Organometallic and Coordination Chemistry: Fundamental and Applied Aspects

International Youth School-Conference on Organometallic and Coordination Chemistry

September 1-7, 2013, Nizhny Novgorod, Russia

ORGANOMETALLIC AND COORDINATION CHEMISTRY: FUNDAMENTAL AND APPLIED ASPECTS

INTERNATIONAL YOUTH SCHOOL-CONFERENCE ON ORGANOMETALLIC AND COORDINATION CHEMISTRY

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Volga and Sheksna rivers
Nizhny Novgorod – Goritsy –Nizhny Novgorod, Russia

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Plenary lectures

FIFTY YEARS OF CARBORANE CHEMISTRY

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Fifty years ago the first papers on synthesis of icosahedral carboranes $C_2B_{10}H_{12}$ have been published, and these publications opened a new page in chemistry history. Carboranes were shown to be important both from fundamental point of view and for practical perspective. In carboranes the unusual to that time two-electron three-centered and multi-centered bonds were realized. Carborane gave an example of three-dimensional aromatic compound (Fig. 1).

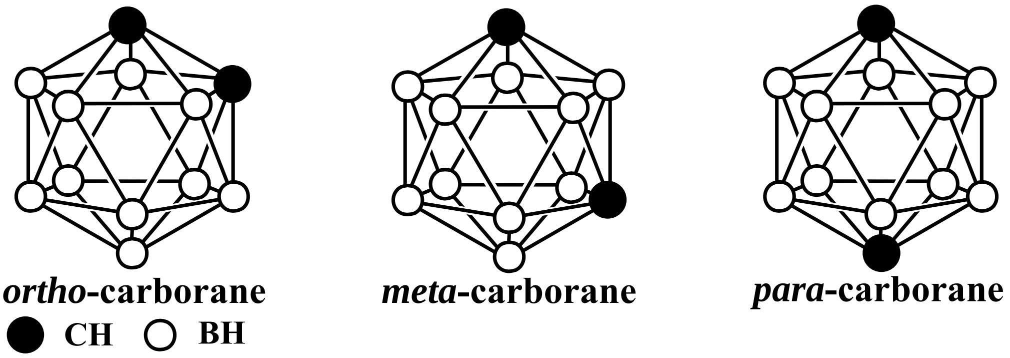

Fig. 1

The history of carborane origin and development of this unusual and exciting field of chemistry are presented in the lecture. It is of interest that synthesis of icosahedral carboranes has been published in one time in USSR and USA in November-December issues of journals [1-4]. In USA two companies were involved to this project: Thiokol Chemical Corporation (Dr. M.S.Cohen, et al) and Olin Mathieson Chemical Corporation (Dr. T.L.Heying, et al). In USSR L.I.Zakharkin and coworkers from INEOS were authors of the first publications. I would like also to underline a great role of Prof. A.F.Zhigach and his coworkers in development of technology of boron hydrides and carboranes production. Theoretical works in the field of carborane and polyhedral borane structure have been made by Prof. W.N.Lipscomb [5] who became Nobel Prize Winner in 1976. Comprehensive monograph on carboranes was presented by Prof. R.N.Grimes [6].

1. T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak and J. W. Szymanski, *Inorg. Chem.*, **1963**, *2*, 1089-1092.
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6. R. N. Grimes, Carboranes; 1st ed., Academic Press: New York, 1970, 260 p.; 2nd ed., Academic Press (Elsevier), 2011, 1246 p.

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REVISITING OLD FAMILIES OF CYANO-BRIDGED COORDINATION POLYMERS AT THE NANOSCALE

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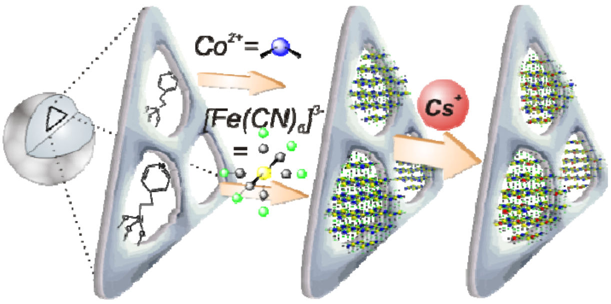
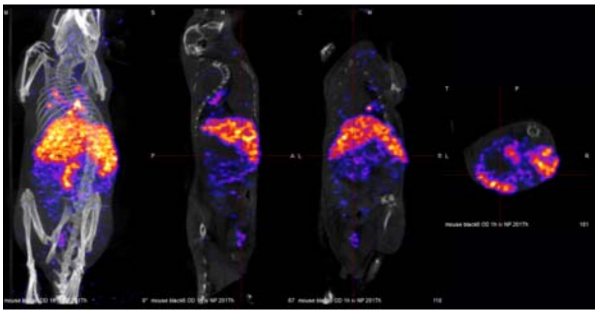
From 1704, year of the discovery of the oldest coordination polymer, Prussian blue, to now, many cyano-bridged coordination polymers were synthesised and extensively studied. This research field remains very active with the development of materials featuring magnetic, photomagnetic, sorption or catalytic properties.



Schematic representation of cyano-bridged coordination polymer based nanocomposites synthesis and their use in Cs decontamination.

A significant part of the current research activity on these materials is devoted to the synthesis and study of size and shape controlled cyano-bridged coordination polymer materials at the nanoscale.[1] These nanomaterials have the same advantages as the corresponding bulk materials. Among them may be mentioned the versatility of precursors that can be assembled, the adjustable porosity and the possibility to combine several properties within a single nano-object by a judicious choice of precursors.

In addition, the ease of synthesis of these nanoparticles under mild conditions allows control of their size, shape and sometimes their organization and thus control over their properties. In this presentation, we will illustrate the latest developments made in our research groups on this topic. We will discuss various synthetic methodologies that we developed for the preparation of nano-objects or nano-composites of these materials and magnetic, magneto-optic or sorption properties associated therewith.



Biomedical imaging using cyano-bridged coordination polymer nanoparticles.

We will also address the potential applications of cyano-bridged coordination polymer nanoparticles and nanocomposites in the fields of medical imaging and decontamination of mobile radioactive elements.

[1] A(a) S. P. Moulik, G. C. De, A. K. Panda, B. B. Bhowmik, A. R. Das, *Langmuir* **1999**, *15*, 8361; (b) S. Vaucher, M. Li, S. Mann, *Angew. Chem., Int. Ed.* 2000, **39**, 1793; (c) J. Larionova, Y. Guari, C. Sangregorio, Ch. Guérin, *New J. Chem.* **2009**, *33*, 1177; (d) F. Volatron, L. Catala, E. Riviere, A. Gloter, O. Stephan and T. Mallah, *Inorg. Chem.*, **2008**, *47*, 6584–6586.

