the band positions and intensities in the UV-visible absorption spectra as well as the mixing of Rydberg and intravalency states. On going from $(\eta^7\text{-}C_7H_7)Cr(\eta^5\text{-}C_5H_5)$ to $(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_5H_5)$ Rydberg transitions from the metal $a_1(3d_z2)$ orbital shift to blue. The configuration interactions involving the $3d_{z^2} \rightarrow R4d_{z^2}$ transition change on replacing Cr with V, the latter complex revealing a mixture of the Rydberg and valence-shell excitations. In contrast to isomeric bis(η^6-benzene)chromium, the $a1(3d_{z^2})1(R4p_z)1$ configuration of trochrocene does not interact with intravalency states. Accordingly, a narrow $3d_{z^2} \rightarrow R4p_z$ peak appears in the experimental gas-phase spectrum. TD DFT calculations predict also the intensity trends for Rydberg excitations. The computed $3d_{z^2} \rightarrow R4p_{x,y}$ /$3d_{z^2} \rightarrow R4p_z$ oscillator strength ratio changes from 0.7 to 11 on going from (C6H6)V to trovacene $(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_5H_5)$. Indeed, the gas-phase spectrum of the symmetric sandwich shows stronger 4pz component while for $(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_5H_5)$ this component is much weaker than $3d_{z^2} \rightarrow R4p_{x,y}$. The energies of Rydberg orbitals decrease on going from $(\eta^7\text{-}C_7H_7)Cr(\eta^5\text{-}C_5H_5)$ to $(\eta^7\text{-}C_7H_7)Ti(\eta^5\text{-}C_5H_5)$.

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COMPLEXES OF S-TRIAZINE WITH RARE-EARTH METAL THIOCYANATES. STRUCTURAL FEATURES AND TRANSFORMATIONS IN SOLUTIONS

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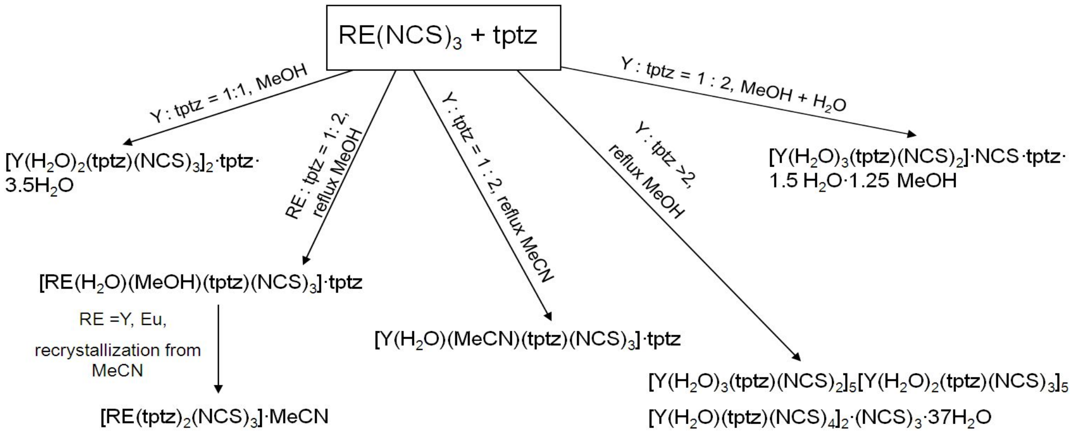
The most stable oxidation state of rare-earth metals (RE) is +3, the large ion radius of RE in combination with the predominantly electrostatic nature of metal–ligand binding results in the formation of compounds with the coordination number up to 9 and higher and stereochemical variety of the formed compounds [1]. Despite exceptional oxophilicity cations RE, in recent decades intensively develops the chemistry of compounds of RE with organic N-donor ligands, that is determined by the current and prospective applications of multifunctional coordination compounds of RE in magnetic and optical devices, sensor systems, biological analysis and medical diagnostic apparatus, etc. For coordination chemistry is of special interest polydentate N-donor s-triazine, 2,4,6,-tris(2-pyridyl)-1,3,5-triazine (tptz) and large π-system in tptz, contributing to the stabilization of the complexes. In the present work we studied the influence of conditions (nature of solvent, ratio of reagents, temperature) on the composition and structure of compounds formed in the interaction of $RE(NCS)_3•6H_2O$ (RE = Y, Eu, Tb) with tptz (scheme).



Structural features of the obtained compounds is determined using the data of the single crystal and powder X-ray analysis, IR spectroscopy and thermoanalytical tests. Depending on the conditions formed a neutral, cationic, mononuclear or supramolecular ensembles, in which there is a link to RE-NCS and the coordination number (CN) of RE is 8.

All the complexes isolated from solutions have two molecules of tptz in its composition, one of them coordinated tridentate, the other is in the *exo*-position. Transformation tptz in *endo*-position occurs on the recrystallization of the samples in aprotic MeCN (scheme), in $[RE(tptz)_2(NCS)_3]•MeCN$ (RE = Y, Eu, Tb), coordination sphere with CN 9 is formed only from nitrogen atoms, six of whish belong two molecules of tptz and three belong to thiocyanate anions.

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STRONG CONFINEMENT EFFECT IN THICK LAYERS OF YTTERBIUM COMPLEX

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The successful synthesis of *nematic* metallomesogens [1] opened up the possibility to obtain and study macroscopically ordered liquid-crystalline phases in metallomesogen. Systematic studies of metallomesogens revealed one more feature, which has not been deliberately investigated so far. In particular, the first-order phase transition from the liquid-crystalline to isotropic phases can take place within a temperature range of one to several degrees [2]. This should give rise to coexistence of the anisotropic and isotropic phases and to effective anisotropy of physical properties being lower in this range than the anisotropy of the proper liquid-crystalline phase.

The liquid-crystalline complex studied in this work was tris[1-(4-(4-propylcyclohexyl)phenyl)octane-1,3-diono]-[5,5′-di(heptadecyl)-2,2′-bipyridineytterbium. It has both smectic-A and nematic phases [1].

We compared the electro-optical properties of the metallomesogen in isotropic (I) phase with the optical and dielectric anisotropy of the metallomesogen determined in the nematic (N) phase on the basis of the Landau–de Gennes theory. The anisotropy measured experimentally near the transition proved to be many times lower than the calculated value.

The cause for phase coexistence was determined by monitoring the phase transition by polarization microscopy. According to polarization microscopy data, the phase transition temperature decreases by more than 10°C as the metallomesogen layer thickness is reduced from 200 to 5 μm. This is the effect of boundaries of the cell containing the sample on the N–I phase transition temperature, i.e., the confinement effect. In the case of classical liquid crystals placed into a thin cell or porous matrix, this effect is manifested if the cell (pore) characteristic dimension is less than a micrometer. The confinement effect found in metallomesogens for order of magnitude greater layer thicknesses was a new and unexpected finding.

Thus, for the first time it was shown that in metallomesogen complexes exist very strong confinement effect. The reason seems to lie in the physical-chemical nature of the complexes, namely in the presence of coordination bonds. It can be assumed that a necessary condition for the observed effect is the strong interaction between neighboring complexes.

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FEATURES OF INDIUM COMPLEXES FORMATION IN EXTRACTION SYSTEMS WITH NITROGEN – CONTAINING OLIGOMERIC ALKYLPHENOLS"

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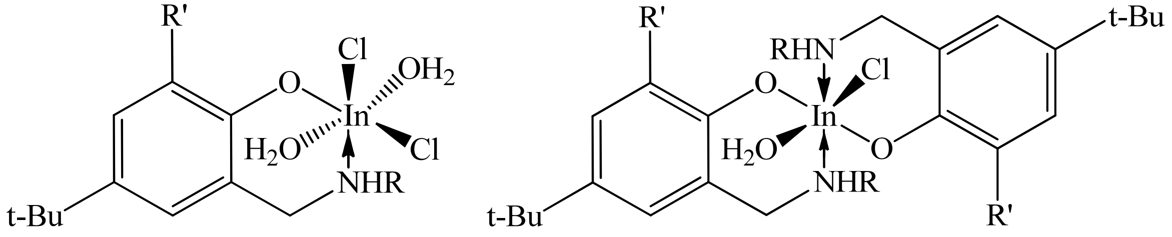
The liquid-liquid extraction of indium (III) from chloride and sulfate aqueous solutions containing mineral acid and corresponding salts by alkyl-phenol-amino-formaldehyde resol oligomer (resin «Yarrezin B», YaRB) in toluene has been investigated under different conditions. YaRB is a technical product of polycondensation of para-tert-butyl-phenol with formaldehyde in ammonia presence. It is as hemi-aza-calixarene – the analog of Salen, Kelex, amino acids and tripod phenolic ligands: tris(2-hydroxy-3,5-dimethylbenzyl)amine [1, 2].

The samples from organic extracts are also examined by infrared spectroscopy. As the results, it is found that in chloride systems HCl competing extraction is resulted and bonds In–Cl, In–O and In–N (it is confirmed indirectly) in organic phase are formed.

The indium (III) complexation with inorganic ions take into account. Non-ideality of aqueous phase is considered using specific interaction theory by Brønsted-Guggenheim-Scatchard (SIT) [3, 4]. The present models are realized in program Mathcad medium. By applying the error method of least-squares analysis to the indium distribution coefficients on equilibrium equations for these extraction systems, the conditional thermodynamic constants of indium complexes and mineral acid extraction have been determined. Non-classic approach is supplied: with regard to mineral acid extraction and with introduction of activity coefficient of YaRB active component (as amine).

Indium is extracted in pH = 2–4.5 similar to zinc and cadmium – with formation of coordinating-unsaturated complexes [5], but with formation of bond In–inorganic anion – similar to scandium [6]. The extracted complex «In^{3+} – YaRB active component» species in hydrochloric acid systems have the following forms:



This work is supervised by deceased Professor of Institute of Fine Chemical Technologies Bukin V.I.

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INFLUENCE OF THE COORDINATION SPHERE OF μ-CARBIDO-DIMERIC BIS(5,10,15,20-TETRAPHENYLPORPHYRINATO)IRON(IV) ON ITS REDOX PROPERTIES IN THE REACTION WITH *TERT*-BUTYLHYDROPEROXIDE

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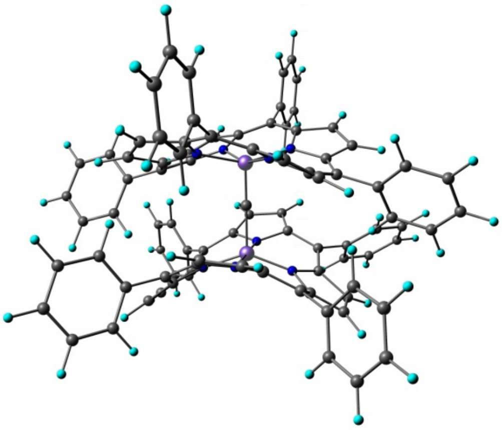
Modeling of enzymatic oxidation processes and understanding of their mechanisms are of great interest in the chemistry of macrocyclic compounds. Analogues of active centers of natural enzymes can be porphyrin complexes of biologically active metals. It has been shown that binuclear bridged iron complexes capable of rapidly losing or attaching an electron, exhibit good catalytic activity. The example of such promising compounds is μ-carbido-dimeric iron (IV) complexes, which are very stable in solutions.



This work is devoted to study of the influence of the environment of the coordination center of the μ-carbide-dimer tetraphenylporphyrinate iron(IV) $(Fe^{IV}TPP)_2C$ on its redox properties in the reaction with *tert*-butylhydroperoxide (TBHP). The composition of the inner coordination sphere was changed by donor-acceptor binding of substrates of various nature to the iron atom (L = imidazole, tret-butanol). During the reaction of $(Fe^{IV}TPP)_2C$ ($c = 6.8 \times 10^{-6}$ mol/l) with TBHP ($c = 2 \times 10^{-5} - 2 \times 10^{-2}$ mol/l), the π-cation-radical form $TPPFe^{IV}{=}C{=}Fe^{IV}TPP^{+\bullet}$ is formed. One-electron oxidation of macrocycle is preceded by the stage of peroxide coordination on the central metal cation. The kinetic characteristics of the investigated process are obtained.

Variation of the complex coordination sphere leads to a change in the composition of the intermediates, products, and the reaction rate during interaction with peroxide. The interaction between TBHP and complexes $(L)(Fe^{IV}TPP)_2C$, having different environment of the coordination center, is a multistage process. Each stage is characterized by a set of spectral curves with clear isobestic points. The orders with respect to the individual reagents and the values of k_v at each stage are determined. The reaction mechanism is established and comparative analysis of the kinetic parameters of the investigated reactions is done. Identification of the intermediate active oxidized forms and products of the reactions was carried out by UV-visible, IR spectroscopy, and mass-spectrometry.

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3D-TRANSITION METAL(II) TRIS-PYRIDINEOXIMATES WITH TERMINAL METHANETHIOSULFONATE GROUP DESIGNED FOR AN EFFICIENT PROTEIN THIOL GROUP BINDING

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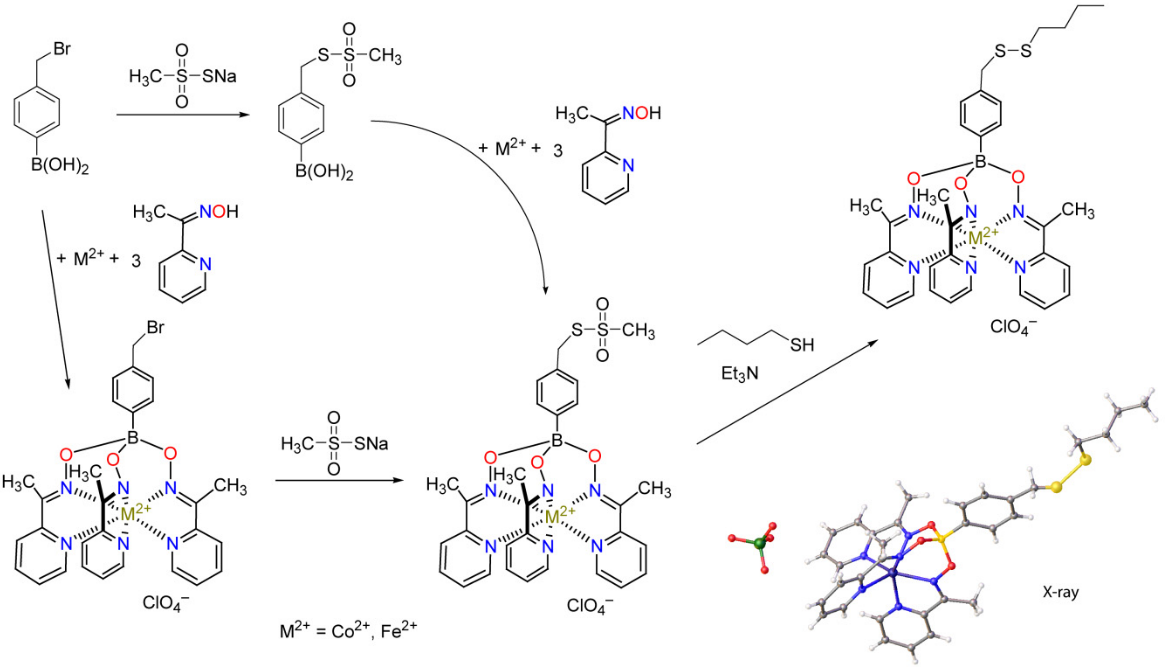
Development of novel agents for the therapy and the diagnostics as well as new types of the paramagnetic tags (including those based on cage metal complexes) with extremely high magnetic anisotropy is one at the most important tasks of modern biochemistry and structural biology. Their selective binding to a given biological target can be improved by the directed functionalization of such complexes by suitable vector groups, thus increasing an affinity to this biomacromolecule. The boron-capped paramagnetic cobalt and diamagnetic iron(II) tris-pyridineoximates with terminal methanethiosulfonate group were prepared using two synthetic approaches shown in Scheme. Most suitable of them for the synthesis of the iron(II) complex of this type used the functionalization of its initially obtained bromine-terminated precursor, while the direct self-assembly on a cobalt(II) ion as a matrix using the corresponding functionalized boronic acid as a capping agent is more suitable synthetic approach in the case of its cobalt(II)-containing analog. We also performed the model reaction of these methanethiosulfonate-teminated iron and cobalt(II) complexes with butanethiol in the presence of triethylamine as organic base giving the corresponding conjugates.



The obtained high spin cobalt(II) cage complexes was found to have a very high axial component of the magnetic susceptibility with a negligible rhombic amount in its value.

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COMPLEX FORMATION OF RE(V) C N-ETHYLTHOMOUSINE AT TEMPERATURES 273-338 K

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Rhenium is a metal whose complex compounds have been studied with such biologically active ligands as thiourea and its derivatives in solution and in solid form. Many rhenium complexes with these ligands are used to increase the stability of polymers. From the literature it is known that when complexes are formed, the coordination of the metal atom occurs through the sulfur atom. The stability constant of complex compounds of rhenium (V) with methyl-, ethylthiourea depends on the nature of the metal, ligand and medium, and their values differ significantly from each other.

Previously, we studied the processes of complexing of rhenium (V) with N-ethylthiourea in a medium of 6 mol/l of HCI at temperatures of 273-288 K. It was found that the values of the constants of the complex forms formed decrease with increasing temperature in this interval. Then, taking into account the effect of temperature, this complexation process was studied at temperatures of 298-338 K. To determine the number of complex forms formed, the potentiometric titration method was used, and in the calculation of their stability constants - by the Bjerrum method.

To obtain the starting material and potentiometric titration, the potassium permanganate powder- $KReO_4$ is used, to which KI and 6 M of HCl are added, the iodine evaporates and the original titrant of $K_2[ReOCI_5]$ remains. In the cell, an ethylthiourea ligand is taken, which is the oxidized R-S-S-R and the reduced R = S form of the system. When it is added to the cell with the ligand of $K_2[ReOCI_5]$, an increase in the potential is observed, which indicates the participation in the complexation process of the reduced form of the ligand.

The values of the potentials of the system of $K_2[ReOCI_5]$-N -ethylthiourea-6M HCl were used to calculate the equilibrium ligand concentration at each titration point at all temperatures. Based on the results of experimental data on the determination of the rhenium (V) complex formation function, the graph of the dependence = f (-Lg [L]) was constructed in accordance with which the values of the instability constants of the complex compounds formed were calculated. All calculations were carried out using the computer program "Excel".

Curves of the formation function of chlorine -N-ethylthiourea Re (V) complexes in 6M of HCl medium revealed that five coordinating compounds of the following composition are formed in the studied system: $[ReOLCl_4]^-$; $[ReOL_2Cl_3]^0$; $[ReOL_3Cl_2]^+$; $[ReOL_4Cl]^{2+}$ и $[ReOL_5]^{3+}$. The increase in temperature does not affect the composition of the complexes that form, but the values of the constants of their formation decrease. Complex compounds become less stable, since the electrostatic repulsive forces between the ligand and the central atom of the complexing agent increase.

Using the values of the formation constants of complex forms, at all temperatures the values of Gibbs energy were calculated, which have a negative sign. The obtained data indicate that the reaction of complex formation of rhenium (V) with the investigated ligand in the studied temperature range is a spontaneous process.

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X-RAY PHOTOELECTRON SPECTRA AND ELECTRONIC STRUCTURE OF BINUCLEAR BORON DIFLUORIDE Β-DIKETONATES

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Boron difluoride β-diketonates possess intensive luminescence, liquid crystal properties and are applied as laser dyes, organic light diodes, optical chemosensors, active components of sunlight collectors, materials for non-linear optics and polymer optical materials. Due to electronic structure of boron difluoride β-diketonates as well as of any chemical compound determines its optical properties, to synthesize new compounds with prescribed properties one needs to establish relations between desired properties of the complexes and their electronic structure. The most complete information about the electronic structure of complexes can be obtained by a combined use of photoelectron spectroscopy and quantum chemistry. Using the absorption spectroscopy together with calculated results within the TDDFT approach makes it possible to determine an effect of substituents on the optical properties of complexes.

The work presents results of electronic structure investigation and optical properties study of five β-diketonates of boron difluoride by the means of X-ray photoelectron spectroscopy absorption spectroscopy, DFT and TDDFT. X-ray photoelectron spectra molecular crystals were recorded on a high-vacuum photoelectron spectrometer (Omicron, Germany) with hemispherical electrostatic analyzer using monochromatic irradiation source MgKα (hν = 1253.6 eV). Calculations were performed using Firefly 8.1.1. G quantum chemical software package using TZVP basis set and the hybrid exchange-correlation functional B3LYP.

In the series of investigated complexes, electronic substitution effects were revealed. Due to the influence of the atomic orbitals Se 4p and S 3p for the binuclear acetylacetonates of boron difluoride, in comparison with the monomer, the energy of the π and n-MO chelate cycles is stabilized by 0.2-0.7 eV. In comparison with dibenzoylmethanate of boron difluoride, are observed for the binuclear complex the transfer of electron density from sulfur atoms to chelate and benzene cycles (S_0-S_1 transition) and the bathochromic shift of the long-wave band of the theoretical absorption spectrum due to destabilization of the level of the highest filled molecular orbital by 0.35 eV. Based on the calculated results, the bands of X-ray photoelectron and absorption spectra are interpreted.

Acknowledgements
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IR-SPECTROSCOPIC INVESTIGATION OF Zn (II), Co (II) COMPLEX COMPOUNDS WITH GARMIN AND GARMALIN

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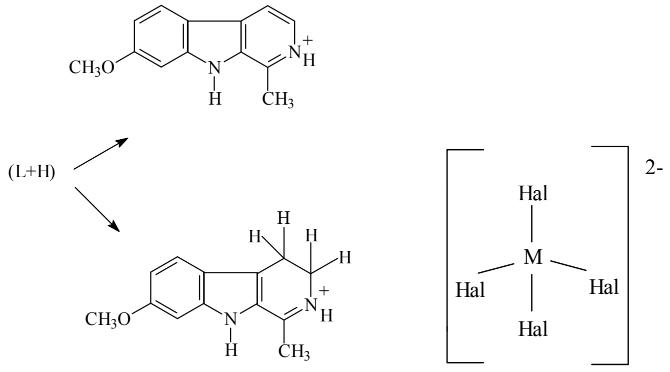
The metal complexes of harmine and harmaline alkaloids from Peganum Harmala have wide range of biological activity. The aim of work is study of FTIR spectra of the metal complexes with harmaline and harmine. In the IR spectra of harmine and harmaline, broad bands at ~ 3400-3050 cm^{-1} are observed which correspond to the valent ossilations of ν(NH) и ν(C-H) in the aromatic systems. In the region of 2830, 2950 cm^{-1} absorption bands ν(C$_{aliphatic}$-H) are also observed. The most intense and characteristic peaks were in the region of ~1630 см$^{-1}$(ν(C=N)), ~1600-1400 см$^{-1}$ (oscilations of the aromatic ring - ν(C=C)), ~ 1375 (δ(CH_3)), ~ 1260 and 1030 (= C-O-C), ~ 1160 (C-O) and ~ 800 (substituted aromatics) см$^{-1}$. In the IR spectra of Zn (II) and Co (II) complexes, broad characteristic peaks related to ν(NH) and ν(CH) in the 3400-3100 cm^{-1} region are clearly manifested. In this case, the frequencies of ν(NH), (CH) and ν(OH) overlap each other when the crystallization water molecules are included in the complex.

As a result of ligand protonation in the spectra of of the $[MX_4](L+H)_2$ onium type complexes, where M = Zn (II), Co (II); X = Hal$^-$, O^{2-}; L = GRN, GLN, there was a small shift in the characteristic ν(C=N) bands, as well as, in the system of conjugated bonds of the aromatic system ν(C=C) at ≈1600-1500 cm^{-1} in the high-frequency region (Δ=1-8 см$^{-1}$).

In the case of GRN complexes, the intense doublet band in the 1627, 1565 cm^{-1} region is split into a triplet, and for the GLN coordination compounds, three bands in the 1626, 1566, 1542 cm^{-1} region are broaden and become a doublet. Obviously, this is due to a decrease in the symmetry of the GRN molecule as a result of coordination. In the case of GLN, at the contrary coordination leads to an increase in symmetry and IR spectrum is simplified.

This dependence is observed for synthesized onium compounds of the type $[MX_n](L+H)_2$, (L=GLN, GRN; X=Cl$^-$, Br$^-$, O^{2-}, CN$^-$, NO_2^-; n=4,6; M= Zn(II), Co(II), where the ligand is in the protonated form. The structure of complex anions can be represented as follows:



M = Co^{2+}, Zn^{2+}; Hal = Cl$^-$, Br$^-$

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REDOX PROPERTIES OF Cu(II) AND Pd(II) COMPLEXES WITH LIGANDS CONTAINING THE CUMARINE FRAGMENT

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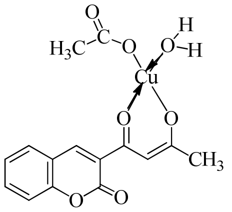
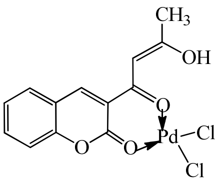
The compounds containing a coumarin fragment in their structure have a wide range of physiological effects (anti-inflammatory, analgesic, antitumor, etc.). The 3-substituted chromen-2-ones are polyheteroatomic cyclic systems including several potential donor centers. Complexes **1**,**2** were previously obtained (SU, Saratov) on the basis of the reaction of polyoxocompounds of *2H*-chromen-2-one with salts of transition metals – $Cu(CH_3COO)_2$ and $PdCl_2$.



1



2

	1	2
Ox:	E_{pa1}=1,66V, E_{pa2}=1,86V;	E_{pa1}=1,74V, E_{pa2}=1,92V;
Red:	E_{pc1}= -0,66V, E_{pc2}=-0,87V, E_{pc2}=-1,4 V;	E_{pc1}=0,45V, E_{pc2}=-1,16V.

In this work the redox properties of copper (II) **1** and palladium (II) **2** complexes were studied by the cyclic voltamperometry method (CVA). Atoms of metals coordinate the organic ligands containing the coumarin fragment, over different oxygen atoms. Compounds **1**, **2** were analyzed in anodic (0; -2.0 V) and cathodic (0; 2.2 V) environments in CH_3CN. The CVA of oxidation and reduction of complexes **1**, **2** are shown on the Fig.**1** (***a***, ***b***).

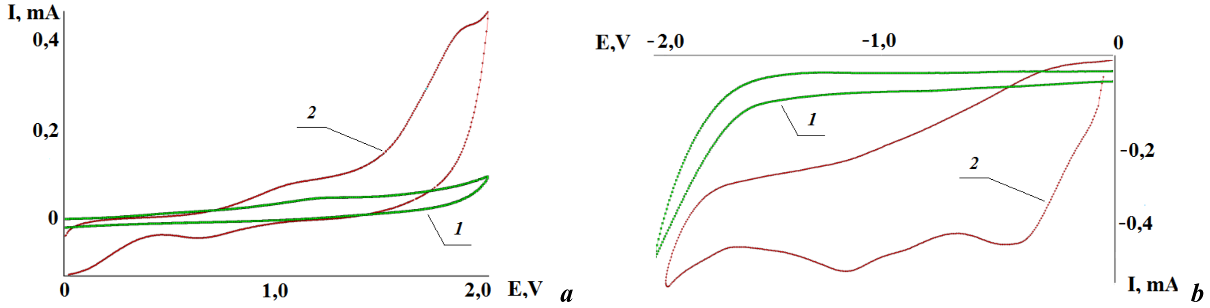


Fig. **1.** CVA of the oxidation (***a***) of complex **1** and reduction (***b***) of complex **2:** ***1*** – 0,1 *n*-Bu_4NClO_4; ***2*** – compounds **1**, **2** (CH_3CN, Pt-anode, Ag/AgCl, C = $5 \cdot 10^{-3}$ M, V=0,2V/c)

The oxidation of complexes **1**, **2** occurs analogously with the participation of a ligand. It proceeds along the heteroatom of the piran ring and this redox process is described by the *EEC* mechanism (*E*-electrochemical stage, *C*-chemical stage). The anodic peaks have similar potentials and they are better separated at a scan speed of the potenitsal higher than 0.2V/c. The mechanism and oxidation potentials of complexes **1**, **2** are consistent with the data obtained earlier for the original substituted coumarins. The reduction of compounds **1**, **2** occurs in two one-electron stages with the participation of metal atoms. The complex **1** has a third cathodic peak at a higher potential, which corresponds to the presence of a free carbonyl group in its structure. Between the oxygen atom of the carbonyl group and the palladium atom there is a chemical coordination bond in complex **2**. This carbonyl group is not capable of taking an electron. The nature of metals has an insignificant effect on the values of redox potentials of complexes **1**, **2**.

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MULTIFUNCTIONAL SUPRAMOLECULAR SMART PLATFORM BASED ON OLIGO(ETHYLENE OXIDE) DERIVATIVES AND LANTHANIDE IONS

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Increased interest to lyotropic liquid crystal (LLC) systems is caused by that processes of self-organizing, their underlying formations, are used in nanotechnology and biomedicine. Supramolecular assemblies of metal complexes in anisotropic LLC phases are of great interest and provide new promises in today’s materials science. The combination of anisotropic LC properties and electrical, magnetic and optical characteristics of a metal ion suggest great potential for the design of new multifunctional materials.

In this work we present data of structure organization and liquid crystal properties lyotropic lanthanide containing (La^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}) systems based on oligo(ethylene oxide) derivatives several types of compounds: nonionic surfactants with various EO chain lengths $C_{12}EO_{10}$, $C_{12}EO_4$ and cholesteryl oligo(ethylene oxide) amphiphile $CholEO_{10}$. Liquid crystal and thermal properties, structure parameters of lanthanide containing LLC were established by methods of POM, DSC and SAXS. Phase diagrams for ternary systems $C_{12}EO_n/Ln(III)/H_2O$ were drawn. It is shown, that is not dependent on type of Ln ions, systems on the basis of $C_{12}EO_{10}$ form hexagonal mesophase, while systems based on $C_{12}EO_4$ exhibits lamellar molecular order. The effect of the type of the supramolecular organization on the luminescence efficacy due to the structure of the $C_{12}EO_{10}$ and $C_{12}EO_4$ ligands, forming different types of lyotropic mesophases, hexagonal and lamellar, were studied. To study the effect of the liquid crystal state on the luminescence efficiency, time-resolved spectra were obtained at different temperatures. NMR ^1H with a pulsed magnetic field gradient has been used to characterize molecular motions in the $C_{12}EO_4/La^{3+}/H_2O$ systems with different water contents [1].

Lyotropic liquid crystals based on cholesteryl oligo(ethylene oxide) amphiphiles and Ln^{3+}– La, Dy, Tb, Eu ions were synthesized. For binary systems $CholEO_{10}/Ln$ the smectic phases were obtained. In ternary systems in the present of water (5-30 % wt) the lyotropic mesomorphism were observed. The phase’s transformations from hexagonal via cubic to lamellar mesophases were found. Investigation of the luminescent properties of $CholEO_{10}/Ln^{3+}$ complexes, where Ln^{3+}-Dy, Tb, Eu showed the characteristic luminescence in the yellow, green and red regions of the spectrum. The biomezogenic complex $CholEO_{10}/Tb^{3+}$ demonstrates a long lifetime in comparison with the analogue $C_{12}EO_{10}/Tb$ (III).

The good luminescent characteristics allow using these mesophases in future as biocompatible delivery systems for various molecules with the possibility of spectral monitoring.

[1] N. Selivanova, A. Konov, K. Romanova, A.Gubaidullin, Yu. Galyametdinov. *Soft Matter,* **2015**, *11*, 7809-7816.

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WATER-SOLUBLE COMPOUNDS OF IRON(II)

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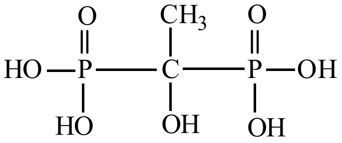
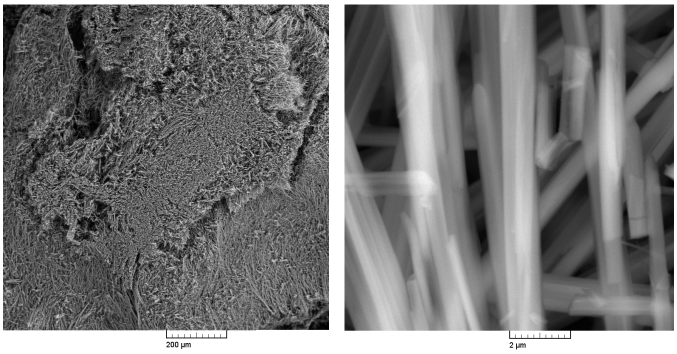
The reaction of an aqueous suspension of fine iron with one equivalent of 1-hydroxyethylidenediphosphonic acid (H_4L) has yielded a poorly soluble iron(II) 1-hydroxyethylidenediphosphonate ($FeH_2L \cdot H_2O$).



$$HO-P(=O)(OH)-C(CH_3)(OH)-P(=O)(OH)-OH$$

H_4L

The compound is precipitated from the solution in the form of closely packed whiskers (fig. 1).



a *b*

Fig. 1. SEM images of whiskers $FeH_2L \cdot H_2O$: *a* - areas with a parallel and erratic arrangement, *b* - tight fusion of fine filaments.

Reaction of fine iron with two equivalents of acid gives a water-soluble compound $Fe(H_3L)_2$ which is disproportionated to $FeH_2L{\bullet}H_2O$ and H_4L at heating. The interaction of an aqueous suspension of $FeH_2L{\bullet}H_2O$ with an organic amine (solubility promoter) leads to the dissolution of the iron(II) compound. As the solubility promoters, 2-aminoethanol $H_2NCH_2CH_2OH$, 2-amino-2-(hydroxymethyl)propane-1,3-diol $H_2NC(CH_2OH)_3$ and $2,2'$-(ethylidenedioxy)bis (ethylamine) $H_2NCH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$ were used. Heating the aqueous suspension of $FeH_2L{\bullet}H_2O$ in an autoclave at 150° C in the presence of catalytic amounts of KF causes the formation of a new crystalline phase and an X-ray amorphous impurity. The obtained compounds were studied by elemental analysis, infrared spectroscopy, scanning electron microscopy, X-ray phase analysis.

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CRYSTAL STRUCTURE OF THE BISMUTH COMPLEX WITH 2-AMINO-1-METHYLBENZIMIDAZOLE AND DIIZOPROPYLDITHIOPHOSPHATE

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Study of mixed ligand metal complexes is very important for establishment of competitive coordination in N,P,S–containing organic ligands. In addition, the dialkyldithiophosphate and benzimidazole ligands have many practical applications in industry, medicine and agriculture. The aim of this work is to synthesize, study the structures of the coordination compound Bi[(i-$C_3H_7O)_2PS_2]_3$ 3 with 2-amino-1-methylbenzimidazole (MAB) and determine the nature of the interaction of molecules in their crystal structures. The crystals of the [Bi (MAB) (i-Pro$_2$PS$_2$)$_3$] compound belong to the triclinic syngony. Basic crystal structure data: $P2_1/c$, a = 11.389 (5) Å, b = 29.984 (5) Å, c = 12.898 (5) Å, β = 101.063 (5)°, V = 4322.66 Å^3, Z = 4. Crystal structure and packing of molecules of the complex are shown in Fig. 1. In the structure of the synthesized mixed ligand complex with bismuth, introduction of the bulk molecule of 2-amino-1-methylbenzimidazole into the distorted pseudo-octahedral configuration of bismuth tris-diisopropyldithiophosphate is observed. As a result, 6 sulfur atoms from 3 diisopropyldithiophosphate ions and 1 nitrogen atom from the aminobenzimidazole molecule are bidentately coordinated around the bismuth ion. Hydrogen bonds are not observed in the structure, which leads to the formation of individual island monomeric complex particles, which are joined together by a π-stacking interaction. The bond lengths and valence angles in the complex practically do not differ from the normal values.

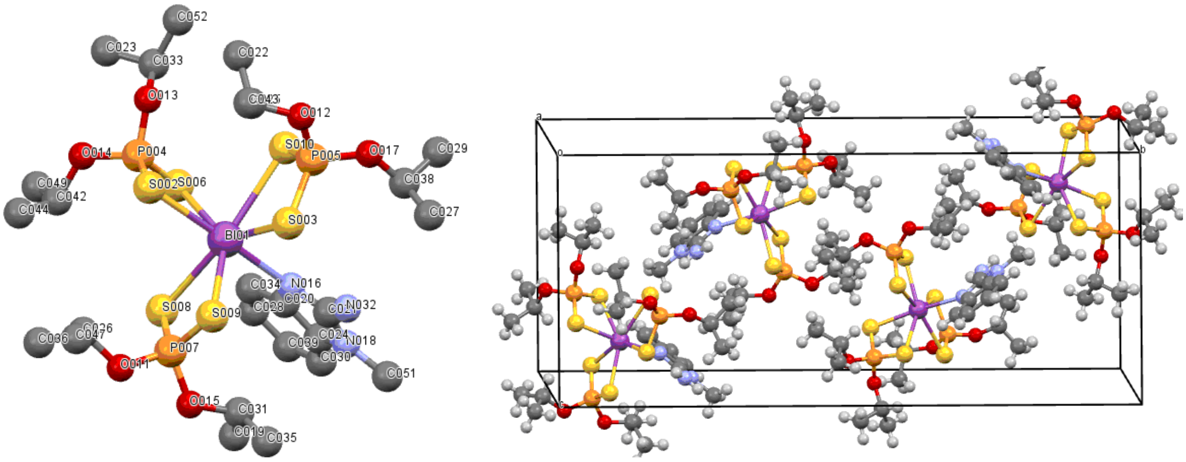

Fig. 1. Crystal structure of [Bi(MAB)(i-Pro$_2$PS$_2$)$_3$] and its complex packing in crystal.

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COMPLEX FORMATION OF Pt (II) IN THE PROCESS OF SORPTION BY PHOSPHORUS AND SULFUR-CONTAINING IMPREGNATED SORBENTS

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It is known that solid sorbents based on dialkyldithiophosphoric acids (DADTPA) have complexing properties with respect to ions of certain transition metals, in particular copper, nickel, iron, cobalt, silver, and gold. There is a direct relationship between sorption properties from solutions and the possibility of formation of complex compounds of extractable metal and DADTPA.

In order to obtain additional data regarding structure and mechanism of complexation of Pt (II) with impregnated sorbents on the basis of dialkyldithiophosphates, the IR absorption spectra of the new synthesized impregnated sorbents were recorded before and after sorption of the Pt (II) ion. The commercially available hydrophobic chemically inert PAD600 sorbent used as an initial polymer matrix in the preparation of impregnated sorbents has a well-developed macroporous structure, which makes it suitable for use as an impregnated sorbent matrix with virtually any impregnating organic ligands.

In the IR spectrum of PAD600, the frequencies specific to polystyrene were observed in the frequency interval of 400-4000 cm^{-1}. Absorption bands in the range of 1600-1700, 705-795 cm^{-1} were identified as the frequencies of valence and deformation oscillations of monosubstituted aromatic hydrocarbon. The presence of absorption bands at 2925-3081 cm^{-1}, as well as at 1350-1512 cm^{-1}, refer to the ν_s and ν_{as} oscillations of the C-C, C-H, CH_2-, CH_3-aliphatic hydrocarbon bonds. The absorption bands of styrene at 708, 795, 1605 and 1699 cm^{-1} are clearly visible. In addition, there are so-called "five-fingerprint" bands in the region of 1700 and 2000 cm^{-1}.

Regarding the sorbent, which contain PSS-functional groups in its structure, in addition to the indicated bands, new intense bands in the region of 1372-1353, 975-899 cm^{-1} are also observed. These bands are related to the oscillations of the P-O-R group. In addition, in the region of 745-760 cm^{-1}, valence oscillations of the P-O group are observed. The P = S oscillations were attributed to the bands at 688 cm^{-1}.

The presence of an asymmetric band with a maximum of 512 cm^{-1} is associated with the oscillations of the P-S group. The spectra of chelates differ significantly from the spectra of sorbents, which indicates a fundamental difference in the nature of the bond with the dithiophosphoric fragment. In addition, in the transition from sorbents to chelates (complexes), a low-frequency shift of the P = S groups bands was observed, due to a decrease in the order of the P-S bond and indicating the formation of a metal-sulfur bond. The band in the range of the P-S-bond oscillations also changed in a significant way.