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CARBORANES AND METALLACARBORANES: A HISTORIC PERSPECTIVE

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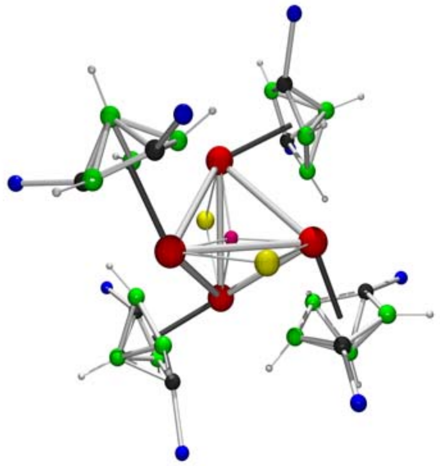
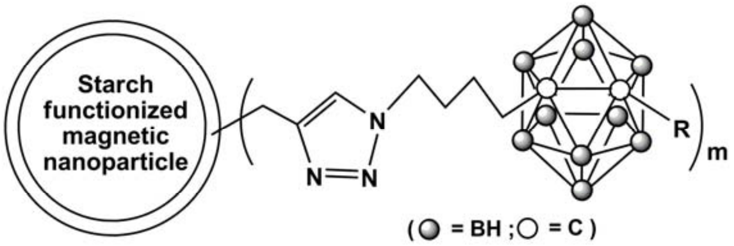
Most of the carborane derivatives of the icosahedral (C2B10) or small cage (C2B4) systems are formed by varying the groups on the cage carbons. This is usually accomplished in the original carborane synthesis by reacting substituted acetylenes with either the decaborane(14) or pentaborane(9) precursors. These reactions led directly to the “carbons adjacent” carboranes in which the carbon atoms occupy adjacent positions in the cage. The larger cages are obtained as closo-icosahedra, while the small cage, C2B4-carboranes, have nido-structures. In the small cage system there is another cage geometry in which the carbon atoms are separated by a boron atom. Although these “carbons apart” or nido-2,4-(CR)2B4H6 species are thermodynamically more stable and are more symmetric than the “carbons adjacent” isomers, they are not as well studied. The main reason for the relative scarcity of information on the “carbons apart” systems lies in their method of preparation; they must be synthesized from their “carbons adjacent” analogues through a sequential series of oxidative cage closure/reductive cage opening reactions. In light of complete destruction of pentaborane stockpile at the US Edwards Airforce Base, we have also directed our attention to the development of a safe, bench-scale preparation of the small-cage carboranes, that does not require isolating and handling dangerous, volatile and toxic borane precursors, such as pentaborane(9). The historic perspective of the chemistry of carboranes and metallacarboranes along with the latest findings in our research involving boron nanomaterials will be presented in detail.





Boron concentration in tumour: 51.4 ugB/g tumour;
Tumour : normal tissues: ~ 10:1

Hosmane, N. S.; Maguire, J. A. *Organometallics,* **2005**, *24*, 1356-1389.
Satapathy, R.; Dash, B. P.; Maguire, J. A.; Hosmane, N. S. *Dalton Trans.,* **2010**, *39*, 6613-6625.

THE MODULATION OF ORGANIC PHARMACOPHORE’S ACTIVITY BY THE INCORPORATION OF A METAL. A NOVEL WAY TO THE METAL-BASED PHARMACEUTICALS

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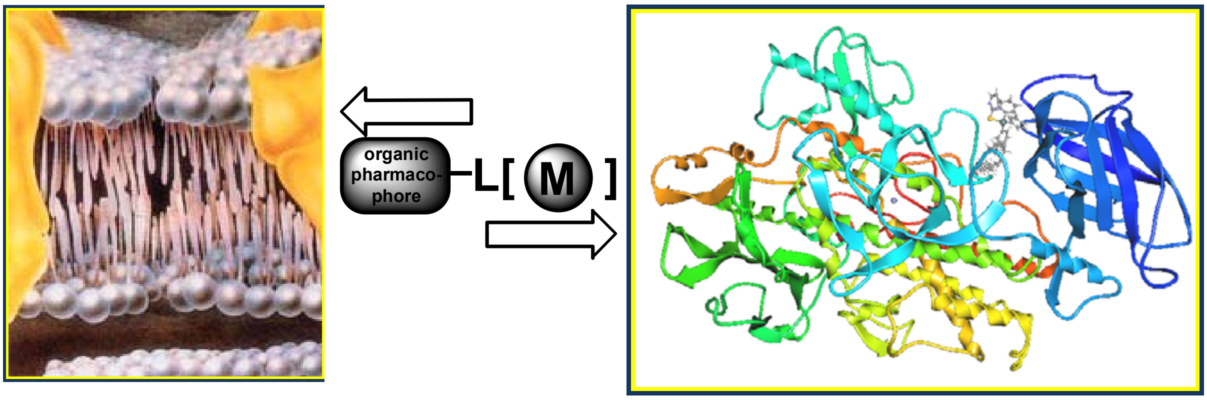
The question if the metal is “boon or bane” in medicine has been answered by bringing a good deal of metal-based drugs to the pharmaceutical market in recent time. Nowadays there is a strong need of the design of novel potential therapeutic candidates based on organometallic and coordination metal compounds since the metal-based physiologically active substances posses a wide spectrum of activities. This short review will focus on a novel approach for the molecular construction of the target-oriented metal complexes combining in one molecule both an organic pharmacophore and a metal center. The synthesis and biological screening of organometallic compounds and metal complexes where metal is either a biogenic element (Fe, Mn, Cu, Co, Zn) or a pharmaceutically important metal (Pt, Ru, Sn, Sb) will be discussed. The metal is considered to play a key role in biomolecular mechanism of metal complex actions as antiprolifirative and neuroprotective agents.



*The assay has been performed by using model reactions (DPPH, CUPRAC-tests, liposome system), enzymatic methods (*tubuline, lipoxygenase, xanthine oxidase*,* gluthathione reductase, thioredoxine reductase*),* in vitro *and* ex vivo *lipid peroxidation in mitochondria and homogenates from Wistar rat brain and liver. The* in vivo *study and molecular doking were performed for the lead compounds.*

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THE UNIVERSE _ A GUIDE TO NEW CHEMISTRY

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In the interstellar space a number of compounds with low valent elements have been spectroscopically characterized. In our ongoing research we are trying to synthesize those compounds with low valent elements with the support of N-heterocyclic carbenes. Preferentially I will report the results on aluminum(1), silicon(0), silicon(I), silicon(II), germanium(I), and germanium(II). Compounds such as RAl: and $:SiCl_2$ can be prepared and their striking properties are created through the metals, which function as Lewis bases as well as Lewis acids. Tailor-made N-heterocyclic carbenes are used for the stabilization of radicals and biradicals. The resulting products can be used for the activation of molecules, due to the radical or biradical centers in the coordination sphere of the metals.

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THERMAL ACTIVATION OF METHANE BY METAL OXIDES IN THE GAS PHASE

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In terms of selective oxidation of hydrocarbons, oxygen-based systems represent a keystone in contemporary catalysis. However, a detailed mechanistic knowledge of the elementary processes is still rather limited. Thus, gas-phase chemistry of transition-metal oxide cations $[M_xO_y]^+$ has received considerable attention with the aim to uncover mechanistic details of catalytic transformations [1]. Different types of methane activation by metal-oxide species have been observed in the gas phase, including hydrogen- as well as oxygen-atom transfer (HAT, OAT), and carbene as well as formaldehyde formation [2]. Examples of these types of reactions are described including mechanistic details, and properties of the reactive species are identified which are required to bring about the wanted transformation. For example, the bond-dissociation energy $BDE(M^+–O)$ determines the ability to transfer an oxygen atom to methane while relativistic effects play a role for carbene formation. Particular emphasis will be paid to the concept of oxygen-centered radicals, i.e. the presence or absence of a high spin density located at a terminal oxygen atom which turned out to be crucial for thermal HAT reactions [3].