The frequencies of valent oscillations of the P-S-bond are shifted by 10-40 cm^{-1} in sorbents containing Pt (II) ions.

Thus, the processes of complexation of Pt (II) with dialkyldithiophosphoric acids on the surface of impregnated sorbents were studied by IR spectroscopy. Based on the shift of the characteristic bands in the spectrum, it is shown that impregnated organic ligand interacts with the Pt (II) ions to form metal complexes.

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SYNTHESIS OF AROYLHYDRAZONE TIN(IV) COMPLEXES WITH THE SPECIFIED STRUCTURE FROM FRAGMENTS OF HYDRAZIDE COMPLEXES OF TIN TETRACHLORIDE AND AROMATIC ALDEHYDES

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The problem of selective synthesis of tin(IV) hydrazone complexes, perspective for creation of modern biomaterials and medicinal preparations, is topical not only for biocoordination chemistry, but also for biology and medicine. For the first time there were obtained molecular chelates $[SnCl_4(HLg)]$ with O(C=O)–N(NH_2)-coordination and zwitter-ionic $[SnCl_4(Lg{\cdot}H)]$ with O(C–O)–N(NH_2) by interaction of $SnCl_4$ with hydrazides of 2- and 4-R-benzoic (R = H, OH, OCH_3, NH_2), 3-R-2-naphthalic (R = H, OH) and pyridine carbonic acids (HLg). The complexes of these types were also synthesized with corresponding hydrazone of 2- and 4-R-benzoic (R = H, $N(CH_3)_2$, OCH_3, OH, Br) and also 2-R-naphthalic (R = H, OH) aldehydes (HL) with different composition of coordination knot: $\{SnCl_4ON\}$ – $[SnCl_4(HL)]/[SnCl_4(L{\cdot}H)]$ and $\{SnCl_3O_2N\}$ in case of R = 2-OH – $[SnCl_3(HL)]/[SnCl_3(L{\cdot}H)]$, where hydrazone is H_2L.

The received data set – approximately ~50 complexes with the structures defined by means of IR, NMR spectroscopy, mass-spectrometry, thermogravimetry methods as well as 21 molecular and crystalline structures defined by X-ray diffraction analysis method – was used as a scientific background to determine the conditions for the directed synthesis of tin(IV) aroylhydrazone complexes with the specified structure by the reaction of intrasphere condensation of its hydrazide complexes and aromatic aldehydes.

Results:
– coordinated Sn←NH_2-group enters the condensation reaction with aldehydes with formation of azomethine, at the same time connection Sn← N is preserved here;
– hydrazone molecular chelates of $SnCl_4$ with coordination knot $\{SnCl_4ON\}$ and the ketonic form of $O_{(C=O)}$–$N_{(CH=N)}$-ligand can be intentionally synthesized on the basis of the same type hydrazide complexes provided the absence of aldehydes of nitrogen containing substitutes, in particular R=$N(CH_3)_2$, in a benzene ring; their presence results in formation of zwitter-ionic complexes with $O_{(C–O)}$–$N_{(CH=N)}$-coordination of hydrazone and knot $\{SnCl_4ON\}^-$;
– as a result of condensation of zwitter-ionic hydrazide complexes with aldehydes analogical hydrazone complexes appear with a coordination knot $\{SnCl_4ON\}^-$ and enolic form of $O_{(C–O)}$–$N_{(CH=N)}$-ligand independently of substitutes (R) in the aromatic ring of aldehyde, except for R = 2-OH;
– the presence of 2-OH-group in an aldehyde fragment during condensation does not cause the modification of the type of appearing hydrazone complex, its deprotonation and binding to Sn(IV) leads to the change of composition of coordination knot – $\{SnCl_3O_2N\}/\{SnCl_3O_2N\}^-$ in comparison with hydrazide $\{SnCl_4ON\}/\{SnCl_4ON\}^-$;
–regularity in organizing of hydrazone tautomeric form in the complexes of Sn(IV) is kept similar to initial hydrazide: ketonic – in absence of vacant atom of nitrogen both in hydrazide, and in an aldehyde, and enolic – at its presence;
– the positive charge appearing as a result of (Npy, $N(CH_3)_2$, NH_2) groups protonation compensates negative on coordination knots $\{SnCl_4ON\}^-$ and $\{SnCl_3O_2N\}^-$; protonation is kept on hydrazide at the presence of nitrogen atoms in two fragments of hydrazones.

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NAPHTHOPHOSPHACYCLOPHANES AS BIDENTATE LIGANDS IN THE SYNTHESIS OF COMPLEXES OF RHODIUM (I)

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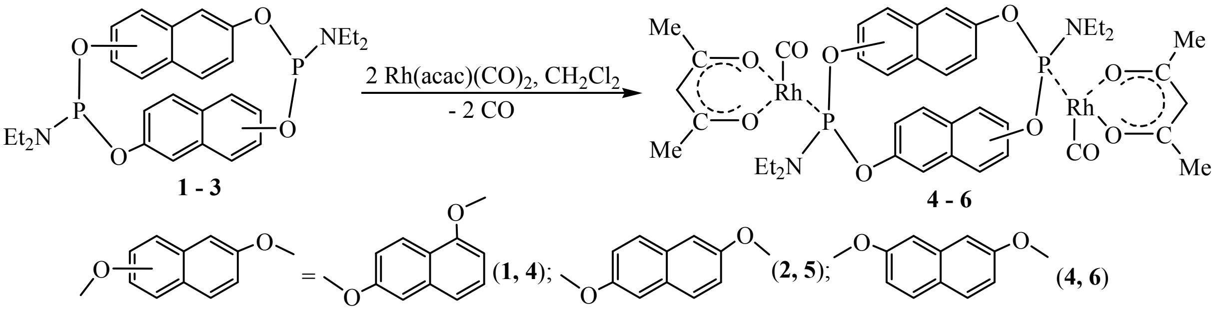
Rhodium(I) complexes based on uniform naphthophosphacyclophanes were synthesized and characterized by physical-chemical methods.

The uniform naphthophosphacyclophanes are bidentate ligands, containing two amidophosphite centers [1−3]. Reaction of 2 moles of acetylactonatocarbonyl rhodium(I) with 1 mole of naphthophosphacyclophanes **1−3** afforded binuclear complexes **4−6**:



Reactions were carried out in dichloromethane at room temperature during 4 hours. Complexes **4−6** were isolated as yellow or light-brown powders in 70−80% yields by precipitation from reaction mixture. They were well-soluble in dichloromethane, chloroform, acetone and 1,4-dioxane. Their ^{31}P-NMR spectra revealed doublet signals at 134 ppm with $^{1}J_{P,Rh}$ = 260 – 264 Hz, which are characteristic for square-planar Rh(I) complexes. Resonance signals in ^{1}H-NMR spectra were broadened, apparently, because of the existence of the macrocyclic ligands in several conformations. IR-spectra of complexes **4−6** revealed three strong bands at 1990 cm^{-1} (Rh−CO) and 1510, 1570 cm^{-1} (Rh−acac), as well as bands corresponding to naphthophosphacyclophane ligand.

The synthesized complexes were found to be unstable upon storage in solution, particularly in chlorinated solvents, resulting in formation of viscous insoluble olygomeric substances.

The catalytic activity of the synthesized compounds will be investigated.

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A STUDY OF THE THERMAL STABILITY OF THE COMPLEX TYROSINE COPPER

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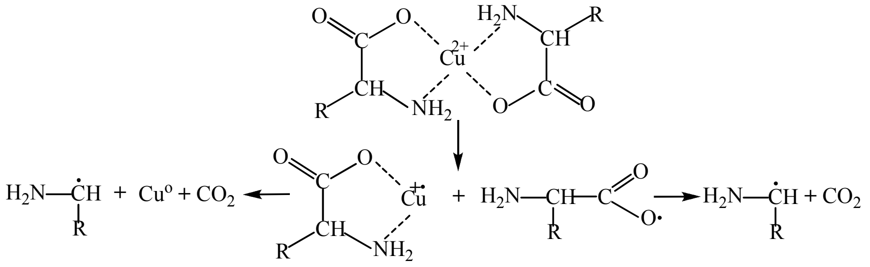
The mechanism and rate of decomposition of the amino acid metal complexes is of interest in connection with thermal processing of protein foods. The aim of this work is to study the thermal stability of the copper complex of tyrosine ($CuTyr_2$) in the solid phase in vacuum. The reaction rate was determined by the increase in pressure of the volatile decomposition products [1]. The effective rate constant of the decomposition process was calculated from the reaction equation of the first order in the temperature range of 200°to 230 ° C. Set of kinetic reaction parameters: activation energy E = 225кДж/mol, lnk0=57,9. The main gaseous reaction product is carbon dioxide. It is assumed that the primary act of thermal decomposition is intramolecular redox process of formation of ion-radical monovalent copper and the radical $H_2NCH(R)COO.$, where $R = HOC_6H_4CH_2$ (see scheme).

Previously, it was found that thermal decomposition of the complex of copper with glycine (R=H) is a two-stage process, accompanied by the formation of CO_2, Си^0, CH_2=NH (HC≡N) and diketopiperazine. Speed homolysis contacts in other metal complexes $Cu[H_2NCH(R)COO]_2$, where $R \neq H$, is directly dependent on the stability of the resulting decay of free radicals [2]. It becomes clear the range of reactivity of the studied copper complexes of amino acids, where it fits perfectly $CuTyr_2$: $CuAla_2 < CuGly_2 < CuVal_2 < CuIle_2 < CuLeu_2 < CuTyr_2 < CuPhe_2$.

With the increasing volume of the substituent R increases the stability of the radicals formed upon homolytic decomposition of the complexes, and, accordingly, increasing the speed of the process of decomposition.



The decay of the complex $CuTyr_2$, where $R = HOC_6H_4CH_2$, in the solid phase in a vacuum is approximately 2 moles of CO_2 and the products of disproportionation of the radical H2N(R)H., which confirms the above chart.

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RELATIVE CYTOTOXICITY OF COMPLEXES OF PLATINUM(II) AND PALLADIUM(II) ON HUMAN CELL LINES A431 AND HACAT

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It is well-known, that cisplatin (cis-[$Pt(NH_3)_2Cl_2$]) just as *in vitro,* in a physiological values of pH and temperature, so too *in vivo,* in conditions of reduced concentrations of chloride ion, easily hydrolyzes with formation of cis-$[Pt(NH_3)_2(OH_2)Cl]^+$, and then - cis-$[Pt(NH_3)_2(OH_2)_2]^{2+}$. Both particles are able to engage into processes of oligomerization forming bi- or oligonuclear complexes, e.g., $[(H_3N)_2Pt(\mu\text{-}OH)_2Pt(NH_3)_2]^{2+}$. Supposed, that cisplatin and his hydrolysis forms are intercalated and covalently bound with nuclear DNA, replacing aqua- or hydroxo ligands to nucleobases of DNA, thereby blocking reparation, replication and transcription processes, subsequently initiating mechanism of apoptosis cancer cells. A large amount of researches of cytotoxicity of new platinum complexes are known [1]. Nevertheless, there are no works in that field of study for hydrolysis products of *in vivo* complexes and inactive forms of cisplatin and relates, that are used in an oncological diseases therapy.

In this work, a number of Pt(II) и Pd(II) *model* complexes, that are isostructural to cisplatin and its pharmacological analogues were synthesized: [M(dipy)Cl_2], [(dipy)M(μ-OH)$_2$M(dipy)]$(NO_3)_2\cdot 2H_2O$ and [(dipy)M(μ-aet)$_2$M(dipy)]$(NO_3)_4\cdot 5H_2O$ (M = Pt or Pd, dipy – 2,2’-bipyridyl, aet – 2-aminoethanethiol), that are analogues products of complexes hydrolysis *in vivo* and inactive forms of cisplatin. All the compounds are described by structural and elemental analysis and IR-spectroscopy. Using MTT-test and calculations of coloured apoptotic cells the relative cytotoxicity of complexes was discovered, in comparison with cisplatin on human epidermoid carcinoma A431 cells and its normal histological analogue - human marginally transformed ceratinocytes of HaCaT. All the data were shown in Table 1.

Table 1 IC_{50} of complexes, μM

	A431	HaCaT
cis-[$Pt(NH_3)_2Cl_2$]	35.42±0.92	31.1±1.06
[Pt(dipy)Cl_2]	58.13±0.71	48.1±1.15
[Pd(dipy)Cl_2]	38.27±1.25	29.2±1.51
[(dipy)Pt(μ-OH)$_2$Pt(dipy)]$(NO_3)_2\cdot 2H_2O$	0.98±0.50	0.6±0.78
[(dipy)Pd(μ-OH)$_2$Pd(dipy)]$(NO_3)_2\cdot 2H_2O$	0.02±0.05	0.01±0.04
[(dipy)Pt(μ-aet)$_2$Pt(dipy)]$(NO_3)_4\cdot 5H_2O$	89.52±1.21	52.14±0.93
[(dipy)Pd(μ-aet)$_2$Pd(dipy)]$(NO_3)_4\cdot 5H_2O$	32.91±1.18	24.85±0.75

Analysis of data shows that hydrolysis forms ($M_2(\mu\text{-}OH)_2$) have the greater toxicity (more than 100 times) than the chloride complexes of platinum and palladium (including cisplatin); also they are more toxic for normal cells, in comparison with tumoral. Inactive thiol-forms ($M_2(\mu\text{-}SR)_2$) are non-toxic for cells. Also it should be noted that hydrolysis and inactivated forms of cisplatin practically don’t induce apoptosis of cancer cells.

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SYNTHESIS AND CRYSTAL STRUCTURE OF CHELATE COPPER(II) AND NICKEL(II) COMPLEXES WITH 2-*TERT*-BUTYL-5-(N,N-DIMETHYLAMINOMETHYL)TETRAZOLE

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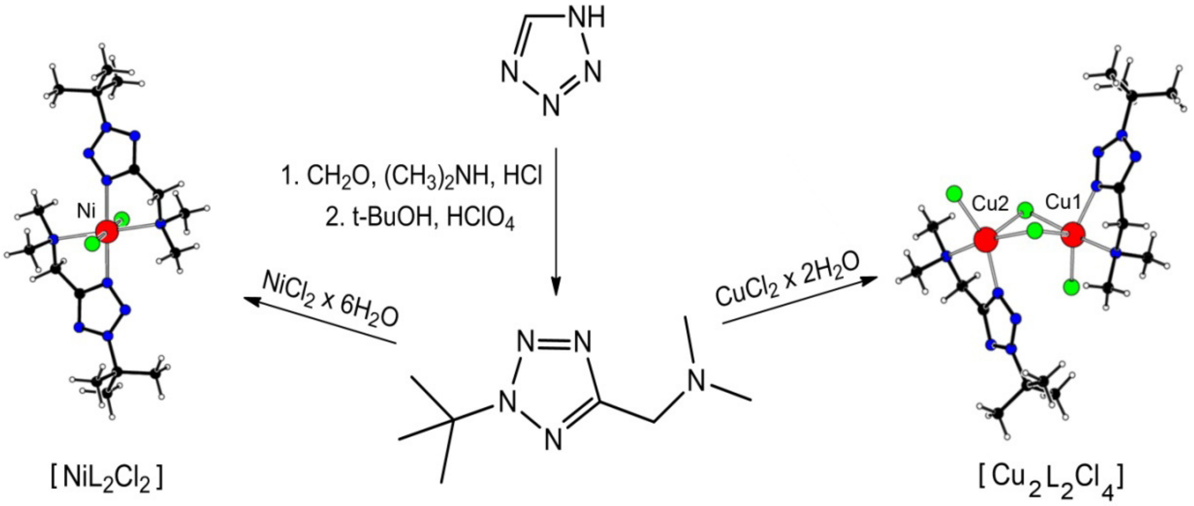
Complexes of copper(II) and nickel(II) chlorides with a new chelating ligand, namely 2-*tert*-butyl-5-(N,N-dimethylaminomethyl)tetrazole, (L), have been synthesized and characterized by elemental, thermogravimetric and X-ray analyses, as well as IR-spectroscopy. The obtained complexes were found to be [$Cu_2L_2Cl_4$] and [NiL_2Cl_2], respectively.



Complex [$Cu_2L_2Cl_4$] crystallizes in the triclinic space group $P\bar{1}$, and presents a binuclear complex. In complex molecule, the copper atoms Cu1 and Cu2 are connected by two asymmetrical chlorine bridges. Each copper atom is surrounded by three chlorine and two nitrogen atoms (the tetrazole ring N^4 and the dimethylamine nitrogen atoms of the same ligand molecule). These atoms form considerably distorted square pyramids, with bridging chlorine atoms in the apical positions, showing the longest Cu–Cl bonds in the coordination environment of each copper atom.

Complex [NiL_2Cl_2] is monoclinic, crystallizing in the space group $P2_1/n$. In shows a mononuclear structure, with the nickel atom lying on inversion centre. The nickel atom is bonded to two chlorine atoms and four nitrogen atoms of two ligand molecules, coordinated *via* the tetrazole ring N^4 and the dimethylamine nitrogen atoms. The coordination polyhedron is a considerably elongated octahedron, with chlorine atoms in the axial positions.

In complexes [$Cu_2L_2Cl_4$] and [NiL_2Cl_2], ligand molecules together with metal atoms form five-membered chelate cycles. In both compounds, coordination polyhedra reveal considerable distortion imposed by chelating coordination mode of ligands L.

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CYTOTOXIC ACTIVITY OF TIN COMPLEXES WITH SUBSTITUTED 8-HYDROXYQUINOLINES

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Organotin compounds are perspective anticancer drugs candidates [1, 2]. The 8-hydroxyquinoline exhibits antiseptic, disinfectant, and pesticide properties, functioning as a transcription inhibitor. Recently the cytotoxic properties of organotin complexes with hydroxyquinolines were discovered [3]. The 5,7-dihalo-8-quinolinolato tin(IV) complexes demonstrated high anti-proliferative activity toward the cancer cell lines with IC_{50} values ranging from nM to μM. Compared with their quinolinol ligands, complexes bind more strongly with DNA and intercalation was found the most probable binding mode for the complexes.

The aim of present work was the study of cytotoxic activity of organotin complexes based on dihalo-8-hydroxyquinoline. Complexes of dimethyl- and dibutyltin with 5,7-di-bromo-8-hydroxyquinoline **1**, **2** were synthesized and characterized by X-ray diffraction analysis.

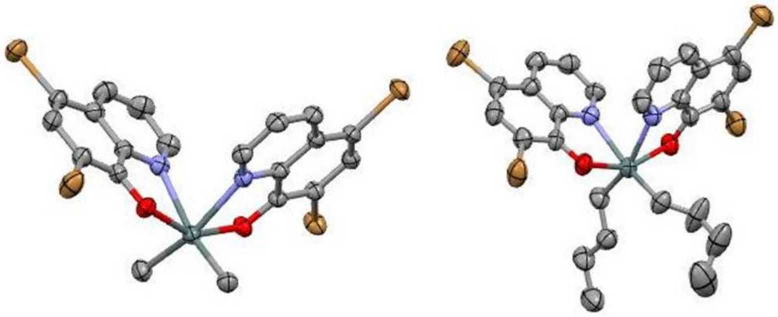

Fig. The molecular structures of **1** and **2**.

The cytotoxicity of the compounds was evaluated on cancer cells by the MTT test. The cytotoxicity of the compounds for the HCT-116 cell lines (colorectal cancer) was evaluated in the presence of complexes **1**, **2** and the IC_{50} values (concentration of the compound at which 50% death of cancer cells was observed) were determined (10 and 1 μM for **1** and **2**, respectively). The activity of the compounds was compared with that of cisplatin (IC_{50} = 5 μM). Thus, dibutyltin complex **2** showed the highest activity that makes it promising for further research as an antitumor agent.