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Section Lectures

POLYNUCLEAR HALOGENIGE COMPLEXES OF BISMUTH AND POLYOXOMETALATES: SIMILARITIES, DIFFERENCES, SYMBIOSIS

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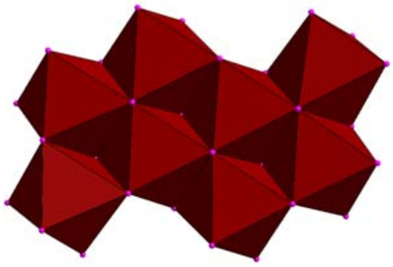
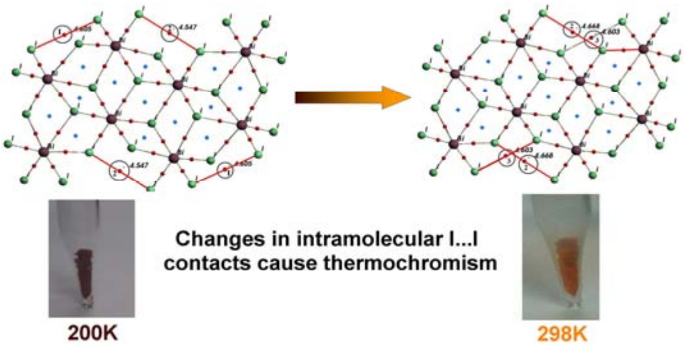
Polyoxometalates (POM) and polynuclear halogenide complexes of Bi represent two large classes of coordination compounds; both attract a growing interest due to their promising properties, related to materials science and catalysis. Here we report our latest results in the chemistry of polynuclear bismuth iodides (PIBs) and a route to the creation of hybride POM complexes containing BiX_3 (X = Cl, Br, I).

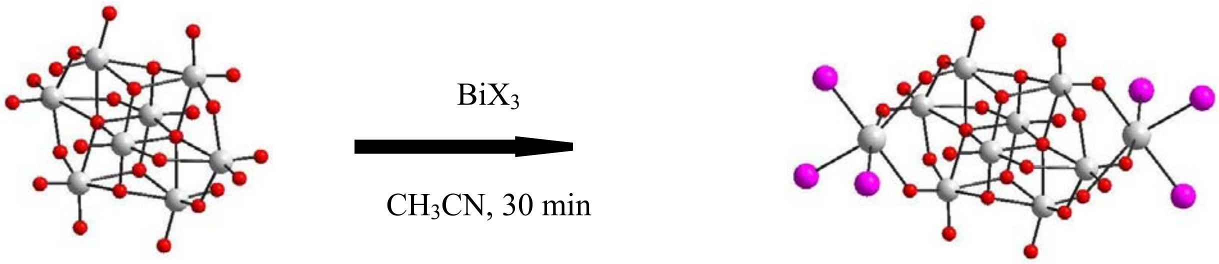
Reaction of BiI_3 and Bu_4NI in acetone leads to formation of a new octanuclear PIB complex, $TBA_4[\beta\text{-}Bi_8I_{28}]$ (**1**). As other PIBs, this compound displays strongly prominent thermochromic behavior. To explain its nature, a combination of physical methods (XRD and DSC) and computational studies has been used. We found that the key role is played by the system of weak intramolecular I...I interactions which dramatically changes with the temperature due to slight thermal distortions of the whole anion structure [1]:





The first PIB complex containing heterometallic octahedral unit, $[Bi_2PtI_{12}]^{2-}$ (**2**), has been obtained by reaction of $H_2[PtCl_6]$, NaI and BiI_3 [2]. The bonding was studied by DFT calculations.

Reactions of $(Bu_4N)_4[\beta\text{-}Mo_8O_{26}]$ with BiX_3 (X = Cl, Br, I) in CH_3CN lead to coordination of two BiX_3 fragments, yielding in family of hybride $[\beta\text{-}Mo_8O_{26}(BiX_3)_2]^{4-}$ polyoxoanions (**3-5**):



We suppose that **3-5** will display catalytic activity of in oxidation of organic substrates; corresponding experiments are underway.

[1] S.A. Adonin, M.N. Sokolov, P.A. Abramov et al., Chem. Eur. J. 2013, submitted
[2] S.A. Adonin, M.N. Sokolov, A.I. Smolentsev et al., Dalton Trans. 2013, accepted manuscript

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PECULIARITY OF THE LUMINESCENCE MECHANISM OF Sm(III), Eu(III) and Yb(III) COMPLEXES

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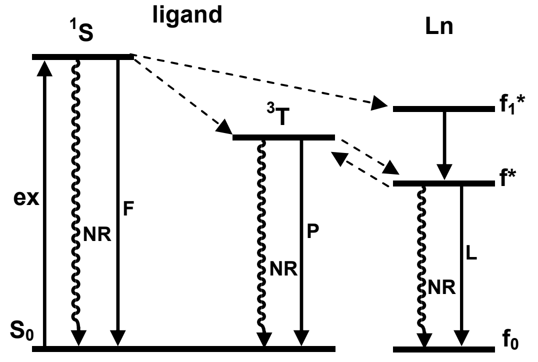
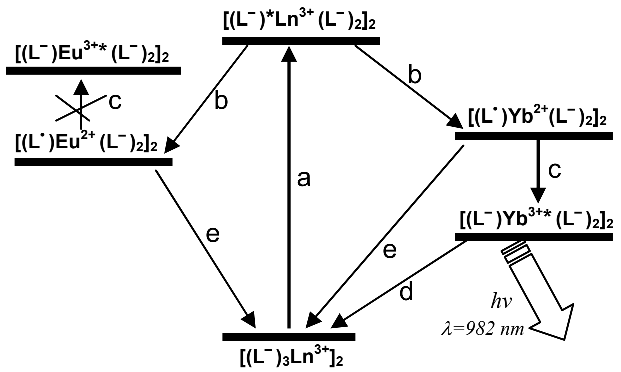
To describe the luminescence mechanism of organo-lanthanide complexes the well-known Jablonski-Crosby energy diagram usually is used (Fig. 1). The scheme is consistent with the vast majority of experimental data but it does not explain the hyperemission of Yb(III) and the lack of Eu(III) luminescence in some recently obtained complexes with substituted phenolate and naphtholate ligands.



(1)



(2)

Fig. 1. Conventional mechanism of sensitized emission of lanthanide complexes (singlet state **^{1}S**; triplet state **^{3}T**; excited state ***f****; fluorescence **F**; phosphorescence **P**; luminescence **L**; excitation **ex**; non-radiative pathways **NR**).

Fig. 2. Redox mechanism of luminescence of lanthanide complexes (ligand excitation **a**; electron transfer from the excited ligand to Ln(III) **b**; back electron transfer from Ln(II) to the radical L° with formation of excited Ln(III) **c**; relaxation and the metal-centered emission **d**;

The alternative mechanism of excitation of Ln(III) (Fig. 2) comprising the stages of Ln(III) reduction to Ln(II) and the reverse process of oxidation of Ln(II) to Ln(III) due to the electron transfer from divalent ion to the radical ligand provides such an explanation. The latter step in this pathway in the case of Yb derivatives results in the formation of excited Yb(III) ions. Since the parity forbidden f-f transitions in these processes do not prevent the formation of excited Yb (III)* ions the efficiency of luminescence is unusually high. The energy level of excited Eu(III) ions is significantly higher than that of Yb(III), which does not allow to reach the excited state Eu(III)* and to get the metal-centered emission. Taking into account the values of Ln(III)/Ln(II) redox potentials for Sm (-1.50 V), Eu (-0.34 V) and Yb (-1.18 V) as well as rather low energy level of Sm(III)* one can suppose that the excitation of metal ions in the samarium complexes also can be achieved through the mechanism of the intramolecular electron transfer according to the scheme on Fig. 2.