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NEW FUNCTIONALIZED SPATIALLY SHIELDED CATECHOLS, O-QUINONES AND COMPLEXES OF TRIPHENYLANTIMONY(V) ON THEIR BASIS

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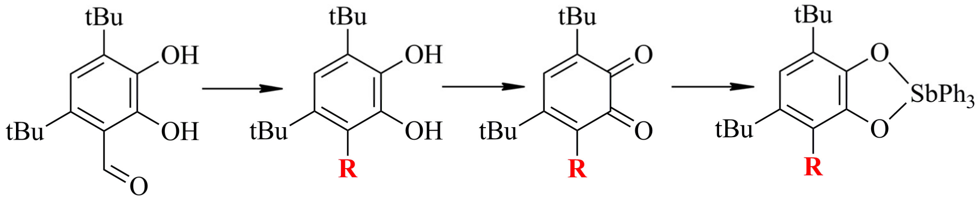
For "green" oxidation, an environmentally safe oxidation system should include molecular oxygen and a non-toxic renewable catalyst that activates molecular oxygen or a carrier of molecular oxygen acting under mild conditions. One of the promising options for solving this problem is the modeling of the biological oxygen carrier. In G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, it was found that triphenylantimony(M) catecholates are able to bind reversibly molecular oxygen under mild conditions [1,2] and do not exhibit pronounced toxicity [3,4].

New functionalized sterically hindered catechols/o-benzoquinones containing various electron-acceptor (p-fluorophenyliminomethyl, p-chlorophenyliminomethyl, p-bromophenyliminomethyl, p-iodophenyliminomethyl) and electron-donor (methoxymethyl, ethoxymethyl, isopropoxymethyl, tert-butoxymethyl) groups and catecholate complexes of triphenylantimony(V) on their basis were synthesized.



The compounds obtained are characterized by means of IR, ^{1}H, ^{13}C NMR spectroscopy, mass spectrometry, elemental analysis. For a number of compounds, the molecular structure in the crystalline state was established by single-crystal X-ray analysis.

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ATR-FTIR SPECTROSCOPY AND QUANTUM CHEMICAL MODELING IN THE IDENTIFICATION OF STRUCTURAL IZOMERS OF d-METAL CHALETE COMPLEXES

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The synthesis and identification of chelate amino acid complexes of d-metals is one of the priority areas of coordination chemistry. It is known that these compounds widely used in industry and pharmaceuticals. Known also that complexes of biogenic metals can play an important role in biological systems and their pharmacological action in the body may depend by the nature of the ligands, as well as on their spatial orientation. Of course, the low-molecular of the amino acid chelates Cu(II) can participate in to *cis-trans*-isomerization in aqueous solutions [1], however, according to other sources, such compounds have some stability in aqueous solutions to normal conditions [2]. Thus, to date, the study of the processes of *cis-trans*-isomerization bis- [3-4] and mix-ligands [5] of amino acid chelates remains an urgent task, the whose solution will allow to establish the mechanism of their pharmacological action and develop on their basis preparations for the regulation of homeostasis in the body.

The structure of bis- and mix-ligand chelate complexes Cu(II), Co(II) и Ni(II) [6] $[M^bL_1{}^bL_2]$ (M=Cu(II), Co(II), Ni(II) ($^bL_1$, $^bL_2$ = gly, *S*-ala, *R,S*-val, (±)-thr, *S*-phe, *R,S*-phe etc.) was studied by the ATR-FTIR spectroscopy and quantum-chemical modeling (M06-L, mPWPW91, OLYP, M06, B3LYP, LC-wPBE, 6-311+G(d) basis set) in the mid region for the characteristic valence vibrations of carboxylate ion.

It is established that the most sensitive to the change in the geometric structure of complexes in the mid region of the IR spectrum are the valence vibrations $\nu_{as,s}$(C=O) (1620-1655 cm^{-1}), $\nu_{as,s}$(CO) + δ(CH) (1360-1398 cm^{-1}). The identification of geometric isomers in the mid-wave region of the IR spectrum was done. It is shown that the experimental IR characteristics of geometric isomers are consistent well with theoretical calculations (method M06-L/6-311+G (d)).

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STRUCTURE OF THE BIS(N,N-DIETHYLDITHIOCARBAMATO)NITROSYL IRON

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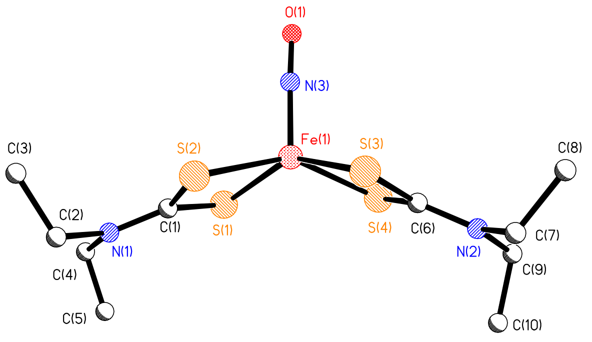
At present, the emphasis in the search for new monomolecular magnets has shifted from obtaining complexes of ferromagnetically bound atoms with a large spin toward the stable single-ion magnets (SIM), in which the magnetic center is the unit atom of the d- or f-element. In the SIM, it is possible to keep higher values of the splitting parameter in the zero field D, which determines the height of the magnetization reversal energy barrier and, accordingly, the practical significance of the magnet. Almost all SIMs known at the moment are unstable in air complexes of magnetic ions with volumetric organic ligands. Thus, the actual problem is the search for stable compounds of d-metals magnetic ions. One such example is bis(N,N-diethyldithiocarbamato)nitrosyl iron, which has unique magnetic and electronic properties.

An X-ray diffraction study of the compound was carried out on single crystals on a “Belok” beamline diffractometer using a Rayonix SX165 detector at λ = 0.96990 Å. According to X-ray structural analysis the complex has formula $[(C_2H_5)_2NCS2]_2FeNO$ and crystallizes in the monoclinic system: space group P2(1)/c, a=15.294(3)Å, b=8.9841(18)Å, c=13.293(3)Å, α=90.0^0, β=67.92(3)^0, γ=90.00^0, V=1692.5(6)Å^3, Z=4. The coordination arrangement around the iron atom is a tetragonal pyramid with the nitrosyl group at the apix (see figure); the symmetry of the molecule approximates to C_{2v}. In the IR spectrum of the complex, one band is observed, responsible for the valence vibrations of the nitrosyl group with a frequency at 1683 cm^{-1}, which is typical for neutral NO with angular geometry [1], i.e. the oxidation number of the iron atom is +1. But the Mössbauer spectrum parameters at 85K (δ_{Fe}=0.363(5) mm/s, ΔE_Q=0.876(2) mm/s) is as for Fe^{3+}. The complex is stable in the solid state under normal conditions, but when heated above 100 °C or dissolving in a number of solvents, NO is released.



[1] M. Fontecave, J.-L. Pierre, *Bull. Soc. Chim. Fr.*, **1994**, *131*, 620-631.

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SYNTHESIS, STRUCTURE AND ANTIPROLIFERATIVE ACTIVITY OF THE ISOMERIC PLATINUM(II) COMPLEXES WITH (2-*TERT*-BUTYLTETRAZOL-5-YL)ACETIC ACID AND ITS ETHYL ESTER

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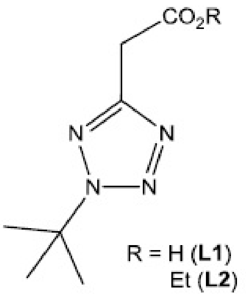
[c] *Institute of Pharmaceutical and Medicinal Chemistry, TU Braunschweig, Braunschweig, GERMANY*

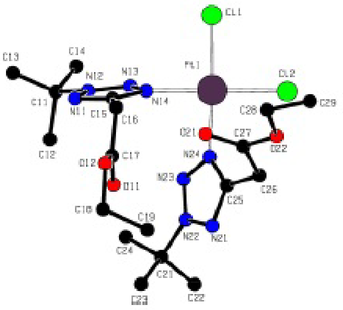
Bearing both carboxyl and tetrazolyl fragments, tetrazolylacetic acids are often considered as amino acid analogs and useful ligands for the molecular design of metal complexes [1]. Owing to the combination of high lipophilicity and good water solubility, alkylated tetrazolylacetic acids were chosen as potent ligands for the elaboration of new platinum-based antiproliferative agents [2].

Cis and *trans*-isomeric platinum(II) chlorido complexes bearing (2-*tert*-butyltetrazol-5-yl)acetic acid and its ethyl ester were synthesized and thoroughly characterized by means of elemental analyses, ESI(+)-MS, multinuclear NMR (^{1}H, ^{13}C and ^{195}Pt), and IR spectroscopy in the range 4000–50 cm^{-1}. Thermal stability of the compounds was confirmed by DCS/TG studies. Molecular and crystal structures of the complexes were established by single crystal X-ray diffractometry.



Antiproliferative activity

PtL_2Cl_2		IC_{50}, μM HT-29 (colon cancer)	IC_{50}, μM MDA-MB-231 (breast cancer)
L1	*cis*	> 100	> 100
	trans	> 100	> 100
L2	*cis*	4.7 ± 0.7	4.3 ± 0.5
	trans	11.4 ± 0.7	11.0 ± 0.9
Cisplatin		7.5 ± 0.4	7.7 ± 0.4



cis-[Pt(L2)$_2$Cl$_2$]

Antiproliferative activity of the title compounds was evaluated in two cancer cell lines using crystal violet assay and compared to cisplatin as positive control. Both isomeric complexes bearing (2-*tert*-butyltetrazol-5-yl)acetic acid turned out to be inactive with IC_{50} values exceeding 100 μM. The ethylated derivatives demonstrated noticeable antiproliferative effects in both cell lines, *cis* isomer with IC_{50} values of approx. 4 μM being more active than its *trans* congener and cisplatin.

[1] E.A. Popova and R.E. Trifonov, *Russ. Chem. Rev.*, **2015**, *84*, 891-916.
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BINUCLEAR COPPER(II) COMPLEX BAZED ON *O*-VANILLIN S-METHYLISOTHIOSEMICARBAZONE

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[b]*Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, MOLDOVA*

For some time, semi- and thiosemicarbazones have been a subject of interest to researchers of different profiles. In view of the fact that these compounds form with many metals complexes of diverse chemical, physical and structural characteristics, they are of special interest to coordination chemists. In addition, many of these compounds have shown a wide spectrum of biological activity, so that they have also become a subject of intense research for pharmacologists.

New binuclear copper(II) complex $[CuL]_2$ has been obtained by interaction of *o*-vanillin S-methylisotiosemicarbazone with salicylic aldehyde and copper acetate (in 1:1:1 molar ratio) in methanol. Compound is soluble in chloroform, dimethylformamide, less soluble in ethanol and methanol and insoluble in water. It has been characterized by IR spectroscopy and X-ray diffraction method.

In the IR spectrum of complex the bands in 3300-3400 cm^{-1} region assigned to NH_2 functional group and in 3113 cm^{-1} band assigned to the oscillations of the OH group are not observed. The intense absorptions recorded in the 1163-1240 and 1024-1139 cm^{-1} domains were attributed to the C_{AR}-O stretching oscillations of the coordinated deprotonated hydroxyl group. Intensive absorption bands in the range of 1496-1526 cm^{-1} are attributed to azomethine groups (-HC = N-). At 1586-1601 cm^{-1} the valence oscillations of the C=N and C=C double bonds of the coordinated fragment are recorded. All these confirm the condensation of the Schiff base with salicylic aldehyde to form the $[CuL]_2$ coordination compound.

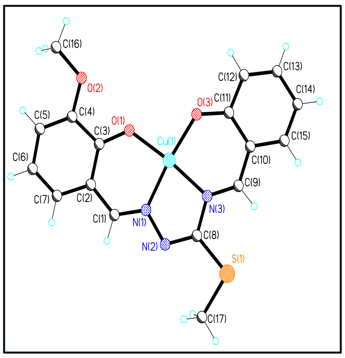

Fig. 1 Molecular structure of CuL

Compound $[CuL]_2$ crystallizes in the monoclinic space group $P2_1/n$. The structural data confirms that bideprotonated L^{2-} ligand coordinates to the metal ion through O_2N_2 set of donor atoms, forming one five membered CuN_3C and two six membered $CuOC_3N$ metallocycles, with the sequence 6, 5, 6 (Fig. 1 and 2). Cu(II) centers are four-coordinated by means of two nitrogen and two oxygen atoms with the distances: 1.903(3) Ǻ (Cu-O1), 1.899(3) Ǻ (Cu-O3), 1.920(3) Ǻ (Cu-N1) and 1.942(3) Ǻ (Cu-N3). Coordination geometry of this compound is square pyramidal with O(1)O(3)N(1)N(3) donors at the base, and O(3) atom of the neighboring complex in the vertex, with Cu(1) – O(3)* bond length of 2.807 Ǻ. As a result, in the crystal, the CuL complexes form centrosymmetric dimers, that are further joined through week C–H...O hydrogen bonds.

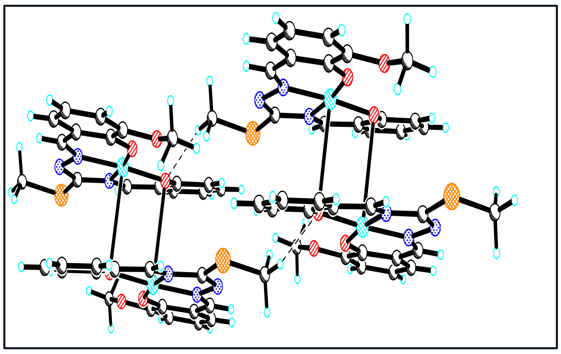

Fig. 2. Fragment of the crystal packing of $[CuL]_2$

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СТРУКТУРА И СВОЙСТВА КОМПЛЕКСОВ МАРГАНЦА, ЖЕЛЕЗА, МЕДИ И КОБАЛЬТА С ПРОИЗВОДНЫМИ ДИГИДРАЗИДОВ МАЛОНОВОЙ КИСЛОТЫ

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Комплексы металлов дигидразидов дикарбоновых кислот и их производных представляют интерес с точки зрения их потенциального применения в биоорганической химии, магнетохимии, химии материалов и др.[1,2]. Известно, что производные гидразидов и дигидразидов склонны к образованию полиядерных структур с ионами переходных металлов [3,4]. В частности, бис(салицилоил)этандигидразид образует девяти и шестиядерные комплексы с ионами Cu(II) и Co(II), соответственно.

Нами исследовано комплексообразование дигидразида бис(салицилиден) малоновой кислоты с ионами Mn(II), Fe(II), Co(II), Ni(II) и Cu(II) и изучена их структура. Согласно рентгеноструктурным данным Mn(II) образуют с бис(3,5-дитретбутилсалицилиден) дигидразид малоновой кислоты биядерный комплекс.

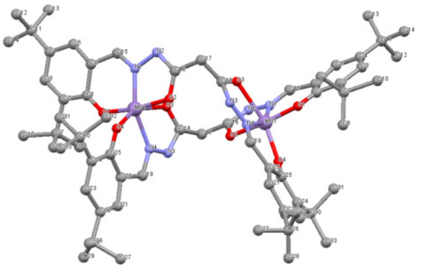

Рис.1. Структура комплекса Mn(II) с бис(3,5-дитретбутилсалицилиден)малондигидразидом.

Октаэдрическое окружение каждого иона Mn(II), осуществляется двумя атомами кислорода двух дипольных групп, двумя атомами азота салицилиден гидразоновых групп и двумя атомами кислорода малоновых гидразидных групп. Измеренный магнитный момент соответствует двухвалентному иону Mn(II) с $\mu_{эфф}$=5.4 м.Б

Согласно данным ИК и электронной абсорбционной спектроскопии комплексы других металлов имеют подобную структуру.

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4th Conference-School for Young Researchers “Physicochemical Methods in Coordination Chemistry”
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THE DESIGN OF MACROCYCLIC METALLIC COMPLEXES FROM A SCHIFF BASE

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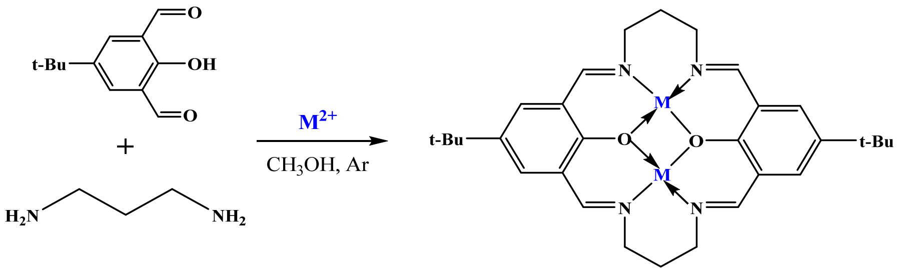
Macrocyclic metal complexes of the transition metals have been attracted extensive attention because of their potential application in magnetic materials as well as their widespread application in homogeneous and heterogeneous catalysis and as catalysts in the various industrial processes.

In this abstract we report the methods of the synthesis of macrocyclic dinuclear metal (II) coplexes and coupled dimeric dodecanuclear metal (II) complexes.

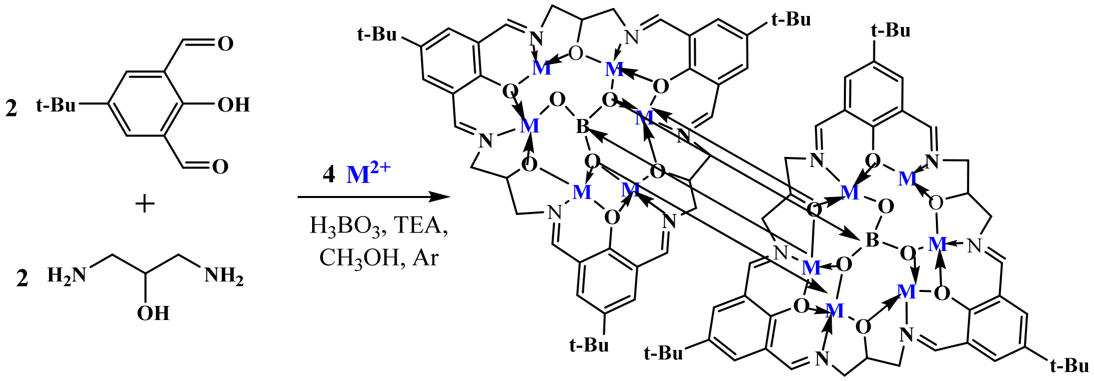
The dinuclear complexes of transition metal (Fe, Ni and Cu) were prepared from a Schiff base condensation reaction [1]. 2,6-diformyl-4-(t-Bu)-phenol and 1,3-diaminopropane in the presence of the corresponding transition metal salt, namely [$Fe(ClO_4)_2.6H_2O$], [$CoCl_2.6H_2O$], [$NiCl_2.6H_2O$], [$Cu(ClO_4)_2.6H_2O$] were reacted with fairly high yields (Scheme 1).

Scheme 1.



The dimeric dodecanuclear metal complexes were derived by reaction between 2,6-diformyl-4-(t-Bu)-phenol and 1,3-diamino-2-hydroxypropane in the presence of the same transition metal salt, boric acid and triethylamine (TEA) (Scheme 2) [2].

Scheme 2.



These reactions were carried out in dry methanol and under argon atmosphere. The structure of all complexes was confirmed and characterized by spectroscopic methods of analysis (^{1}HNMR-, IR- and UV-vis spectroscopy). Catalytic activity these complexes are being studied in the homogeneous and heterogeneous Fischer–Tropsch process.

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PHOTOELECTRON SPECTRA AND ELECTRONIC STRUCTURE OF NITROGEN ANALOGUES OF BORON β-DIKETONATES

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Boron chelate complexes possess important physico-chemical properties. In particular, boron formazanates ($X_2B(N(R_1)$-N-C-N-$N(R_2))$) that are relatively easily synthesized and can be used to produce new phosphors in a broad spectral range. Establishing correlations between spectral characteristics of boron complexes and their electron structure paves the way to targeted synthesis of new luminophores. The most confident information regarding electron structure of chelates one can obtain using simultaneously UV photoelectron spectroscopy and quantum chemistry. As we have shown in [1], the DFT calculations allow to estimate the ionization energy within an accuracy of 0.1 eV for boron complexes with aromatic substituents.

UV photoelectron spectra of vapors of the three boron complexes [2] were obtained on a modified electronic spectrometer ES-3201 with a monochromatic light source He I (hν=21.2 eV). The spectral energy resolution is 0.08 eV, and it was determined by the width at half-maximum of the xenon peak. The temperature of the ionization cell was dependent on the temperature of vapor sublimation of a particular sample and was in the range from 180 to 240°C. DFT computations were performed using Firefly 8.1. G quantum chemical software package using TZVP basis set and the hybrid exchange-correlation functional B3LYP.