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MAGNETIC CONTROL OF THE DNA SYNTHESIS

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DNA synthesis is known to occur by polymerases, magnesium-dependent molecular machines, which attach nucleotide three-phosphate monomer molecule to the growing DNA chain. Chemical mechanism of the attachment was traditionally thought to be nucleophilic which does not imply participation of any spin-carrying, paramagnetic intermediates. By using polymerases β loaded by pure isotopic ions $^{24}Mg^{2+}$, $^{25}Mg^{2+}$ and $^{26}Mg^{2+}$ we have detected magnetic isotope effect: $^{25}Mg^{2+}$ ions with magnetic nucleus ^{25}Mg were shown to suppress enzymatic activity by 2-3 times with respect to that of polymerases β loaded by $^{24}Mg^{2+}$ and $^{26}Mg^{2+}$ ions. No difference in enzymatic activity was found between polymerases β carrying $^{24}Mg^{2+}$ and $^{26}Mg^{2+}$ ions with spinless, nonmagnetic nuclei ^{24}Mg and ^{26}Mg. The rate of DNA synthesis by polymerases β was also shown to exhibit magnetic field effect, in conformity with isotope effect. Polymerase chain reaction is also suppressed by $^{25}Mg^{2+}$ ions. Both isotope and magnetic field effects indicate that in the DNA synthesis a new, ion-radical mechanism functions and coexists with generally accepted nucleophilic one. Magnetic control of the DNA synthesis may be used for medical purposes to regulate trans-cranial magnetic stimulation, gene expression, cell proliferation, biological clocks, apoptosis of the cancer cells, and many other processes related to the molecular functioning of living organisms..

PROSPECTS OF SYNTHETIC ELECTROCHEMISTRY IN THE DEVELOPMENT OF UNUSUAL OXIDATION STATE METAL CATALYSTS FOR C-Cf AND P-Cf BONDS FORMATION REACTIONS AND HYDROGEN-EVOLVING ACTIVITY

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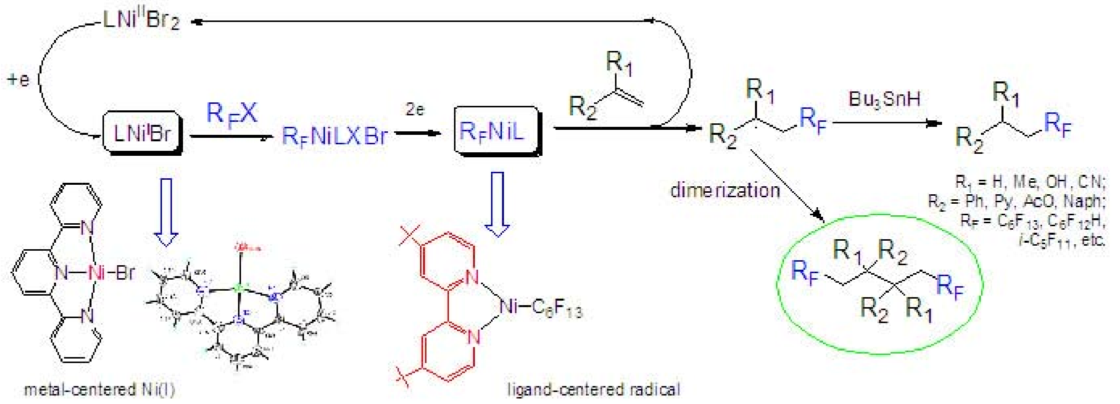
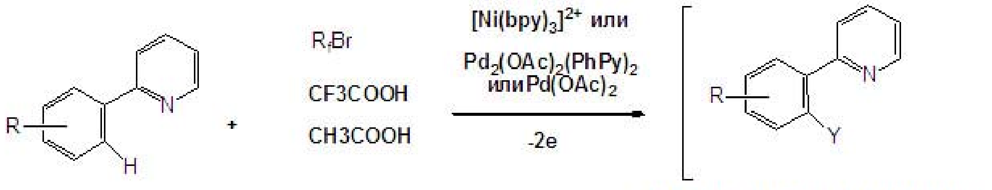
Achievements of electrosynthesis mediated by nickel and palladium complexes in unusual oxidation states will be demonstrated. Important advances are associated with the development of synthetic approaches to the C = C, C-Hal, P-Cl, P-P and C-H bonds functionalization in the one-step mild conditions. The leading role of electrochemistry in the development of biomimetic catalysts for oxidation of hydrogen in the coordination sphere of the complex or H_2 evolution will be discussed. The key intermediates, such as Ni(I)L, Pd (III)L(dimer or monomer complexes) and others have been detected and investigated.



$$PhBr + R_FI \xrightarrow{MX_2L,\ 2F} R_F\text{-}Ph$$

anode: Cu, Zn, Mg

L : 2,2'-bipyridine; terpyridine
2,9-dimethyl-1,10-phenanthroline;
4,4'-di-*tert*-butyl-2,2'-bipyridine; etc.



Y = Rf, CF3, OC(O)CH3, OC(O)CF3

Acknowledgements - *We thank Russian Foundation for Basic Research (grant N 13-03-97025, 13-03-00139, 11-03-92662) for the support of this work*

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SWITCHABLE MAGNETIC PROPERTIES IN PYRAZOLATE-BASED DI- AND TETRANUCLEAR COMPLEXES.

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Pyrazolate-based dinucleating ligands with thioether-containing chelate arms have been used for the synthesis of a family of novel dinuclear nickel(II) complexes $[LNi_2(N_3)_3]\cdot(solvent)_n$ that incorporate one bridging and two terminal azido ligands. Molecular structures have been elucidated by X-ray crystallography.

One of the complexes exists in form of different polymorphs. Two polymorphic modifications of the molecular dinickel(II) complex $[L^1Ni_2(N_3)_3]$ show thermal hysteresis of the magnetic susceptibility for single crystals, in which a $\mu_{1,3}$-bridging azido ligand functions as an on/off-switch for the intramolecular antiferromagnetic coupling between the two metal ions.

The switching function of the $\mu_{1,3}$-bridging azide is closely connected to the order/disorder of the thioether arms and can be even blocked by appropriate chemical modification. The investigation of pressure effects on the magnetic bistability of $[L^1Ni_2(N_3)_3]$ allows to shift the transition temperature more than 80 K towards higher temperatures.

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MULTIDECKER COMPLEXES OF RARE EARTH ELEMENTS WITH TETRAPYROLLIC LIGANDS: HOW MANY DECKS ARE POSSIBLE?

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The discovering of double-decker lanthanide sandwich complexes with unsubstituted phthalocyanine was made almost 50 years ago[1]. Over the years, the complexes of rare earth elements (lanthanides, except Pm, Y, Sc) with a variety of substituted macrocyclic tetrapyrrole ligands were synthesized[2,3]. These compounds are widely used as components of electrochromic displays, sensors, conductive materials, etc. In recent years a large number of triple-decker sandwich complexes containing two metal atoms and three tetrapyrrole ligands were investigated. Is it possible to further increase of decks numbers in sandwiches? Yes, it is possible in the case of weak non-covalent, supramolecular interactions. For, example, once the crown-ether groups are attached to the periphery of double- and triple-decker REE complexes, their properties can be tuned by molecular recognition of metal cations[4]. The report will be devoted to our recent investigations of elaboration of efficient and regioselective synthetic approaches towards heteroleptic crown-substituted REE complexes, including heterometallic complexes and their further thorough characterization (including studies of cation-induced assemblies)[5,6]. The approaches to the investigation of compounds in solution and solid state will be discussed[7-10]. Particular attention will be paid to the development of new functional materials based on the sandwich crownphthalocyaninates REE.