In order to determine effects of heteroatom substitution in the chelate ligand, a comparative analysis was carried out for the electronic structure of three model compounds. In a range of model compounds, the HOMO's nature was revealed to be the same. The HOMO-1 orbital of nitrogen containing compounds is determined by the presence of lone electron pairs of nitrogen. In a range of the complexes under study, the influence of aromatic substituents on the electronic structure was defined. In the imidoylamidinate complex, in contrast to formazanates and β-diketonates, it was found the absence of any noticeable mixing of π-orbitals of the chelate and benzene rings. It was shown that within energy range to 11 eV, the calculated results reproduce well the energy differencies between the ionized states of complexes.

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Acknowledgements
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THE INVESTIGATION OF THE KINETICS OF THE INTERACTION BETWEEN THE CALCIUM IONS AND BIOGENIC AMINO ACIDS

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The investigation of the nature of the interaction of calcium ions and amino acids (AA) is one of the most important tasks. It is due to the formation of the pathogenic organomineral aggregates (POA) in the human body under the influence of the factors which are breaching the physiological existence in norm [1,2]. At the same time, nowadays there's no complex theory which can explain the kinetics of the interaction of inorganic and organic substituents of POA in the human body.

According to this, the aim of this work was the development of the method of estimation of lability of forming complexes between Ca^{2+} and AA, which are involved in the metabolism.

The object of the research were several AA (isoleucine - Ile, aspartic acid - Asp, arginine - Arg, alanine - Ala, glycine - Gly). From the solutions of the given amino acids (C_{amino} acid = 10^{-2} mole per litre) and $Ca(NO_3)_2$ ($C_{Ca(NO_3)2}$ = 10^{-3}моль/л), were selected an aliquots with V=10,0 ml and carried out in the volumetric flask with V=100 ml. Then, from mix were selected 20 ml of process solution, it was acidified to pH = 3 and was titrated by the freshly prepared solution of 0,10M NaOH with the determination of e.m.f. The obtained curves were introduced according to the Gran method (example - fig. 1):

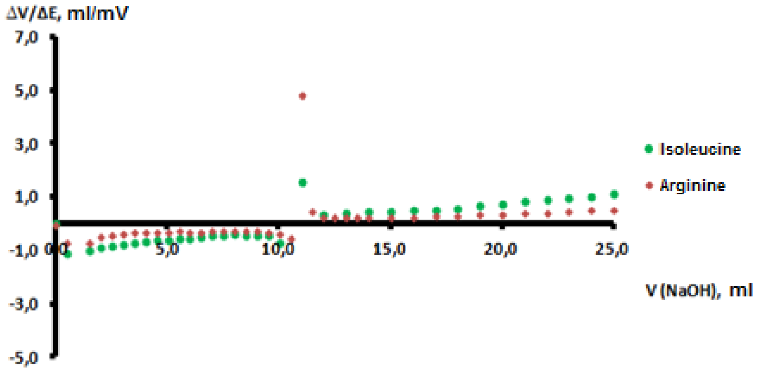

Fig. 1. The curves of potentiometric titration with the Gran method of the mixes of $C_{Ca(NO_3)2} = 10^{-3}$ mole per litre and the amino acid ($C_{amino\ acid} = 10^{-2}$ mole per litre).

For the determination of the lability of all complexes, we suggest semi-quantitative criteria δ:

$$\delta = \frac{\Delta V}{\Delta E}\text{p. after eq. p.} - \frac{\Delta V}{\Delta E}\text{p. before eq. p.}$$

After the calculation, according to their lability, complexes of Ca^{2+} with the given amino acids are standing in the following order: δ (Ca^{2+} - Asp) < δ (Ca^{2+} - Ile) < δ (Ca^{2+} - Ala) <δ (Ca^{2+} - Arg) < δ (Ca^{2+} - Gly), so, the most labile complex is with aspartic acid, the most stable - with isoleucine. Lability of the other complexes could be determined at the same way.

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PROCESSES OF COMPLEX FORMATION OF ZINC WITH TRETTOFAN IN WATER AND PHYSIOLOGICAL SOLUTIONS

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Investigation of the processes of complexation of metals with various natural amino acids containing O, N-donor groups is one of the most promising and priority areas of bioorganic, coordination, physical and inorganic chemistry. Important are the coordination compounds of zinc with tryptophan, which are part of complex biocomplexes of living systems. They have unusual, unique properties, and therefore have great practical and theoretical importance.

The purpose of this study was to study the complexing properties of biologically active tryptophan with zinc in the temperature range 20-60°C, metal: ligand ratio 1: 1 in aqueous and physiological solutions by pH-metric titration. This method is widely used to determine the equilibrium of the system during the interaction of metal ions with amino acids. At the same time, according to the obtained experimental data, the Bjerrum formation function is calculated, which is the average number of ligands associated with the central ion of the complexing metal. To determine it from the experimental data, the equilibrium concentration of the ligand is calculated. It is known that tryptophan, like all amino acids, is in solution in three ionic forms: protonated (H_2L^+), zwitterionic ($HL^\pm$) and anionic (L^-). The protolytic properties of tryptophan have been previously studied by us also by the method of pH-metric titration under conditions identical to the formation of coordination compounds. Experimental data on the complexation of zinc with tryptophan showed that the process proceeds up to a pH of about 9. The formation of complexes proceeds stepwise, coordination compounds are formed with the protonated ligand, anion and mixed ligand hydroxoform: $\mathbf{[Zn(HL^\pm)(H_2O)_3]^{2+}}$; $\mathbf{[Zn(HL^\pm)_2(H_2O)_2]^{2+}}$; $\mathbf{[Zn(HL^\pm)(OH^-)(H_2O)_2]^{+}}$; $\mathbf{[Zn(L^-)(H_2O)_3]^{+}}$; $\mathbf{[Zn(L^-)_2(H_2O)_2]^{0}}$; $\mathbf{[Zn(L^-)(OH^-)(H_2O)_2]^{0}}$.

At pH = 7.5, there is a slight decrease in the titration curve, where a mixed ligand hydroxo complex of zinc appears to be formed. The formation constants of the forming coordination compounds are determined by the iteration method using the computer program "Excel" to the maximum approximation of the experimental and theoretical functions of Bjerrum formation. The expression for the theoretical function of formation is derived taking into account the composition of the complex forms formed above, and their formation constants. It has been established that as the ligand concentration increases, the formation constants of all complex forms of zinc and tryptophan increase. Equations are derived for calculating the degrees of accumulation (mole fractions) of complex forms that are used to construct their distribution diagrams and to identify areas of dominance of coordination compounds. The chemical models of the equilibria existing in the system studied are compiled.It is shown that sodium chloride has no effect on the composition of the resulting coordination compounds, and the formation constants of complex forms of zinc with tryptophan depend on the ratio of components, temperature and pH of the medium. The values of the formation constants of the complexes in the physiological solution are less affected by the temperature and the ratio of the components than the same parameters in the aqueous solution. The obtained information on the composition, the constants of the formation of coordination compounds of zinc with tryptophan supplement the existing gap in the reference literature, the system can serve as a chemical model for studying the equilibrium of complexation of zinc with other natural amino acids.

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SYNTHESIS, CRYSTAL STRUCTURE AND CHARACTERIZATION OF FLUORINATED β-DIKETONATE COMPLEXES OF Ca, Sr, Ba WITH CROWN-ETHERS

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The fluorinated β-diketonate complexes of alkaline earth metals with closed and open polyethers find extensive applications in Chemical Vapor Deposition and Atomic Layer Deposition of several binary and complex oxide films [1].

Here we report the synthesis and characterization of new fluorinated monomeric complexes [M(fod)$_2$(crown)] {M=Ca, crown=15-crown-5 (**1**); M=Sr, crown=18-crown-6 (**2**); M=Ba, crown=18-crown-6 (**3**); Hfod= 1,1,1,2,2,3,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione}. For the synthesis of **1-3** we have used the convenient and easy one-pot synthetic procedure, which included the following stages: (i) refluxing of metal and crown-ether in absolute ethanol; (ii) the addition of Hfod to reaction mixture. The formation of **1-3** was confirmed by their IR-, by ^{1}H, ^{19}F, ^{13}C NMR spectroscopy, elemental analyses and single crystal X-ray structure determinations. The complexes **1-3** are air stable and quite soluble in aromatic hydrocarbons and in coordinating solvents. The X-ray diffraction study showed that the complexes **1-3** are monomeric. In the structure of **1** calcium atom is outside the 15-crown-5 cavity and coordinated by five atoms of 15-crown-5 and four O atoms of two chelating fod ligands arranged in *cis* position. In contrast, in the structures of complexes **2, 3** the M^{2+} ion resides in the center position of 18-crown-6 cavity and is coordinated by 10 oxygens, including four from the two fod ligands arranged in *trans* position. The X-ray crystallograhic data have been deposited on the Cambridge Crystallographic Data Centre, CCDC reference number for **1, 2, 3** are 1558539, 1558540, 1558538, respectively.

The complexes **1-3** are volatile and thermal stable in temperature range 70-230 ^{0}C. The DSC data showed that the melting points are 110 ^{0}C, 184 ^{0}C, 170 ^{0}C for **1**, **2**, **3**, respectively.

The Knudsen effusion method was use to measure the saturated vapor pressure of complexes **1-3** and as function of temperature in the range of T = 340-428 K. Based on results of Knudsen effusion experiments saturated vapor pressure (p, Torr) at each temperature (T, K) were calculated using the Hertz-Knudsen equation. The p-T dependencies are presented by eq. (1)-(3) for complexes **1-3**, respectively

$$\ln p\ (\mathrm{Torr}) = (16.4\pm0.5) - (5580\pm120)/T \qquad (1)$$

$$\ln p\ (\mathrm{Torr}) = (13.7\pm0.2) - (5320\pm132)/T \qquad (2)$$

$$\ln p\ (\mathrm{Torr}) = (8.5\pm0.4) - (4142\pm130)/T \qquad (3)$$

The values of sublimation enthalpy ΔH_S = 52.46±1.8 kJ·mol^{-1} for **1** and ΔH_S = 101.4±1.7 kJ·mol^{-1} for **2** and ΔH_S =79.2±2.3 kJ·mol^{-1} for **3** were calculated from the Clausius-Clayperon equation using the least-squares procedure.

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HIGHLY STABLE GOLD(I) COMPLEXES WITH SULFUR-CONTAINING LIGANDS IN SOLUTION

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Highly stable gold(I) complexes with sulfur-containing ligands find a variety of applications, ranging from medicine (treatment of autoimmune diseases, antitumor therapy) and components of gilding electrolytes to the stability regulators of nanodispersed systems. Nevertheless, there is very little data on the forms in the solution and on their stability (both redox and substitution of ligands). The problem consists in very high stability of these complexes and in the absence of a reliable method of investigation. Gold(I) complexes often do not have an informative spectrum, and the potentials of gold electrodes are usually poorly reproducible.

For the solution of some problems, the sulphite complex $Au(SO_3)_2^{3-}$ is suitable as the initial gold(I) complex. From the one hand, it is highly stable, and from the other hand it is fairly well studied. However, the sulphite complex is unstable to self-reduction in the acidic medium and its use required additional studies. In this work it was found that at pH > 2, $C_{Au} < 5\ 10^{-3}$ M and $C_{Cl} > 0.2$ M the complex is stable for more than an hour and no traces of metallic gold are observed.

A study was performed for the systems of thiosulfate, methioninate, cysteinate and thiomalate gold(I) complexes. The study was carried out using the pH-metry, spectrophotometry and capillary electrophoresis (Agilent ^{3D}CE 1600A). Stability constants and characteristics of species, including of mixed complexes, were determined. The most stable are the cysteinate and thiomalate complexes. It was shown that for them a large role is played by multiple protonation processes of the complexes themselves that usually is not considered. The protonation constants for the complexes are higher than for the corresponding functional groups of ligands. We associate this with the higher negative charge of the complex compared with the charge of the ligand. The results obtained make it possible to explain a number of unusual properties of these systems. For example, the slow rate of the transformations in the system of thiomalate gold(I) complexes can be explained by their polymeric structure.

Methionine complexes have the lowest stability due to the special arrangement of the sulfur atom in the methionine molecule, which does not participate in the coordination. In the case of thiosulfate complexes, a great role is played by mixed forms, in particular, sulfite-thiosulfate complexes. The oxidation-reduction stability of the complexes studied is different. The highest redox stability is observed for thiosulphate and thiomalate complexes.

The obtained results can be used to explain the behavior of complex forms of gold(I) under physiological conditions, and also to optimize some technological processes.

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THE STRUCTURE OF COPPER(II) COMPLEX COMPOUND WITH L-HISTIDINE AND COMENIC ACID

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The investigation of d-elements complex formation with bioactive ligands such as comenic acid and aminoacids is of practical interest in biochemistry. Comenic (5-hydroxy- γ-pyron-2-carboxylic) acid reveals considerable antiradiation and antioxidant activity. But d- and f-elements complex compounds are taken to be more biologically active, than acid, as well as complex compounds of natural amino acids. Biological activity of complex compounds depends on molecular structure. The quantum-chemical calculations of spatial and electronic structure of L-histidine and its ionized species with copper(II) were carried out using DFT method on basis of B32YP functional and 311G(d) basis. The presence of solvent (water) was account within the PEM framework. The equilibrium in the copper(II) - L-histidine system in aqueous solution was investigated by EPR spectroscopy at pH 2-11.The theoretical calculation parameter association and EPR spectrum data suggests following geometric coordinates of copper(II) ion in complex compounds: CuHL1- planar squared, CuL_2, CuHL2’ и Cu2L’ – distorted square pyramid, CuL_2’ - octahedral site.

Zn(II) coordinate to comenic acid with the formation of bisnuclear complex composed of two Zn(II)ions coordinated to carboxyl of two anions of comenic asid, which are associate to dimmer by hydroxyl and keto groups, according to IR, NMR and thermogravimetric data.

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ELECTROCHEMICAL SYNTHESIS OF LANTHANIDES COORDINATION COMPOUNDS WITH CARBOXYLIC ACIDS

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In previous research we indicated that anodic dissolution of *d*-metals in solutions of various organic substances in some cases is accompanied by the formation of coordination compounds [1]. The anode synthesis is a promising method for obtaining anhydrous high-purity coordination compounds as distinct from classic chemical synthesis. The anode synthesis method succeeds in obtaining of thermal stable coordination compounds of 4*f* elements (lanthanides) appearing effective phosphors properties [2]. We carried out the electrochemical synthesis of anhydrous lanthanides complexes with different aromatic and heterocyclic acids such as alkylhydroxybenzoic, benzoylbenzoic, acetylbenzoic, pyridinecarboxylic etc. Terbium and gadolinium were used as zero-valent metals.

Electrochemical synthesis method was described in [1]. Dry acetonitrile was used as nonaqueous solvent at electrochemical synthesis conditions. Ligand concentrations were 0,001 - 0,015 M in depending on their solubility. The time of the synthesis was determined in terms of initial ligand concentration according to the Faraday law, which was in the range of 2-3,5 hours. The processes were carried out in inert atmosphere and in hermetic chamber. In the synthesis of terbium(III) coordination compounds with applied ligands, the optimal current density was 0.008–0.013 A/cm2. To achieve the optimal current density, a voltage of 4–9 V was applied to the electrochemical cell. At lower operating current densities, the rate of the synthesis decreased significantly, whereas higher current densities would result in overheating of the solution. That could lead to side reactions resulting in the target product decomposition or significant contamination (for example, severe erosion of the anode was possible). For that reason, the synthesis was carried out at room temperature. To reach high electrical conductivity of the solution, a background electrolyte ($LiClO_4$) was added at a ratio of 1/10 of the ligand, which was inert in chosen conditions. It should be noted, that adhesion by formed at the anode poorly soluble complexes led to anode passivation. As a result, the total electrical conductivity and current density decreased almost to zero, and the synthesis was significantly decelerated. To prevent such trouble the electrochemical cell was exposed to the ultrasonic treatment during the synthesis? which considerably decreased the anode passivation and stabilized the synthesis rate.

Coordination compounds of the composition LnL_3 or Ln_2L_3 were identified by IR spectroscopy and thermogravimetry. Luminescence properties of synthesized compounds are investigated.

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ASSOCIATION OF IONIC LIQUIDS IN POLAR SOLVENTS

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Ionic liquids (ILs) with low volatilities and high thermal stability have represented a rich field of research because of their many applications in diverse technological areas, but a major problem of practical use of ILs is a lack of understanding of their nature in liquid state and in solutions. The difference between ionic liquids dissolved in polar solvents and inorganic salts, dissolved in this solvents, has now become of particular interest. As for all electrolyte solutions, chemical speciation has major effects on the properties and behavior of ionic liquids. Chemical speciation is especially important for ionic liquids because of the concentration of charged particles and the interactions between them. A full range of concentrations of solution of ionic liquids, which can vary from infinite dilution to neat, should give the insight as to whether the species exist as solvent separated ions, ion pairs or clusters. One of the defining properties of ILs is that they are ionic, and therefore they conduct electricity. Very few serious studies of the conductivity of pure ionic liquids and its solutions have been carried out as a function of composition, concentration and temperature.

In this paper, the conductimetric method is used to determine the thermodynamic characteristics of ionic association of ILs in acetonitrile (AN) and dimethylsulfoxide (DMSO). Specific electrical conductivity (EC) of the diluted solutions of ILs have been measured in the 20 – 65 °C temperature range. By EC data and the Lee-Wheaton equation, the thermodynamic parameters of association of the investigated ILs have been calculated. It was established that with temperature increase, the association constant of the investigated ILs also increases, and the association constants of ionic liquids in DMSO are about 8-10 times higher than in AN. Based on the temperature dependence of the association constants, the enthalpy ΔH° and entropy ΔS° of the association are determined. The enthalpy and entropy of the ILs association in AH and DMSO are positive. The positive ΔS° indicates, that during the association an increase in the disorder in the system occurs, which can be explained by the escape of solvent molecules from the ion solvate shells upon their association. It should be noted that the ΔS° association in the AN is almost three times the ΔS° in DMSO. This is apparently due to the fact that desolvation during association in AN occurs to a greater extent than in DMSO. In dilute solutions ILs are a weakly associated electrolyte in AN and DMSO.

The values of the conductivity of solutions in two solvents are compared. It is important to note that the molar EC an infinite dilution λ_0 of solutions of ILs in AN is significantly higher than in DMSO. At the same time, the difference in the λ_0 values decreases with increasing temperature (at 20 °C, λ_0 in AN is almost 5 times higher than in DMSO, and at 65 °C it is only 3.5). As a result of the investigations carried out, it was established that the relative temperature coefficient β_κ and the activation energy E_κ of the conductivity of the diluted solutions under study do not depend on their concentration. Values of β_κ and E_κ does not depend on the temperature in AN and decreases with its growth in DMSO.

The abnormally high electrical conductivity of the ILs in acetonitrile is explained by the significant magnitude of the limiting high-frequency (HF) electrical conductivity (the ratio of the absolute dielectric constant to the of dipole relaxation time) of this polar solvent. It is shown that as the temperature increases, the specific EC of solutions of the ILs in AN and DMSO increases directly in proportion to the limiting HF EC of the solvent.

REDOX-ACTIVE METAL COMPLEXES WITH 2,2′-DIPICOLOLAMINE CONTAINING FERROCENYL MOIETY: SYNTHESIS, ELECTROCHEMICAL BEHAVIOR AND BIOLOGICAL ACTIVITY

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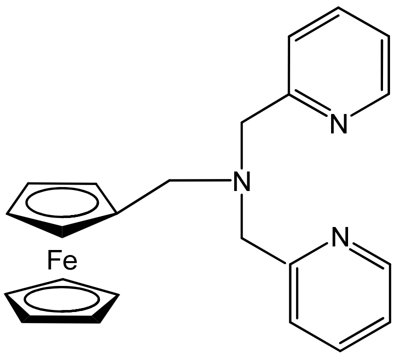
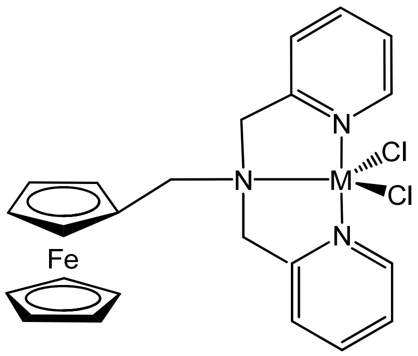
The combining in one molecule a redox active metal center and cytoprotective functional organic moiety with antioxidative function is a promising way to rational metallodrug design in modern medicinal chemistry [1]. The novel metal complexes of general formula $MCl_2 \cdot$**L** (M = Cu, Fe, Co, Mn, Zn) based on the di-(2-picolyl)amine ligand **L** with the redox-active ferrocenyl fragment were synthesized and characterized by elemental analysis, IR, ^{1}H, ^{13}C NMR, UV-vis spectroscopy and MALDI-TOF mass spectrometry [2].



1
L



2-6
$M^{II}Cl_2$ L
M= Cu (**2**); Fe (**3**); Co (**4**); Mn (**5**); Zn (**6**)

The redox properties of complexes were studied using cyclic voltammetry (CV) method and feasible schemes of electrochemical transformations were proposed. The antioxidant activity of compounds was tested by various methods (DPPH-test, CUPRAC, H_2O_2 decomposition, superoxide radical anion and OH· scavenging activity, inhibition of ilnoleic acid peroxidation). The lipoxygenase (LOX) inhibition activity of the studied compounds was evaluated. The *in vitro* biological experiments were performed using rat brain homogenates. The results demonstrate that ditopic compounds containing ferrocene and redox active dipicolylamine fragments act as polyfunctional antioxidants.

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A THERMAL DECOMPOSITION OF SOLID L,D-METHIONINE AND ITS COMPLEX WITH $HgCl_2$ IN EVACUATED SISTEM

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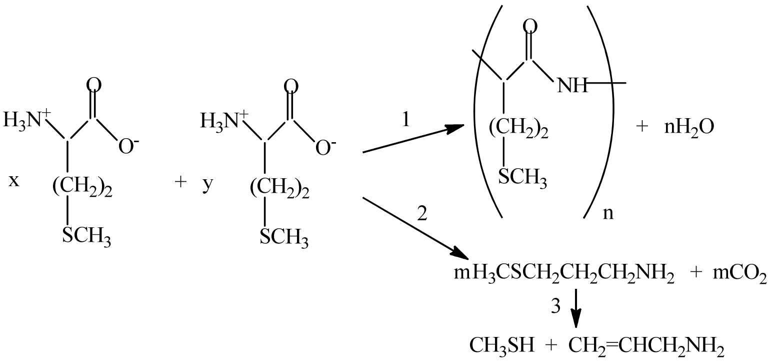
Sulfur compounds play an important role in the life of the human body [2]. Being in the body in the form of thiols (RSH), sulfur binds heavy metals that accumulate in the food chain. L-Methionine (L-Met) by methylation and transsulfuration detoxifies toxic substances, which are then excreted from the body. In this paper, we present a mechanism for the thermal decomposition of L, D-methionine (L, D-Met) and its complex with $HgCl_2$ in a vacuum.

At a small depth of thermal decomposition of crystalline L, D-Met (30-50%), the speed of the gross process obeys the effective reaction order is fist. Within the temperature range of 210-240°C, the effective activation energy of this reaction 193 kJ/mol, $\ln k_0 = 43$ [3]. It is known that the activation energy of decomposition of methionine in the presence of oxygen of air is 230,4 kJ/mol [1]. In the gas phase, in a mass spectrometric method, CO_2, methylthiol CH_3SH, as well as traces of H_2S and $(CH_3)_2S_2$; On the residual pressure at room temperature it is determined that 50% of the gas phase is water - the product of polycondensation. Chromato-mass spectrometric method in the condensed phase revealed: 3-methylthio-1-propylamine, methylthiol and 1-aminopropene-2. The probable thermal transformation scheme of D, L-Met can be represented by the following parallel and sequential reactions.



A thermal decomposition of L, D-Met·$HgCl_2$ complex is observed above 160-190°C. The decomposition mechanism includes parallel and consecntive radical reactions in a multiphase system. The maximum limit pressure of gaseous products in the system is 1.5 times lower than in the decomposition of methionine. Metal mercury, carbon oxides (II), (IY) and hydrogen sulphide catalyze the process. The rate of decomposition increases almost 3. In the volatile products of the decomposition of L, D-MetHHgCl$_2$ by mass spectrometric analysis, CO_2, CH_3SH, $(CH_3)_2S_2$ and CH_3Cl were detected as the main products. Complex L, D-Met with $HgCl_2$ was prepared by mixing aqueous solutions of methionine and mercuric chloride in molar ratios of 1: 1. The precipitated crystals were filtered, washed and dried in a desiccator. The decomposition of crystalline substances: L,D-Met, $HgCl_2$ and complex L, D-Met · $HgCl_2$ was carried out in a vacuumed static system in glass vials of constant volume, with glass membranes.

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APPLICATION OF TETRA-(4-TERTBUTYL)PHTHALOCYANINE AND ITS NICKEL COMPLEX AS MODIFYING AGENT OF THE SURFACE OF DACRON MATERIALS

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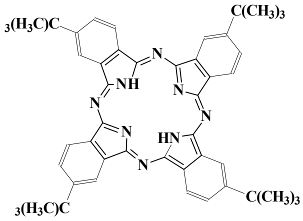
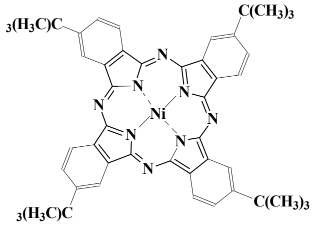
Application of phthalocyanines and their metal complexes is considerably extended by immobilizing them on the polymer matrix. This makes it possible to change the structure of the polymer-carrier surface in the needed direction to impart the desired properties.

The aim of this work was to study modifications of the non-woven Dacron materials of tetra-(4-tertbutyl)phthalocyanine ($H_2Pc(t\text{-}Bu)_4$) and tetra-(4-tertbutyl)phthalocyaninato nickel ($Ni[Pc(t\text{-}Bu)_4]$).



We used non-woven Dacron material surface activated by thermal hydrolysis. This method allows to modify the chemical structure of surface while retaining the strength characteristics of the polymer matrix. The formed functional groups are anchor groups with further immobilization of macrocycles.



The method of electronic absorption spectroscopy in an environment *o*-xylene was used to determine the conditions and quantity of immobilized macrocycles. In this light scattering of nonwoven material decreases dramatically, which allows to register the electronic absorption spectra of sorbed phthalocyanine. Fixing $H_2Pc(t\text{-}Bu)_4$ on the polymeric substrate is carried out through the formation between them the hydrogen bonds, electrostatic and dispersion interactions, $Ni[Pc(t\text{-}Bu)_4]$ additionally binds through coordination interaction of central cation of nickel with the functional containing oxygen groups on polymer surface.

The surface concentration of macrocycles on the polymer-carrier was determined and its dependence on the conditions of immobilization: temperature, time and concentration of the macrocycle was established.

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SILVER COMPLEXES WITH 2-METHYLQUINOLINE

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Special attention paid to the compounds of quinoline (Quin) derivatives with metal ions is caused by a wide range of its application (electroluminescence, photoluminescence, in parti cular, materials for OLEDs). We obtained three novel methylquinoline complexes $[AgL_2(NO_3)]$ (**I**), $[AgL_2(CH_3SO_3)]\cdot H_2O$ (**II**) (L = 2-MeQuin), $[CdI_2(4\text{-}MeQuin)_2]$ (**III**), determined their crystal structures and examined ^{1}H and ^{13}C{H} NMR spectra in deuterated acetonitrile. Emission spectra compounds I and II have been studied. The obtained NMR data agree with the above described compositions of complexes I-III in a solution. The ^{1}H and ^{13}C{H} NMR spectra of solutions of I and II in CD_3CN are almost identical, except the appearance, in the latter case, of the signal of the methyl group of the methanesulfonate anion. This can indicate the ionization and solvation of the initial complexes by acetonitrile. Structure **I** consists of discrete neutral $[AgL_2(NO_3)]$ complexes. The Ag+ ion is coordinated to two nitrogen atoms of two crystallographically nonequivalent ligands L with the *trans* orientation of the methyl groups of L The 2-methylquinoline molecules form infinite columns through π–π stacking with a horizontal displacement of the aromatic moieties. Structure of the discrete $[AgL_2(CH_3SO_3)]\cdot H_2O$ complex in **II** is a similar to that in **I**; however, the methyl groups of ligands L are in *cis* position, which is likely due to steric hindrances of the sulfonate anion in **II**; like in **I**, this anion acts as a chelating ligand weakly binding the Ag+ ion. The H_2O molecules are involved in the hydrogen bonds, in which the terminal oxygen atoms of the sulfonate anions are proton acceptors and combine centrosymmetrically arranged Ag+ complexes into supramolecular dimeric moieties. There is π–π-stacking interaction with a horizontal displacement of aromatic moieties between the pairs of parallel planes of molecules L. Complex **III** is mononuclear and tetrahedral. The Cd^{2+} ion is coordinated by the two nitrogen atoms of crystallographically nonequivalent 4-MeQuin ligands and two independent iodine atoms angles at the Cd atom vary within 98.3°–121.8°. The tetrahedron is appreciably distorted, and the angles between the nitrogen atoms of 4-MeQuin ligands have a minimum value of 98.3°, and the angles between the iodine atoms have a maximum value of 121.8°. The luminescence spectrum of solid I is a superposition of several bands in the yelloworange spectral range at 633 and 611 nm and a weaker band at 592 nm. In addition, a weak peak at ~680 nm is observed. For compound II the fluorescence bands corresponds to the peaks centered at ~550, ~600, ~646, and ~665 nm. Comparison of the spectra of an acetonitrile solution of 2-MeQuin and compounds **I** and **II** reveals a bathochromic shift of basic bands in the spectra of the solid phase.

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ON SOME REGULARITIES OF SYNTHESIS AND STRUCTURE OF HETEROPOLYOXOMETALLATES WITH 3d-ELEMENTS

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Heteropolyoxometallates (or heteropolycompounds) with the general formula $Kt_q[X_xM_mO_y] \bullet nH_2O$, M - tungsten, molybdenum, vanadium, niobium, tantalum or a mixture of these elements in the highest oxidation state (configurations d^1, d^0) form a separate class of complex compounds and have characteristic principles of their formation and structure, as well as their physicochemical properties. Areas of application of these compounds include analytical chemistry, biochemistry, catalysis, materials science, medicine, etc. [1, 2]. To date, several hundred heteropolycompounds containing 3d elements (Cr, Mn, Fe, Co, Ni, Cu, Zn) have been synthesized and their number is constantly increasing. The purpose of this work is to systematize the synthesis methods of these compounds, to establish the regularities and basic methodological methods of obtaining heteropolyoxometallates and the relationship between their composition and structure.

The systematization of methods for the synthesis of heteropolycompounds depending on the functions of 3d-elements in the complex (central atoms, ligands entering the internal coordination sphere, or outer-sphere cations) has been carried out. It has been established that the main factors influencing the formation of various structural types of heteropolyanions with 3d elements are: the stoichiometric ratio of the reagents, the pH and temperature of the reaction mixture, the chemical nature of the solvents, the order of addition of the components, the presence of specific catalysts or the specific effect of cations (counterions) and other factors.

The influence of the structural features of heteropolyanions and the electronic configuration of 3d-elements on the formation of priority structural types of heteropolyoxometallates (the Anderson, Keggin, and Dawson structures and structures based on them) is shown. Some regularities of the influence of elements of the polyoxometallate sphere (tungsten, molybdenum, vanadium, niobium) on the stabilization of electronic configurations of 3d-elements in these complexes are established.

The established regularities make it possible to predict the composition and structure of heteropolycompounds with 3d-elements, depending on the synthesis conditions, the nature of the ligands and the central complexing agent.

A promising intensively developing direction for the synthesis of new heteropolycompounds, including those with 3d-elements, is the use of polyoxometallates as building blocks for the production of nanosized molecular complexes and coordination polymers, and the chemical design of polyoxometallate clusters containing organic and organometallic compounds.

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INVESTIGATION OF THE CATALYTIC PROPERTIES OF HETEROPOLITUNGSTATES AND THE PRODUCTS OF THEIR THERMOLYSIS

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Heteropolycompounds and their thermolysis products are part of multicomponent catalysts for processing and hydrotreating hydrocarbon feedstocks, oxidative reactions of organic synthesis, etc. This research presents the results of the study of the catalytic activity of potassium salts of heteropolytungstates (HPT) with the general formulas $K_m[X_2W_{11}O_{39}(H_2O)]$ X-Fe^{3+}, Co^{2+}, Zn^{2+}, $K_5[H_2W_{11}O_{38}Cr(H_2O)_2]$ with the Keggin’s structure of anions and $K_n[XW_6O_{24}H_n]$ X-Ni^{2+}, Mn^{4+} with the Anderson’s structure of anion and the products of their thermolysis (compounds with pyrochlore-type structure $K_{4x}X_xW_{2-x}O_6$) in the reaction of isopropyl alcohol oxidation with air oxygen.

The study of their acid properties allowed us to establish that there are acid centers of medium strength $-3 < Ho < 1.5$ on the surface of the products of thermal decomposition of HPT. The selectivity of the process of oxygen oxidation of air of isopropyl alcohol to the acetone in the presence of products of thermolysis of HPT correlates with the concentration of acid sites on the catalyst surface and increases in the Fe-Zn-Co-Mn row. It is shown that the reaction of oxidation of isopropyl alcohol to the acetone proceeds with the participation of Lewis acidic centers. The maximum conversion occurs at the temperatures of 320-350 °C. The highest selectivity among the products of thermolysis of HPT is observed in potassium tungstenmanganate (IV), - 97% with a conversion degree of 34%. The selectivity increases with increasing degree of conversion, which indicates a high selectivity of the catalyst.

For the initial HPT, as catalysts for the oxidation of isopropyl alcohol with air oxygen, the degree of conversion is 30-70% at 310-325 °C. The most active catalyst, potassium tungstic chromate (70% conversion rate) is the least selective (12-17%), which indicates the predominant course of side processes. Tungstenferrat(III) potassium is the most selective among the studied HPT (88% with a conversion of 24%). It can be assumed that the chromium-substituted tungstenferrate of composition $K_6[FeW_{11}O_{39}Cr(H_2O)]$ will combine high potassium tungstate chromate activity and selectivity of tungstenferrat in the process of oxidation of isopropyl alcohol to the acetone with air oxygen. In general, increasing the degree of alcohol conversion in the presence of initial HPT leads to a decrease in the selectivity of the process. It is shown that when the reaction regime changes (decreasing air supply), the dehydrogenation process becomes predominant. Thus, both the initial HPT and the products of their thermolysis are also catalysts for high-temperature dehydrogenation.

The regularities allow to predict the catalytic activity of similar compounds in the development of new catalysts.

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TIN (IV) COMPLEXES WITH ANTIOXIDATIVE FRAGMENTS AS FARMACOLOGICAL AGENTS

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Tin (IV) complexes are perspective candidates for the creation of specific anticancer drugs. The toxicity of these compounds is related with the binding of Sn atom with proteins SH-groups as well as the promoting of oxidative stress in living organisms.

The hindered 2,6-di-*tert*-butylphenols are widely used antioxidants in industry and medicine as vitamin E mimetics.

The goal of present work was the study activity of new hybrid tin complexes with fragment of 2,6-di-*tret*-butylphenol. A series of new Sn(IV) complexes $RN{=}C(H)PhOH\cdot Me_3SnCl$ (**1**), $[RNH{=}CHPhO]_2\cdot Me_2SnCl_2$ (**2**), $Me_2Sn(RCOO)_2$ (**3**), $Bu_2Sn(RCOO)_2$ (**4**) (R = 3,5-di-*tert*-butyl-4-hydroxyphenyl) were synthesized and characterized by NMR, IR, X-Ray and elemental analysis.

The antioxidant radical scavenging activity of the complexes was measured spectrophotometrically using a DPPH-test and CUPRAC-test. It was shown that introduction of the protective group of 2,6-di-*tert*-butylphenol leads to a reduction in the overall toxicity of complexes.

The potential cytotoxic activity of new tin complexes was evaluated *in vitro* against panel of human cancer cell lines using the MTT test. The activity of the compounds was compared with that of cisplatin.

IC$_{50}$, µM (for compound 1)								
PC-3	**MCF-7**	**HCT-116**	**SNB-19**	**A-498**	**M-14**	**HEK-293**	**NCI-H332M**	**CaCo-2**
5.31±0.59	**8.14± na**	**2.64± 2.28**	**2.16±0.45**	**16.03±5.49**	**12.32±1.34**	**<0.01**	**5.73±0.79**	**>10.5**

It was shown that new tin(IV) complexes exhibited lower cytotoxic activity against the normal cell line compared to the tumour cell lines HCT-116 and SNB-19. For example the cisplatin IC$_{50}$ value is 32 µM on the HCT-116.

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THE STUDY OF THE PROCESS OF COMPLEXATION OF 1,5-BIS(2-DIOXAPHOSPHORAN-4-ETHYLENOXY)-3-OXAPENTANE WITH Sm(III)

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Phosphorylcontaining podands showed itself as an effective ion-selective reagents in the separation of rare earth elements. Work is underway on identifying the influence of the structure like its complexing and sorption properties.

In this work we have studied the system of 1,5-bis(2-dioxaphosphoran-4-ethylenoxy)-3-oxapentane – Sm(III) – H_2O.

The method of pH-metric titration using the calculation method of Swarzenberg determined acidity constants of 1,5-bis(2-dioxaphosphoran-4-ethylenoxy)-3-oxapentane (H_4L): $pK_{a,1} = 3,09$; $pK_{a,2} = 4,43$; $pK_{a,3} = 8,19$; $pK_{a,4} = 9,24$. In similar conditions (μ = 0,1, KCl) was built curve of potentiometric titration (PMT) solution of H_4L with Sm(III), which calculated stability constants of the formed complex particles (fig., table). The complexation process starts after the formation of the first proton from the ligand at pH = 4. In addition, the PMT curve analysis allowed us to conclude that the coordination sphere of samarium shaped like molecule and does not contain solvent molecules.

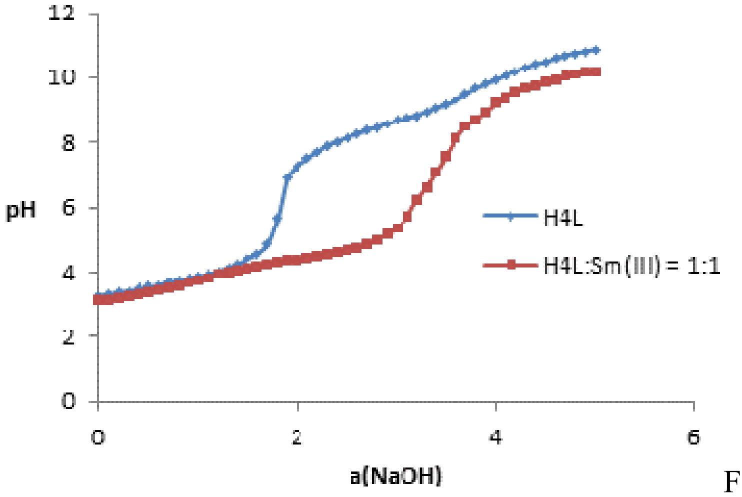

Fig.

Potential curves of titration

Table. Stability's constants

Complex particle	β	lg β
SmH_2L^+	$8{,}1 \cdot 10^3$	4,13
SmHL	$1{,}86 \cdot 10^6$	6,27
SmL^-	$4{,}38 \cdot 10^7$	7,64

The composition of complex particles (1:1) confirmed by the method of conductometric titration. The experiment was carried out, titrating a solution of samarium(III) fully neutralized with a solution of podand (L^{4-}). The conductivity before the equivalence point was dropping, which is due to the flow of chelation reaction: $Sm^{3+} + L^{4-} \rightarrow SmL^-$. With further increase in concentration of the ligand, the conductivity increased.

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1-AMINOETHAN-1,1-DIFOSFONIC ACID IN REACTIONS OF COMPLEXATION WITH GADOLINIUM(III)

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The study of complexes of rare earth metals with aminopolyphenone acids promising both from the point of view of the development of the coordination chemistry of complexes with polyfunctional ligands, and to obtain new biologically active compounds. Currently as drugs for the treatment of osteoporosis and some bone disease apply diphosphonate and their complexes with lanthanides.