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SYNTHESIS, STRUCTURES AND UTILITY OF ORGANO-GALLIUM AND -INDIUM COMPLEXES WITH OXO AND THIO LIGANDS

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The chemistry of organo-gallium and -indium complexes with internally functionalised oxo-ligands and dithiolate has been explored. The reactions of triorgano-gallium and -indium etherate with a variety of internally functionalized oxo lignads such as anionic and dianionic Schiff bases [e.g., 2-hydroxy-Nsalicylideneaniline, 2-hydroxy-N-(2-hydroxy-3-methoxybenzylidene)aniline and 2-mercapto-N-salicylideneaniline] and benzoazole ligands [e.g., 2-(2′-hydroxyphenyl)-benzoxazole (Hhbo), 2-(2′-hydroxyphenyl)benzothiazole (Hhbt) and 2-(2′-hydroxyphenyl)benzimidazole (Hhbi)] yielded complexes of the types $[RML]_n$ and $[R_2ML]_n$ (where R = Me, Et; M = Ga, In; L = deprotonated oxo ligand) in nearly quantitative yields [1,2]. These complexes have been characterized by elemental analysis, IR, UV−vis, and NMR spectroscopy. Several of these complexes have been structurally characterized. The nuclearity of these complexes depends on the nature of the metal atom and the ligand. Some of the gallium complexes exhibited polymorphism. Photoluminescence studies of these complexes showed that the quantum yield is always higher than that of the corresponding ligands due to reduced intermolecular interactions in complexes as compared to free ligands. With 1,1-dithiolate ligands both classical and organometallic complexes of gallium and indium, $[M(S^\frown S)_3]$, $[RM(S^\frown S)_2]$ and $[R_2M(S^\frown S)]$ (where R = Me or Et; M = Ga or In; $S^\frown S$ = RCS_2, $ROCS_2$, R_2NCS_2 and $(RO)_2PS_2$) have been isolated. Indium dithiolate and selenolate complexes have been used as molecular precursors for the preparation of mono dispersed β-$In_2S_3$and In_2Se_3 nano-particles [3].

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COORDINATION CHEMISTRY OF 1,2-DICHALCOGENOLATO CARBORANE LIGANDS

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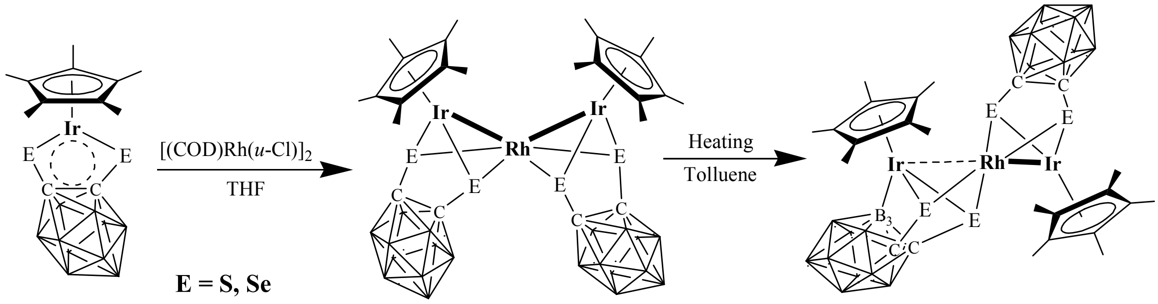
Half-sandwich transition metal complexes ($Cp*M$, $Cp* = \eta^5$-C_5Me_5) are useful model compounds [1] in which one hemisphere of the coordination shell is blocked by the voluminous Cp* rings. In the protected space below the Cp* ligands, 1,2-dichalcogenolate carborane ligands can be accommodated, e.q. 16-electron “pseudo-aromatic” mono-nuclear rhodium and iridium complexes $Cp*M(E_2C_2B_{10}H_{10})$ [2] (M = Rh, Ir; E = S, Se), and they can be used as starting materials to react with low valence transition metal complexes to give heteronuclear complexes, such as, binuclear complexes: $Cp*M[E_2C_2(B_{10}H_{10})]Fe(CO)_3$, $Cp*Rh[E_2C_2(B_{10}H_{10})]W(CO)_4$ and $Cp*Ir[E_2C_2(B_{10}H_{10})]Rh(COD)$ (M = Rh, Ir; E = S, Se), tri-nuclear complexes $\{Cp*M[E_2C_2(B_{10}H_{10})]\}_2Mo(CO)_2$, $\{Cp*M[E_2C_2(B_{10}H_{10})]\}_2W(CO)_2$ and $Cp*M[E_2C_2(B_{10}H_{10})]$ $[CO(CO)_3]_2$, tetra-nuclear complexes: $Cp*_2Rh_2[E_2C_2(B_{10}H_{10})]_3Rh_2(CO)$, $\{Cp^*Ir[E_2C_2(B_{10}H_9)]\}$ $Rh_2(COD)\{Cp^*Ir[E_2C_2(B_{10}H_{10})]\}$ which contain metal-metal bonds.



$Cp*Ir(E_2C_2B_{10}H_{10})$ reacts with $[(COD)RhCl]_2$ to form cis-$\{Cp^*Ir[Se_2C_2(B_{10}H_{10})]\}_2Rh$ and In refluxing toluene solution, the cisoid complex can be converted in more than 95% yield to corresponding transoid trans-$\{Cp^*Ir[Se_2C_2(B_{10}H_9)]\}Rh\{[Se_2C_2(B_{10}H_{10})]IrCp^*\}$ which contains a boron-iridium bond.

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ACTIVATION OF THE HYDROPEROXIDES FORMATION AND DECOMPOSITION BY THE 3D METALS MONO- AND POLYNUCLEAR CARBOXYLATES AND CARBOXYLATE-PYRAZOLATES

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In the recent years, an active discussion about the analogy between pyrazolates and carboxylates metal complexes and, first of all, their chemical and magnetic properties (for example, see [1]), takes place.

In this presentation, on the examples of the cyclohexene (CH) and the dibenzyl ether (DBE) liquid phase oxidation by air oxygen and hydrogen peroxide (H2O2), and transformations of the corresponding hydroperoxides and H2O2 decomposition, the catalytic properties of more than hundred mono- and polynuclear and homo- and heteroligand carboxylate, pyrazolate and carboxylate-pyrazolate complexes of Co, Cu, Ni, Zn, and Pd were examined.

It is shown that the growth of Co complexes nuclearity, generally leads to an increase of the rate and depth of CH oxidation and the selectivity of products of its hydroperoxide (HPCH) further transformations. The close connections between the rates of HPCH decomposition and formation, as well as the H2O2 decomposition in the presence of the studied complexes were revealed and suggested that in these cases the formation and the gap of the O-O bonds takes place on the same "catalytic sites".

The catalytic properties of the complexes with metal cores MPd or M_2Pd in the DBE oxidation, to a first approximation, are similar to those of the corresponding complexes with the cores M_2 and M_3.

Two groups of the catalysts of DBE alternative routes oxidation, its hydroperoxide (HP) decomposition and the benzaldehyde (BAld) and benzoic acid (BAc) formation were identified.

The complexes of Cu, Fe, Co and Pd with DBE, BAld and BAc formed by oxidation of DBE, are first isolated and identified by XRA. The possible mechanisms of these complexes formation and their role in the studied processes are discussed. An attempt was made by the QSPR approach to reveal the key factors of the studied complexes’ structure and composition, determinant their catalytic properties.