In this work the results of a study of the complexation of 1-aminoaniline-1,1-diphosphonic acid (AEDP) with Gd(III) are showed.

The composition of complex particles formed in aqueous solution, was determined by the method of potentiometric. The capacity of the system with a constant content of Gd^{3+}, by varying the concentration AEDF are measured. The curve of dependence of the EMF of the concentration AEDF has breaks corresponding to the ratio metal : ligand equal to 1:1 and 2:1. When excess content of the ligand, when virtually all the metal is bound in the complex, there is a linear dependence of E from lnC AEDF, which, using the methodology [1] calculated the composition and stability constant of formed in these conditions is complex (table).

The influence of acidity on the composition and stability of the complex particles were studied by means of the curves of potentiometric titration (PMT) solutions AEDF in the absence and in the presence of ions Gd^{3+}. On curves of PMT solutions containing components in the ratio 1:1 and 2:1 (Gd^{3+} : AEDF) an algebraic method of Swarzenberg calculated stability constants are dominant in different pH regions of the complex particles (table).

Buffer area	Complex particle	lgβ	Complex particle	lgβ
0≤a≤1	$[GdH_3L]^{2+}$ $[GdH_2L]^{+}$	2,29 (2,04)* 5,72	$[Gd_2H_2L\ ]^{4+}$	11,39
1≤a≤2	$[GdH_3L]^{2+}$ $[GdH_2L]^{+}$ [GdHL]	2,37 5,45 9,02	$[Gd_2H_3L]^{5+}$ $[Gd_2H_2L]^{4+}$	7,44 11,34
2≤a≤3	$[GdL]^{-}$	10,83	$[Gd_2HL]^{3+}$	19,10
3≤a≤4	-	-	$[Gd_2HL]^{3+}$	14,57

* on curve dependence of EMF on $\ln c_{AEDF}$

[1] E.V. Dorozhko, E.I. Korotkov, O. A. Voronova, etc., Basic researches, 2013, № 8, 601-604.

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THE ROLE OF Se-Se COORDINATION TO ALLYLIC CHLORINATION OF BETULIN AND DIACETYLBETULIN

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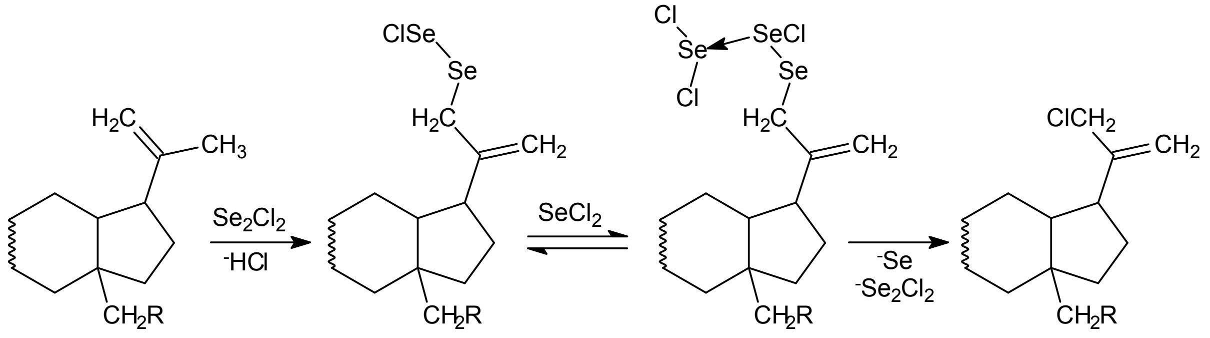
Betulin and some other derivatives of lupane are biologically active compounds, so the actual task is the search of selective methods for the synthesis of betulin derivatives. Chlorination of diacetylbetulin with *tert*-butyl hypochlorite leads to the mixture of vinyl and allyl isomers [1]. It was established that in the reaction of selenium dichloride with betulin and diacetylbetulin occur regiospecific allylic substitution of hydrogen by chlorine atom with formation of a single product – an unsaturated chloride of allylic type [2].

Combination of Se powder and SO_2Cl_2 has been employed to generate "$SeCl_2$" in situ. ^{77}Se NMR spectroscopy is the best method for the quantitative analysis of mixtures of selenium halides. Both $SeCl_2$ and Se_2Cl_2 $\delta(^{77}Se)$ 1762 and 1277 ppm are observed in $CDCl_3$ solution.



R = OH, OAc

Quantum-chemical calculations were carried out with the program Gaussian 09. The calculated activation energy of Se-Cl bond breakage and HCl formation in the complex of betulin with $SeCl_2$ is 39 kcal/mol. The activation energy of the electrophilic substitution of hydrogen by means of Se_2Cl_2 molecule is 10 kcal/mol. Therefore, in the first stage diselenium dichloride reacts. Formation of intermediate perselenide allyl type was confirmed by ^{1}H NMR method. Next, the intermediate compound is converted to allyl chloride. The calculations demonstrate that the complex between a molecule of perselenide and $SeCl_2$ is formed without activation energy. Then, in the complex terminal chlorine atom displaces selenium from the allylic position. Coordination Se→Se plays a key role in regiospecific allylic chlorination.

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ANTICANCER Pt(IV) COMPLEXES WITH LONIDAMINE AND BEXAROTENE LIGANDS: INFLUENCE OF LINKER

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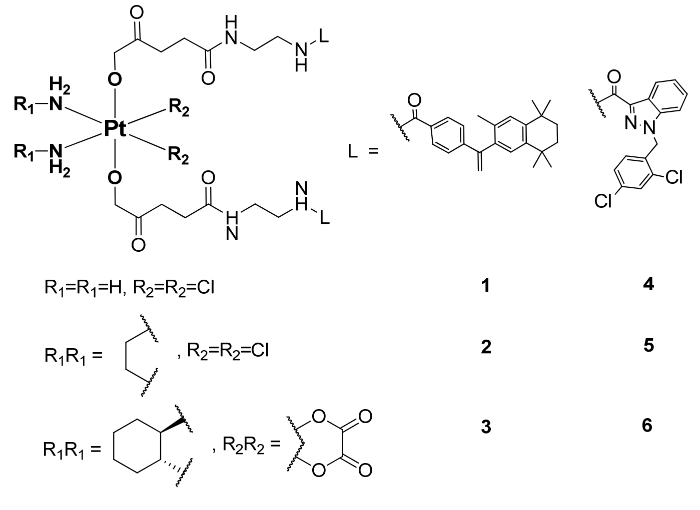
In cancer chemotherapy, drug combinations are almost general rule and platinum (IV) complexes may be considered as an ideal scaffold for incorporation of targeting ligand due to their stability and lower general toxicity. Conjugation with such ligands can increase the activity or selectivity of new complexes and lead to controlled release of an active organic molecule into cancer cell.

In this work two series of Pt(IV) complexes with bioactive ligands were prepared. Glycolysis inhibitor lonidamine or retinoid X receptor agonist bexarotene were utilized as the bioactive ligands in cisplatin or oxaliplatin pharmacophore. In contrast to our previous work [1,2] ligands were introduced by using the mixed amide linker to separate metal center and organic drug.

All synthetized compounds were characterized by NMR (^{1}H, ^{13}C, ^{195}Pt, ^{15}N) spectroscopy, ESI-MS and elemental analysis. The antiproliferative activity of the Pt(IV) complexes was investigated against several cancer cell lines (A549, SW480, MCF7). Most of complexes showed higher *in vitro* activity in comparison to lonidamine and bexarotene. Complex **2** exhibit low nanomolar cytotoxicity (IC_{50} 0.7÷1.0 **μM**) and is notably more active than cisplatin.



IC50	SW480, µM	A549, µM
bexarotene	80±10	85±9
1	24±0.8	>100
2	**0.8±0.1**	**1±0.01**
3	35±0,6	52±5
lonidamine	>90	>90
4	48±6	>100
5	43±1	>100
6	>100	>100
Cisplatin	17.6±5	20.1±1.9

[1] Y. N. Nosova, Foteeva L. S.; Zenin I. V.; Fetisov T. I.; Kirsanov K. I.; Yakubovskaya M. G.; Antonenko T. A. ; Tafeenko V. A. ; Aslanov L. A.; Lobas A. A.; Gorshkov M. V.; Galanski M.; Keppler, B. K.; Timerbaev A. R.; Milaeva E. R. and Nazarov A. A. *Eur. J. Inorg. Chem.,* **2017**, 12, 1785-1791

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PLATINUM(II)-MEDIATED COUPLING OF THIAZOL-2-AMINES AND COORDINATED ISOCYANIDES

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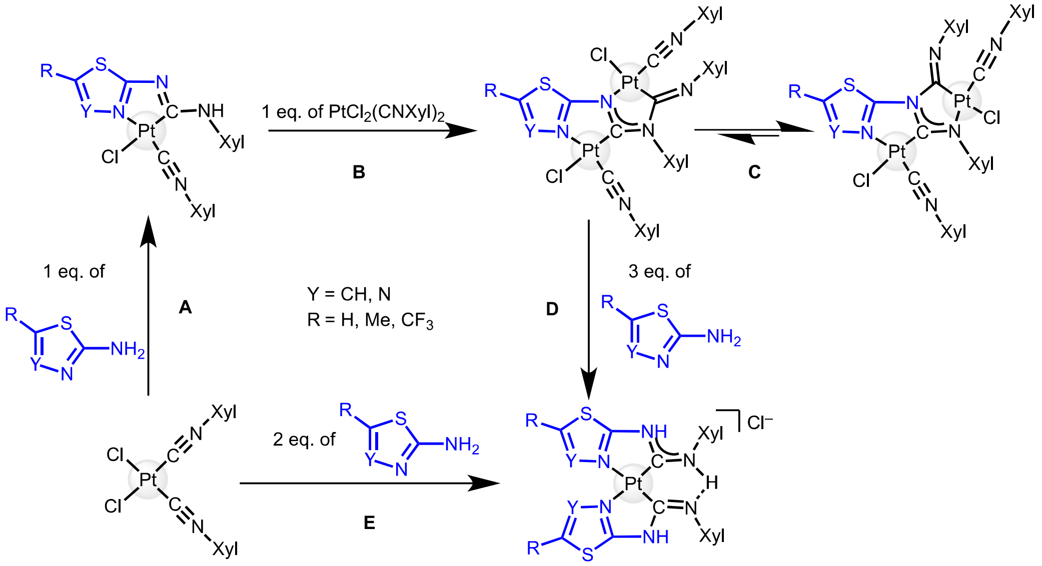
Coordination of isocyanides to metal-centers activates RNC species toward their coupling with various nucleophiles. As a result, the addition of weak NH-nucleophiles becomes possible, what normally does not procced under mild conditions. This reaction leads to transition metal acyclic diaminocarbene complexes, which are difficult-to-obtain by other methods. Previously we have found that the coupling of Pd^{II}-isocyanide complexes with thiazol-2-amines leads to carbene complexes, which can act as nucleophiles themselves and capable of attacking one more isocyanide complex thus forming binuclear species [1]. Herein we studied the coupling of Pt^{II}-xylylisocyanide complex with various thiazol-2-amines. We found that the reaction proceeds via different routes depending on reaction conditions (**Scheme 1**).



Scheme 1. Reaction of *cis*-[$PtCl_2(CNXyl)_2$] with various thiazol-2-amines.

The regioisomeric binuclear Pt^{II}-complexes formed upon the coupling of thiazol-2-amines with *bis*-xylylisocyanide Pt^{II}-complex are in equilibrium with each other in a $CHCl_3$ solution. All products depicted in Scheme 1 were isolated and characterized by HRESI$^+$-MS, IR, ^{1}H and ^{13}C{^{1}H} NMR spectroscopies, and also by single-crystal X-ray diffraction.

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КОЛИЧЕСТВЕННОЕ ИССЛЕДОВАНИЕ РАВНОВЕСИЯ И КИНЕТИКИ КООРДИНАЦИИ ПИРИДИНА ТРИХЛОРО(5,10,15,20-ТЕТРАФЕНИЛПОРФИНАТО)НИОБИЕМ(V)

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Количественно, методами спектрофотометрического титрования и химической кинетики изучена реакция комплекса трихлоро(5,10,15,20-тетрафенилпорфинато)ниобия(V) с биологически активным молекулярным лигандом пиридином (Py). Система исследована в среде инертного по отношению к реагентам толуола при 298 К в широком диапазоне концентраций Py ($4.96\cdot10^{-4}$ – 3.1·моль/л) и при постоянной концентрации $C_{(Cl)_3NbTPP}$ равной 3,63 10^{-6} моль/л. Реакция с Py представляет сложный многоступенчатый процесс: в диапазоне концентраций ($4.96\cdot10^{-4}$ – $2{,}98\cdot10^{-2}$моль/л) константа равновесия $K_p = 2{,}19\cdot10^5$ л^2/моль^2 (tgα ≈ 2); в диапазоне ($2{,}98\cdot10^{-2}$ – 3.1·моль/л) K_p = 5,19· л/моль/ (tgα ≈ 1). Реакция Cl_3NbTPP с Py идет до состояния равновесия, устанавливающегося сразу при сливании растворов во всем диапазоне соотношений компонентов. Однако далее наблюдали медленный необратимый процесс, который сопровождался батохромным смещением ЭСП и вытеснением ацидолигандов $3Cl^-$ во вторую координационную сферу.

Для медленных реакций получено полное кинетическое описание. Ранее в лаборатории были изучены подобные реакции O=Mo(OH)TPP [1], $(Cl)_2HfTPP$ [2], $(Cl)_2ZrTPP$ [3] с Py. На основании полученных ранее данных с учетом результатов этой работы сделан вывод, что изученные комплексы, в том числе и Cl_3NbTPP, могут быть использованы на практике в качестве рецепторов азотистых N-оснований, которые являются строительными блоками для фармацевтических препаратов и компонентов пищи.

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СИНТЕЗ И СВОЙСТВА ГИДРОКСООКСО(5,10,15,20-ТЕТРАФЕНИЛ21Н,23Н-ПОРФИНАТО)(2'-(2-Py)-5'-(2-Py)-1'-(3-PyMe)-ПИРРОЛИДИНО[70]ФУЛЛЕРЕН)МОЛИБДЕНА(V)

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Свойства фуллеренов и их функциональных производных активно изучаются с целью создания на их основе новых лекарственных средств, биоматериалов т устойств оптоэлектроники. Получены [1] комплексы водорастворимого поликатионного производного фуллерена C_{60} с ксантеновым красителем эозином Y и обнаружена эффективная дезактивация синглетных возбужденных состояний эозина Y, по видимому, за счет переноса электрона с красителя на фуллерен. Это открывает возможность создания на основе фуллеренов эффективных фотосенсибилизирующих систем. Огромный интерес вызывают полимер-фуллереновые органические солнечные фотоэлементы (СФЭ), рабочими компонентами которых выступают молекулы или комплексы, построенные по принципу донор – акцептор электронов. Установлено, что высшие фуллерены, например C_{70}, имеют существенно более высокое светопоглощение, поэтому в наиболее эффективных СФЭ используется метано-фуллерен PCBM[C_{70}]. СФЭ на основе нанокомпозита PCPDTBT с PCBM[C_{70}] показал очень высокий кпд 5,5% [2]. Дисбаланс между попытками практического применения донорно-акцепторных систем и изучением реакций их образования тормозит прогресс в упомянутой области.

В настоящей работе равновесие и кинетика реакции гидроксооксо(5,10,15,20–тетрафенилпорфинато)молибдена(V) (O=Mo(OH)TPP) с 2'-(2-Py)-5'-(2-Py)-1'-(3-PyMe)-пирролидино[70]фуллереном (Py_3F) изучены в толуоле при 298 K методами молярных отношений и избыточных концентраций. Измерения оптической плотности для серии растворов с постоянной концентрацией $C_{\mathrm{O=Mo(OH)TPP}}$, равной $1.06 \cdot 10^{-5}$ моль/л, и концентрациями основания, изменяющимися от $3.54\ 10^{-5}$ до $6.02\ 10^{-4}$ моль/л, проводили на рабочей длине волны 462 нм в начальный момент времени ($\tau = 0$) и во времени. Было установлено, что во всем изучаемом диапазоне концентраций равновесие исходного комплекса с внешнесферным дигидроксо-комплексом $[Mo(OH)(Py_3F)_2TPP]^{2+}\ 2OH^-$ с константой $K = 2.94 \times 10^7$ л^2/моль^2 устанавливается сразу при сливании растворов. Однако далее во всех равновесных смесях наблюдали медленный необратимый процесс нулевого порядка по Py_3F - вытеснения ещё одного OH^- во внешнюю сферу. Конечный продукт реакции, $[Mo(Py_3F)_2TPP]^{3+}\ 3(OH)^-$ идентифицирован с применением современных спектральных приборов.

Обнаружено эффективное тушение флуоресценции ($\lambda_{exc} = 435$ нм) молибден-порфирина в составе $[Mo(Py_3F)_2TPP]^{3+}\ 3(OH)^-$, что служит доказательством фотоиндуцированного внутримолекулярного переноса электронов в порфирин-фуллереновом донорно-акцепторном комплексе при облучении видимым светом.

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FIRST REPORT OF THE DIRECT CONFIRMATION OF A TRIPLE INSERTION OF PHENYLISOCYANATE INTO A Ti-OR BOND. CRYSTAL STRUCTURE OF ISOPROPYL(Z)ANILINE(PHENILIMINO)METHYL(PHENYL)CARBAMATE

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Earlier, authors of the article [1] devoted to a multiplet insertion by EtNCO into Ti(JPr)4, on the basis of physical and chemical studies suggested that it contains the associated alkoxy group, on which the insertion took place, representing 1-nylon.This is in stark contrast to our previous results for products of partial and complete hydrolysis of similar products of insertions into the W-Cl bond [2,3], which were accompanied by either the inner-sphere cyclization with the formation of a corresponding ligand, or a formation of a triisocyanuate..

Unexpected results of an X-ray diffraction analysis of the crystals of the intermediates, which are formed at the first stage of interaction, when carrying out the synthesis of products of heteromolecular insertion of PhNCO and CO_2 into $Ti(OPri)_4$, are presented in this report. (The theses describing the final products of reaction are submitted in conference materials). It is expected that at the first stage of reaction there is an instant insertion of the phenyl isocyanate, because it was added to a reaction mixture completely, in contrast with the adding of carbon dioxide, which gradually was allowed to pass through reaction solution Thus, it is natural, that this crystal is the hydrolyzed product of the isocyanate insertion product when standing solution, however its decarboxilation , wtich takes plase is unsurprising.

The assumption of authors [1] about obtaining product of hydrolyzys in course of our X-ray diffraction investigation was confirmed, however, in this case, there was a decarboxylation giving isopropyl (Z) aniline (phenilimino) methyl (phenyl) carbamate. Most likely, this was caused by the difference in heating environments of an experiment, namely due to carrying out the reaction at the boiling point of the solution, which stimulates decarboxylation.

The X-ray date for determination of a structure of the crystal bond I (C23 H23 N3 O2) is received using .an automatic diffractometer Enraf-Nonius CAD-4 at ambient temperature, using graphite monochromator CuK□ α radiation (θ max = 64^o). Structure solution by a method of least squares for 1830 [I - ≥2σ(I)] (R1 = 0,035, R_2=0,092)using SHELX-97 and SHELXL-97 programs, respectively. Crystals are triclinic, the space group: P-1, Z = 2, $\rho_{calc.}$=1.219 g/cm^3, V = 1017.2(3) Å^3, a = 9.474(2) Å, b = 10.646(2) Å, c = 10.720(2) Å α = 81.41(2)^o, β = 71.98(2)^o, γ = 88.41(2)^o.

Main interatomic distances:O(1) - C(1) = 1.209(2) Å (double bond),O(2)-C(1) = 1.328(3), O(2)-C(9) = 1.468(3) , N(2)-C(2) = 1.268(3) (double bond), there is hydrogen bond: (N(1)_H(1a). O(1) (3,083 A, 148.9).C(9) –C(10) 1.498(3), C(9) –C(11)–1.507 (single bond). Another distances: N-C (covalent bond) and C-H(1.365 –1.447),.(1.362-1.387) (phenyl ring).

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27th International Chugaev Conference on Coordination Chemistry
4th Conference-School for Young Researchers “Physicochemical Methods in Coordination Chemistry”
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VERY FAST CROSS-COUPLING REACTIONS WITH LOW LOADING OF ISOXAZOL-1,2,3-TRIAZOLE PALLADIUM COMPLEXES IN AQUEOUS MEDIA

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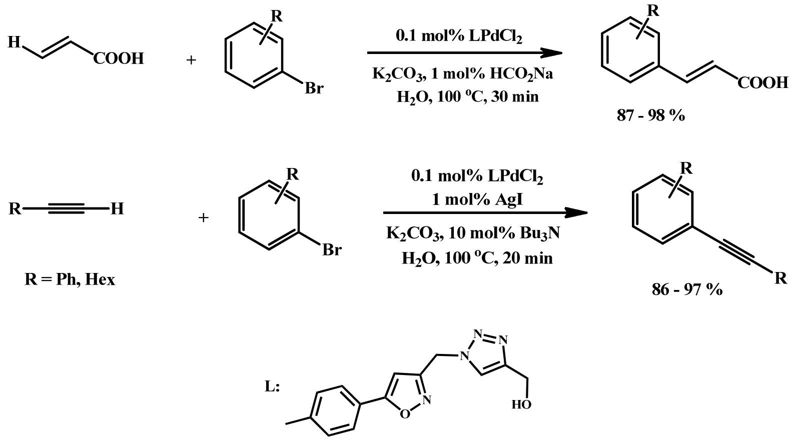
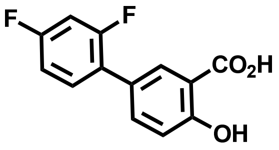
The palladium-catalyzed Suzuki–Miyaura, Heck and Sonogashira reactions represent straightforward and highly effective tools for carbon–carbon bond formation in the synthesis of biaryls and arylated unsaturated compounds [1]. Although many efficient palladium catalysts with novel P- and N-ligands have been discovered for these reactions, also of great importance are the protocols that utilize low loading of Pd-catalysts in water or aqueous media. Water has clear advantages as a solvent for use in this type of reactions because it is cheap, readily available, and nontoxic. Here, we report that isoxazol-1,2,3-triazole palladium complexes exhibit very high catalytic activity in Suzuki, Heck and Sonogashira reactions in aqueous media and allow to synthesize the cross-coupling products in high yields.

$$\mathrm{Ar - B(OH)_2} \quad + \quad \mathrm{Ar' - Br} \quad \xrightarrow[\substack{\mathrm{K_2CO_3,\ (1\ mol\%\ Bu_4NBr)} \\ \mathrm{H_2O,\ 100\ ^oC,\ 10\ min}}]{\mathrm{0.001\ mol\%\ LPdCl_2}} \quad \underset{\text{90-98 \%}}{\mathrm{Ar - Ar'}}$$



Examples of the biaryl, olefin, and acetylene compounds synthesized are presented below.



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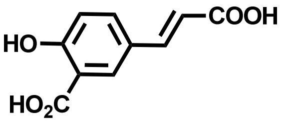

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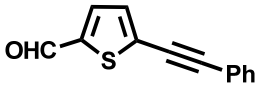

97 %

[1] T.W.J. Cooper, I.B. Campbell and S.J.F. Macdonald, *Angew. Chem. Int. Ed.*, **2010**, *49*, 8082.

Acknowledgements: We thank the Belarusian Republican Foundation for Basic Research (grant № X16P-006) and the Russian Foundation for Basic Research (grant № 16-58-00059-Bel_a) for financial support of this work.

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"GREEN" SUZUKI REACTION CATALYZED BY MESOPOROUS OXIDES SUPPORTED ISOXAZOL-1,2,3-TRIAZOLE-NICKEL-PALLADIUM COMPOSITE

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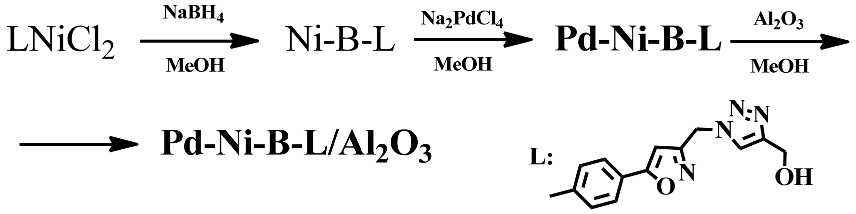
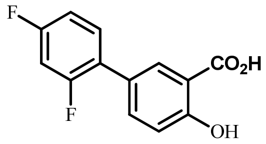
Heterogeneous catalysts have recently drawn much attention in organic synthesis based on sustainable and industrial standpoints, as they have many advantages over homogeneous catalysts, owing to their stability, recoverability, reusability, etc. We report here an efficient heterogeneous catalytic systems (**Pd-Ni-B-L** and **Pd-Ni-B-L/Al_2O_3**, Ni:Pd=99:1) for cross-coupling reactions based on the precipitation of Pd nanoclusters on nanoparticles of modified nickel boride, prepared by reduction of isoxazol-1,2,3-triazole nickel complex $LNiCl_2$ (L= (1-((5-(p-tolyl)isoxazol-3-yl)methyl)-*1H*-1,2,3-triazol-4-yl)methanol) with $NaBH_4$. Catalyst characterization was performed using FTIR, XRD, XPS, and TEM. The method developed has shown to be efficient for the preparation of the catalytic materials and uniform deposition of palladium nanoclusters on nanoparticles of other metals (Fe, Co, Cu etc).



The resulting Pd materials, **Pd-Ni-B-L** and **Pd-Ni-B-L/Al_2O_3**, show homogeneous distribution of palladium clusters (TEM images) with sizes < 1-2 nm. The **Pd-Ni-B-L/Al_2O_3** hybrid is found as highly effective recyclable catalysts in Suzuki, Heck and Sonogashira reactions in water as a green solvent. The cross-coupling reactions were performed at low Pd content using various aryl(heteroaryl) bromides, 1.2 equiv of an arylboronic acid, olefins (acrylic acid or styrene) and phenylacetylene in the presence of ~0.01 mol% of Pd and 2.5 equiv of K_3CO_3 in water under reflux. All of the cross-coupling reactions exhibited high yields within 10-30 min even though they were carried out in air atmosphere.. The new heterogeneous catalysts could be recovered by simple filtration (centrifugation) and reused 5 times without any loss of the catalytic activity. Furthermore, no leached Pd was found in the filtrate and products after the removal of the catalyst by the inductively coupled plasma (ICP) assay. Examples of the compounds synthesized are presented below.



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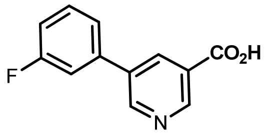

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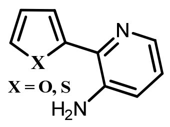

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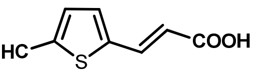

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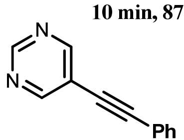

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Acknowledgements: We thank the Belarusian Republican Foundation for Basic Research (grant № X16P-006) and the Russian Foundation for Basic Research (grant № 16-58-00059-Bel_a) for financial support of this work.

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INVESTIGATION OF COMPLEXATION OF Fe(II) AND Fe(III) WITH TIRON IN AQUEOUS SOLUTIONS AND ON THE AMINATED SURFACE OF SILICA USING EPR METHOD

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4,5-dihydroxybenzene-1,3-disulfonicacid (Tiron) is one of the most selective reagent for photometric determination of Fe(III); it forms intensively colored compounds with iron. Fe(II) and Fe(III) form with Tiron compounds that have the identical color and absorption spectra with maximum at 500 nm (regardless of the oxidation level) [1, 2]. It allows to suggest that complexes have the identical composition and comprise iron in the same oxidation level.

EPR method was used in the present work for determination of the oxidation level of iron in complexes which are formed by mixing aqueous solutions of Fe(II) or Fe(III) and Tiron and on the surface of silica, non-covalently modified with Tiron (SiO_2-PHMG-Tiron). Interaction of Fe(II) or Fe(III) with Tiron in solutions in various pH media leads to formation of Fe(III) complexes of various stoichiometry Fe:Tiron = 1:1, 1:2, 1:3. These complex compounds have various colors from blue to red. In the EPR signals the characteristic transitions are observed during varying pH values (in the low-field region signals typical for Fe(III) in the high-spin state (5/2) with different symmetry of the ligand environment are observed). The most intensive signal with g=4.27 and other weaker transitions in the region of g=5-10 are present in the EPR spectrum. The shape and intensity of the signals depends on the pH of the solutions. Fe(III) complex compound is formed as the result of interaction between Fe(II) and Tiron in the pH range of 6.0–7.5 (even in the presence of 0.01M hydroxylamine) with intensive signal g=4.27 in the EPR spectrum. The shape of the spectra and EPR signals intensities are identical for the solutions obtained by mixing of the same concentrations of Fe(III) or Fe(II) with Tiron. The identity of EPR spectra in this case indicates that hydroxylamine does not prevent oxidation of iron (II) during complexation with Tiron.

An intensive signal at g=4.27 in the EPR spectra of SiO_2-PHMG-Tiron after Fe(III) and Fe(II) adsorption at pH 3-8 is observed. That is an evidence of the oxidation state of iron within the surface complex +3. On the basis of EPR data it can be concluded that during interaction of Fe(II) with Tiron both in solution and on the surface of the adsorbent it is oxidized up to Fe(III). Both dissolved in water oxygen and the reagent itself can be an oxidants of Fe(II). The rate of Fe(II) oxidation increases in the presence of acetate ions at pH > 5.

[1] M.J. Sever and J.J. Wilker, *Dalton trans,* **2004**, 1061-1072.
[2] O.V. Kuznetsova, V.M. Ivanov, N.V. Kazennov // *Moscow University Chemistry Bulletin,* **1997**, *38,* 53–56.

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COORDINATION COMPOUNDS OF THE WAUGH-STRUCTURE IN THE PRACTICE OF PREPARATION OF HYDROTREATING CATALYSTS

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[a]*Tomsk State University, Tomsk, RUSSIA.*
[b]*Surgut State University, Surgut, RUSSIA.*

In connection with the growing need for the development of new highly effective hydrotreating catalysts for middle distillates, heteropolycompounds of the Waugh-structure become increasingly important as sources of catalytically active metals.

One of these remarkable heteropolycompounds is the coordination compound of the composition $(NH_4)_6[NiMo_9O_{32}]$. In this complex, the central atom - the complexing agent Ni - is in an extremely rare and high oxidation state 4+. In the coordination compound of composition $(NH_4)_6[NiMo_9O_{32}]$, the cation Ni (IV) is in the pseudo-octahedral environment of oxygen atoms, has a d^6-electron configuration and is diamagnetic. A number of scientists suggest that Ni (IV) with d^6-electron configuration can be formed in the edge positions of the active phase of hydrotreating catalysts due to the process of oxidative addition of the hydrogen molecule to Ni (II) with the d^8-electron configuration. This conclusion is in good agreement with the results of X-ray photoelectron spectroscopy [1].

The results of the study of the behavior of coordination compounds of the composition $(NH_4)_6[NiMo_9O_{32}]$□$6H_20$ и $(NH_4)_6[NiMo_9O_{32}]$□$8H_20$ by the method of synchronous thermal analysis in combination with differential scanning calorimetry indicate a sufficiently high stability of coordination compounds of composition $(NH_4)_6[NiMo_9O_{32}]$□$6H_20$ и $(NH_4)_6[NiMo_9O_{32}]$□$8H_20$ over a wide temperature range [2,3]. X-ray phase analysis showed the presence of individual phases of MoO_3 in samples of catalysts prepared on the basis of ammonium paramolybdate and subjected to heat treatment at a temperature of 400 ° C, when individual MoO_3 phases were absent in catalyst samples prepared under similar conditions on the basis of coordination compound of the composition $(NH_4)_6[NiMo_9O_{32}]$. It is also worth noting a sufficiently high conversion of dibenzothiophene on catalysts prepared on the basis of heteropoly compounds of the Waugh-structure in comparison with catalysts prepared on the basis of classical ammonium paramolybdate [4].

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[2] H. Guoyan, H. Guotang, W. Yupin, Natural Science Editio, **2003**, *2*, 151-157.
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[4] J. Liang, Y. Liu, J. Zhao, X. Li, Y. Lu, M. Wu, C. Liu, *Catal Lett*, **2014**, *144*, 1735–1744.

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HETERONUCLEAR COMPLEXATION IN THE SYSTEM «GADOLINIUM(III) – IRON(III) – 1-HYDROXYETHYLIDENEDIPHOSPHONIC ACID (HEDP)» IN AQUEOUS SOLUTIONS

O.V. Bogatyrev, F.V. Devyatov and G.I. Zaripova

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Contrast reagents (CR) in MRI to generate the image by changing the time of the spin-lattice (T_1) and spin-spin (T_2) relaxation of protons of water surrounding the CR. Most often used as a CR complexes of Gd(III) and Fe(III) due to the high value of the spin-spin relaxation coefficient of efficiency (CRE_2) [1].

Previously, our research group due to the method of pH-potentiometry, PMR relaxation and mathematical modeling has established a diverse set of complex forms in the system "Gd^{3+}-HEDP" – with varying degrees of deprotonization ligand, in particular education 16 integrated forms, of which three binuclear [2]. For the "Fe^{3+} – HEDP" is the same as [2] was established a 8 complex of forms, including two polynuclear By the method of proton magnetic relaxation it was found that complexes of iron (III) with HEDP does not have significant advantages when used in MRI, since the value $КРЭ_2$ in the simulation of the introduction of the complexes into the human body, accompanied by about 1000-fold dilution with pH of 7.4 is not high enough for the contrast reagent and is about 1100 $mol^{-1}s^{-1}l$.

Using data on complexation in homonuclear systems "Gd^{3+} - HEDP," and "Fe^{3+} – HEDP" was described heteronuclear system "Gd^{3+} – Fe^{3+} – HEDP". It has been established that in the heteronuclear system a variety of forms and high stability of heteronuclear complexes are observed, due to which the homopolynuclear forms [2] are replaced by heteronuclear. When the two cations are jointly present in the solution, the accumulation of heteronuclear forms in the acidic region is observed only in the absence of an excess of the ligand, but as the pH increases, as a result of the detachment of the protons, the homonuclear forms go over to heteronuclear complexes with the ratio Gd:Fe:HEDP, equal to 1:1:1 and 1:1:2. In this case only four complexes are found from homonuclear forms in a strongly acid solution: $GdH_5L_2^0$, $GdH_7L_2^{2+}$, $GdH_4L_2^-$, $FeH_6L_3^{3-}$. In a heteronuclear system CRE_2 (for calculation was used the sum of the concentrations of paramagnetic materials) has a value of 3700 $l•mol^{-1}•s^{-1}$ (and higher: ~ 8000 $M^{-1}•s^{-1}$ when the ratio of the concentrations 1:1:2). Heteronuclear system shows the dominance of heteronuclear forms that is characterized by a higher percentage of their accumulation in areas of practical importance for medicine pH = 7.40, in the simulation the introduction of a solution with heteronuclear compounds in the human body, providing a 1000-fold dilution, there is a very low presence (<10-18 mol/l) of free cations which allows us to talk about their actual non-toxicity. Thus, the considered heteronuclear system may recommend itself as a MRI contrast reagent.

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THE NATURE OF ACTIVE PALLADIUM SPECIES IN THE REACTION OF DIRECT ARYLATION OF INDOLE USING LIGANDLESS CATALYTIC SYSTEM

E.V. Larina, A.A. Kurokhtina, E.V. Yarosh, N.A. Lagoda and A.F. Schmidt

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Direct arylation of (hetero)aromatic compounds is one of the most useful ways to construct new aryl-(hetero)aryl C-C bonds. In spite of great attention to the development of effective catalytic systems for these reactions a lack of fundamental knowledge in this field exists. Particularly, for the direct arylation of indole derivatives being the very attractive for the production of fine chemicals the nature of active species is unclear at the moment. We attempted to establish the nature of such species by competitive reaction method in the reaction of indole with aryl iodides using the ligandless catalytic system (Figure).

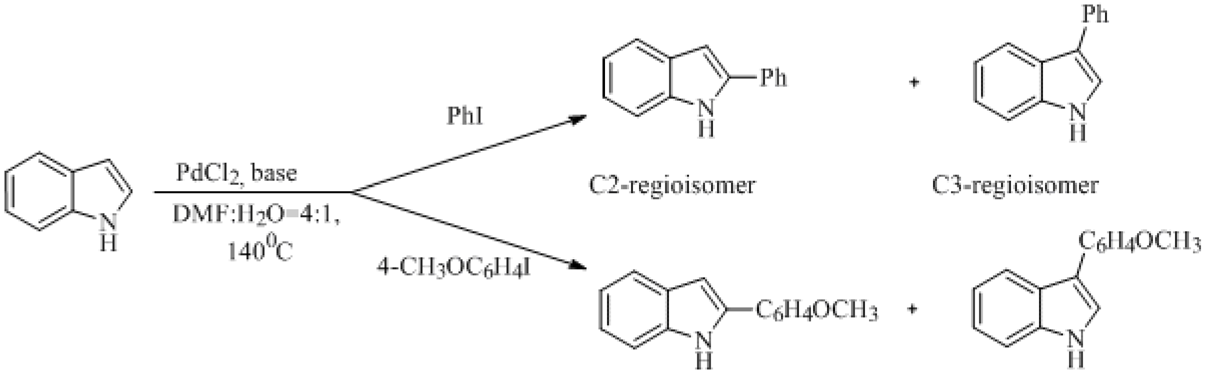

Figure. Arylation of indole by two competing aryl iodides using ligandless catalytic system.

We studied differential selectivity of the reaction using two competing aryl iodides. As differential selectivity of catalytic reaction is independent on amount of active species and is determined by their nature only, any changes of the selectivity under varying the reaction conditions indicate a change of such species nature [1]. It was establish that the differential selectivity of competitive arylation of indole by iodobenzene and 4-iodoanisole (estimated as the ratio of the rates of total accumulation of C2- and C3-aryl indoles) was sensitive to the nature of the inorganic base used (carbonates, acetates, and butyrates of alkali metals) and insensitive to the base concentration. More specifically, the differential selectivity was dependent on the nature of anion of the base used. We believe that such the dependence clearly indicates the anions of base entry into the active Pd complexes determining the selectivity of the catalytic cycle step where two aryl iodides compete. Accordingly to common view, such step is the oxidative addition of aryl halide to Pd(0). Consequently, the results obtained point to the Pd(0) complexes containing base anions are the active species in the indole arylation using ligandless catalytic system.

[1] A. F. Schmidt, A. A. Kurokhtina and E. V. Larina, *Cat. Sci. Technol.*, **2014**, *4*, 3439-3457.

Acknowledgements – this work was supported by Russian Foundation for Basic Research (Project 16-29-10731 ofi_m)

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В ПРОШЕДШЕМ ГОДУ «ЖУРНАЛ НЕОРГАНИЧЕСКОЙ ХИМИИ» ОТМЕТИЛ СВОЕ 60-ЛЕТИЕ

Журнал основан 1956 г. в результате объединения журналов «Известия Института физико-химического анализа» и «Известия Института по изучению платины и других благородных металлов». Почти с самого начала своего существования журнал в полном объеме переводится на английский язык под названием «Russian Journal of Inorganic Chemistry».

«Журнал неорганической химии» публикует результаты оригинальных теоретических и экспериментальных работ по химии неорганических соединений, координационной химии, физико-химическому анализу, физикохимии растворов, обзоры и рецензии. 14 выпусков в год: 12 основных и 2 номера только на английском языке, содержащих обзорные статьи.

За годы существования ЖНХ в его редколлегии состояли выдающиеся ученые, академики и члены-корреспонденты АН СССР и РАН, лауреаты Государственных премий, среди них Ю.А. Буслаев, В.И. Спицын, М.А. Порай-Кошиц, В.Б. Лазарев, А.В. Новоселова, К.Б. Яцимирский, Г.Г. Девятых, В.И. Нефедов и другие. Организатором и первым главным редактором журнала был директор ИОНХ им. Н.С. Курнакова, академик И.И. Черняев. В настоящее время главным редактором журнала является академик РАН Н.Т. Кузнецов, в состав редколлегии входят известные академики и члены-корреспонденты РАН.

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