In the case of complexes with metal cores Pd, CuPd, NiPd, Cu_2Pd and Co_2Pd, the dependences between the rate of H_2O_2 decomposition and concentrations of substrate and catalyst (CAT) have an extreme character, which indicates a substantial passivation of the catalytic system at a certain ratio H_2O_2:Cat. For complexes with composition $Cu_2(\mu\text{-Piv})_4L_2$ the nature of terminal ligands (L) significantly influences the activation energy of H_2O_2 decomposition ($NEt_3 < CO(NH_2)_2 < PCy_3 < MeOH < PPh_3 < Hdmpz < OPPh_3$), whereas for the complexes with composition $Co_2(Piv)_4L_2$ this tendency is virtually nonexistent.

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TRANSITION METAL COMPLEXES OF 1,5-DIAZA-3,7-DIPHOSPHACYCLOOCTANES AS A PROMISING BASIS OF BIOINSPIRED MIMETIC CATALYSTS.

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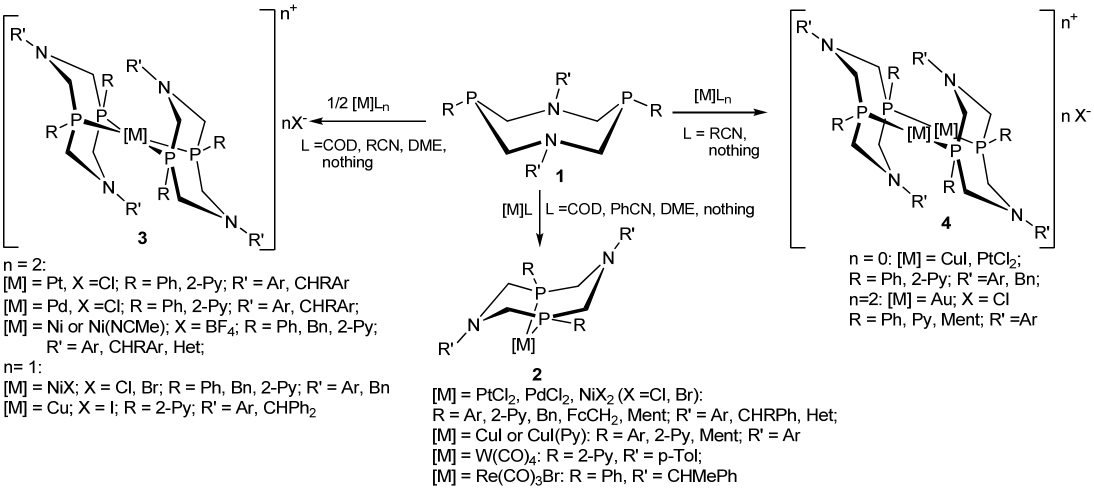
During the last two decads 1,5-diaza-3,7-diphosphacyclooctanes attracted a steady attention as available P,P-chelating ligands possessing relative conformational rigidity [1], and the recent discovery of electrocatalysts of hydrogen evolution and hydrogen oxidation among their nickel (II) complexes inspired a renaissance of the chemistry of these heterocycles containing intramolecular amines that mimic the function of hydrogenase enzymes[2]. The present survey of the coordination chemistry of 1,5-diaza-3,7-diphosphacyclooctanes **1** shows the possibility of the targeted design of their transition metal complexes of various structures which possess the desired properties. Main types of these complexes are P,P-chelate monoligand (**2**) and bis-P,P-chelate bis-ligand complexes **3**[1-3], but recently the varying of exocyclic groups of the ligands and the metals allowed to obtain cage binuclear complexes **4** where diphosphines **1** are bridging ligands.



n = 2:
[M] = Pt, X =Cl; R = Ph, 2-Py; R' = Ar, CHRAr
[M] = Pd, X =Cl; R = Ph, 2-Py; R' = Ar, CHRAr;
[M] = Ni or Ni(NCMe); X = BF_4; R = Ph, Bn, 2-Py; R' = Ar, CHRAr, Het;
n= 1:
[M] = NiX; X = Cl, Br; R = Ph, Bn, 2-Py; R' = Ar, Bn
[M] = Cu; X = I; R = 2-Py; R' = Ar, $CHPh_2$

[M] = $PtCl_2$, $PdCl_2$, NiX_2 (X =Cl, Br):
R = Ar, 2-Py, Bn, $FcCH_2$, Ment; R' = Ar, CHRPh, Het;
[M] = CuI or CuI(Py): R = Ar, 2-Py, Ment; R' = Ar
[M] = $W(CO)_4$: R = 2-Py, R' = p-Tol;
[M] = $Re(CO)_3Br$: R = Ph, R' = CHMePh

n = 0: [M] = CuI, $PtCl_2$;
R = Ph, 2-Py; R' =Ar, Bn;
n=2: [M] = Au; X = Cl
R = Ph, Py, Ment; R' =Ar

The introduction of pyridyl substituents to phosphorus atoms of complexes **3** ([M]=Ni [4a]) allowed to increase their catalytic activities in electrochemical hydrogen evolution [4b]; the testing of these complexes in fuel cells showed the increase of the cell power up to 55% [4b]. These results indicate the unexausted potential of 1,5-diaza-3,7-diphosphacyclooctanes ligands and the necessity of a wide screening of their metal complexes in various catalytic and electrocatalytic reactions.

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FUNCTIONAL POROUS COORDINATION POLYMERS OF 3d METALS: MAGNETIC, SORPTION AND REDOX PROPERTIES

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Porous coordination compounds (PCPs) of 3d metals are considered as promising objects for creation of functional materials, such as materials with tunable magnetic properties, selective sorbents or catalysts of different reactions. In contrast to porous materials of other classes, the structure of PCPs can be easily modified and certain functional groups can be included, which opens the way for creation of compounds, possessing desired properties.

The presentation contains the results of studies of three groups of PCPs:

- compounds, bearing chiral centers, which show different absorption of optical isomers;
- polymers, containing redox-active sites, which show electrocatalytic activity in dehalogenation of organic substrates;
- compounds which magnetic properties can be modified by thermal treatment.

Chiral PCPs $Co(L1)(CH_3OH)(H_2O)$ (H_2L1 = bis-2,4-(N-S-prolyl)-6-chlorotriazine), $[Li(H_2O)(EtOH)][Fe(Lact)(LactH)_2]$, $[Na(H_2O)_2][Fe(Lact)(LactH)_2]$ (H_2Lact = S-lactic acid), $Co_2(H_2O)(L2)(pyridine)_4$ (H_2L2 = *trans*-1R,2R-cyclopropanedicarboxylic acid) were synthesized. X-ray structures of these compounds were determined. Sorption of pure isomers of 2-S-butanol and 2-R-butanol by these complexes was studied. Analysis of sorption/desorption isotherms allowed to show the differences in interaction with these substrates.

PCPs with redox-active sites $\{Fe_2MO(Piv)_6\}\{M'L_2\}_{1,5}$ were prepared by linking of trinuclear complexes $Fe_2MO(Piv)_6$ with mononuclear compounds $M'L_2$ (M = Ni, Co; M' = Co, Ni; Piv = pivalate, L = Schiff base from isoniazide and 2-pyridinecarbaldehyde). It was shown by cyclic voltammetry (CVA), that $M'L_2$ fragments could undergo reversible one-electron process $M'L_2^{0/-1}$ both in corresponding discrete complexes (in solutions) and being incorporated in PCPs (in suspensions). The cathodic current of this process grew at presence of halogen-containing substrates ($CHCl_3$ or CF_2Cl-$CFCl_2$), which could evidence for electrocatalytic dehalogenation of these compounds.

Due to co-existence of paramagnetism and ability to exchange volatile ligands or guest molecules, magnetic properties of PCPs can be modified. It was shown that magnetic properties of several PCPs ($Co(L1)(CH_3OH)(H_2O)$, $Co(Piv)_2(4\text{-}ptz)(EtOH)_2$ and some others, where 4-ptz = tris-(4-pyridyl)triazine) significantly changed in the whole temperature range from 2 to 300 K upon their thermal desolvation.

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HETEROLIGAND LANTHANIDE COMPLEXES WITH REDOX-ACTIVE LIGANDS: A REPORT ABOUT RECENT RESULTS

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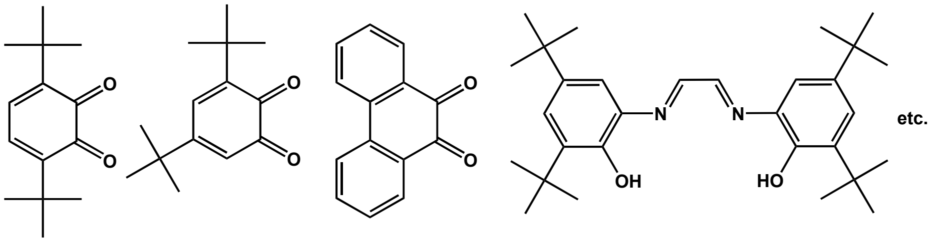
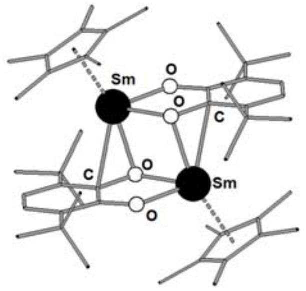
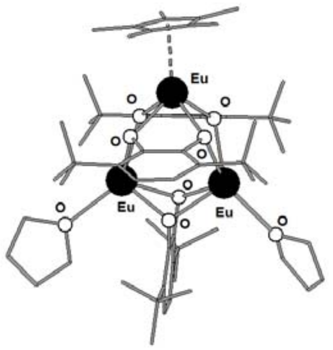
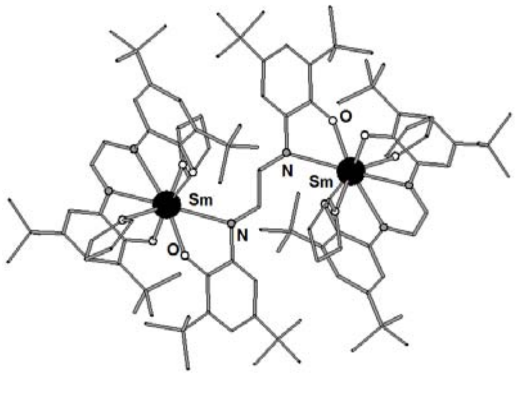
The report is focused on reactions of a few Ln(II) and Ln(III) complexes (lanthanocenes, amides and diimine complexes) with a number of quinones (both in neutral and reduced anionic forms) and their derivatives kindly granted by colleagues from IOMC RAS:



The reactions were found to cause different redox processes and lead to the compounds with different coordination modes depending on the nature of Ln and other ligands. Some of the compounds obtained are represented below:







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MULTIFUNCTIONAL CYANO-BRIDGED COORDINATION POLYMERS

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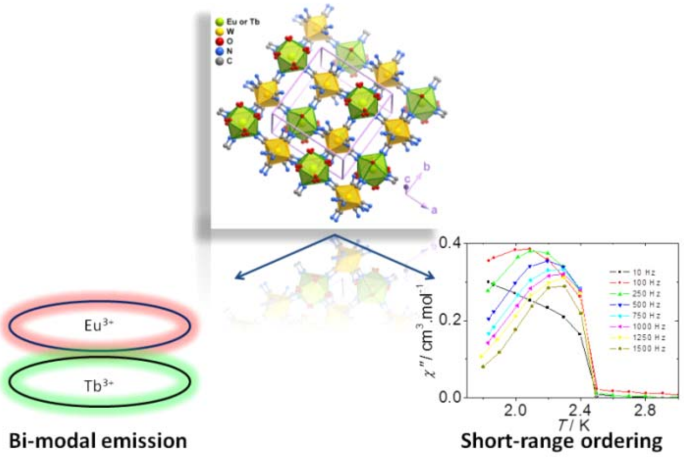
In the scope of multifunctional molecular materials, magneto-luminescent coordination polymers constitute a new class of promising materials for numerous applications such as telecommunications or luminescent imaging.

In this regard, cyano-bridged coordination polymers incorporating lanthanide ions can exhibit strong magnetic interaction between the spin carriers as well as high magnetic anisotropy. In addition, the lanthanide ions can also exhibit strong luminescence with well-resolved emission bands and long lifetimes.

The self-assembly reaction between the paramagnetic cyanometallate core $[M(CN)_8]^{3-}$ (M = Mo, W) and a lanthanide ion Ln^{3+}, yields to a bi-dimensional $Ln(H_2O)_n[M(CN)_8]$ coordination network presenting a long-range ordering and the characteristic luminescence of the lanthanide ion.[1] In order to enhance the luminescence properties, it is possible to introduce antenna ligand in the coordination sphere of the lanthanide ion yielding to a one-dimensional coordination polymer emitting in the Near-Infra Red region. [2]



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HOMO- AND HETERONUCLEAR TRANSITION METAL COMPLEXES PRODUCED BY DEPROTONATION OF PYRAZOLE AND ITS ANALOGUES

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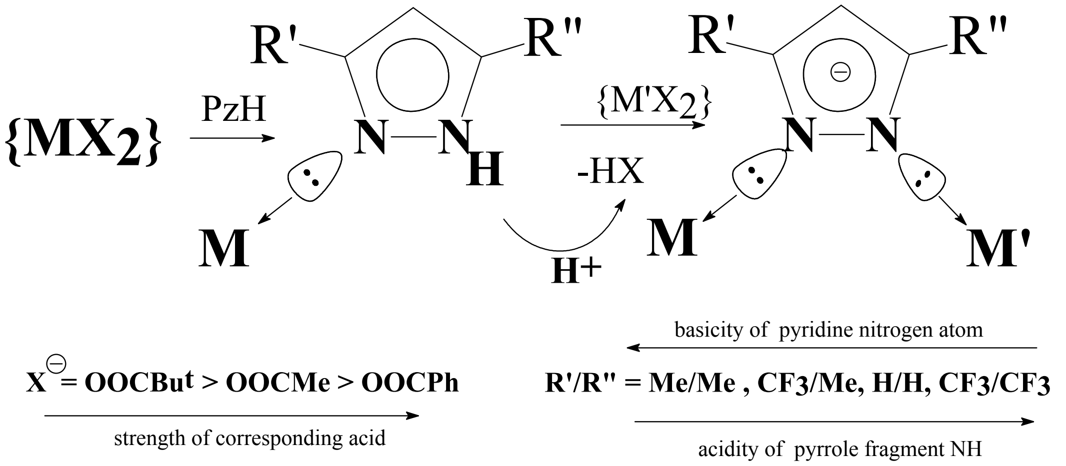
Systematic studies of reactions of pyrazole and its analogues with carboxylates of 3d transition metals, palladium and platinum are presented. Key point in these reactions is the deprotonation of the pyrrole NH fragment. The pyrazolate anion that formed coordinates the metal atoms, producing pyrazolate-bridged homo- or heterometallic compounds. The composition and structure of the complexes obtained are determined by the metal nature, donor ability of the carboxylate anion and R’, R” groups at 3,5 position of the pyrazole cycle.



Acknowledgements- This work was supported by RFBR (projects 11-03-00824, 11-03-01157, 12-03-31339, 13-03-90412) and the Presidium of the Department of Chemistry and Materials Science, Russian Academy of Sciences, and the Council for Grants of the President of the Russian Federation (MK-4452.2013.03)

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CHEMICAL DESIGN OF CHALCOGEN-CONTAINING ORGANOMETALLIC CLUSTERS

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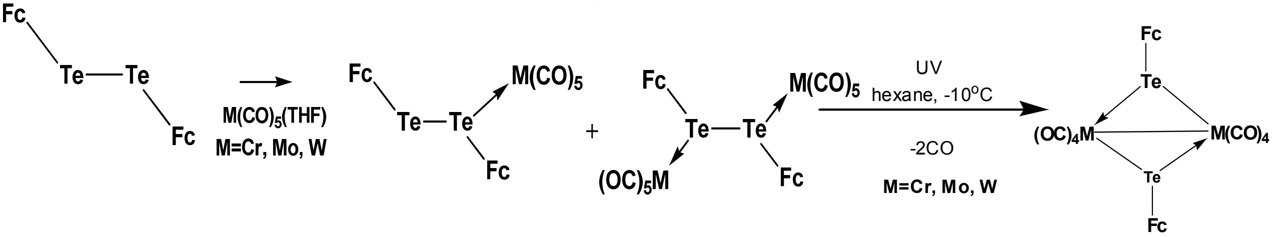
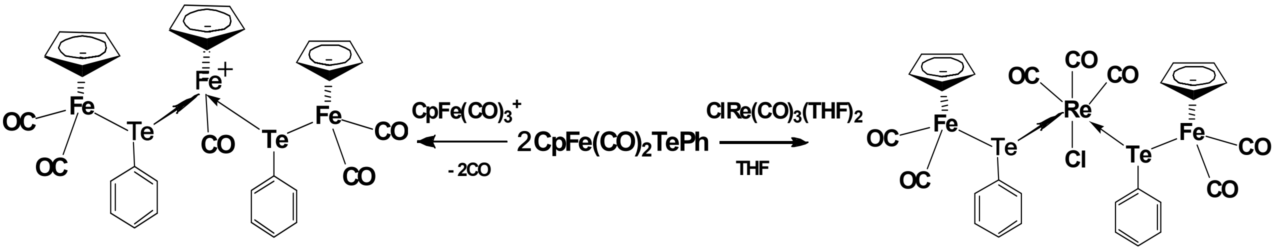
The chalcogen-containing organometallic complexes were used as ligands to complexes of different transition metals (M). X-Ray analyses data showed the common features: a) sharp shortening (from 0.15 to 0.3 A) of formally ordinary M-E bonds (E = S, Se, Te) and M-P bonds[1] compared to the covalent radii sum (CRS) [2] ; b) electron-compensating rearragment of clusters.

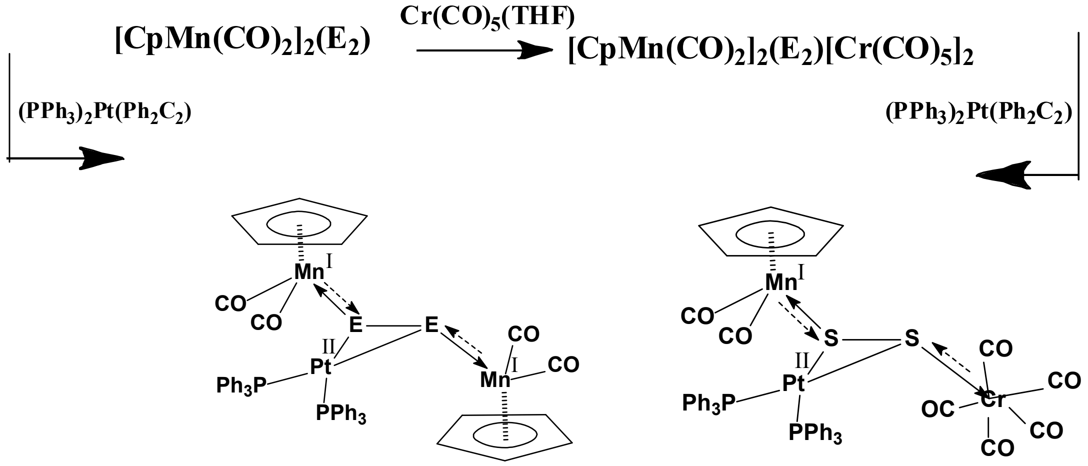
1. The coordination of Fc_2Te_2 (Fc – ferrocenyl) and dissociation of Te-Te bond:



2. The coordination of $CpFe(CO)_2TePh$.



3. The coordination and transmetallation of $[CpMn(CO)_2]_2E_2$ (E = S, Se, Te)



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SLOW MAGNETIC RELAXATION AND PHOTO-INDUCED ELECTRON TRANSFER IN TETRATHIAFULVALENE-BASED COMPLEXES OF LANTHANIDES

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Lanthanide complexes exhibit magnetic hysteresis and luminescence with very long lived excited state lead to potential application in quantum computing, spintronic, OLED, biomedical imaging…[1][2] Our approach consists in the combination of Dy(III) and Yb(III) ions to redox active Tetrathiafulvalene (TTF) ligands to elaborate Single Molecule Magnet (SMM) and Single Ion Magnets (SIM) involving multi physical properties.

[Dy(hfac)$_3$(**L**^{1})] (**L**^{1} = 4,5-bis(propylthio)-tetrathiafulvalene- 2-(2-pyridyl)benzimidazole) displays a SIM behaviour only in solution while [Dy(hfac)$_3$(**L**^{2})] (**L**^{2} = 4,5-bis(propylthio)-tetrathiafulvalene- 2-(2-pyridyl)benzimidazole-methyl-2-pyridine) is a SIM in both solution and solid-state. The SIM behaviour is obtained if the hydrogen bond is broken by dissolution or by alkylation. Multiple relaxation processes were identified for [Dy(hfac)$_3$(**L**^{2})] with two competing processes: fast one acting in zero field and slow one acting for high field. Both processes cohabit for intermediate field. Magnetic dilution and frozen solution measurements drive us to conclude that the origin of these multiple relaxation processes is not due to the property of one single molecule.[3]

Irradiation in the intra-ligand charge transfer bands provoked the Yb(III) luminescence in both [Yb(hfac)$_3$(**L**^{n})] complexes. The alkylation enhanced the two intensity and lifetime of the Yb(III) luminescence. The shape of the Yb(III) luminescence spectra is directly correlated to the energy splitting of the M_J states coming from the $^2F_{7/2}$ multiplet ground state. Yb(III) luminescence process can involved a photo-induced electron transfer from the excited **L**^{n} chromophores to the Yb(III) ion making them good candidates for photo-induced conduction.[4]

Finally, we will show through the study of a redox-active luminescent single molecule magnet that the two infrared-luminescence and dynamic magnetic properties can be correlated.[5]

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CHEMISTRY OF BORON HYDRIDES ORCHESTRATED BY DIHYDROGEN BONDS

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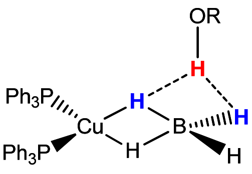
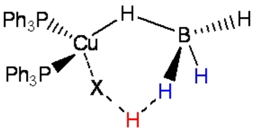
An increasing application of polyhedral boron compounds in medicine induced the intensive investigations of their interaction with biomolecules. One type of such interactions determining the polyhedron behavior *in vivo* is hydrogen bonding of polyhedral boron compounds with acidic and basic sites of biomolecules. The results of systematic investigation of intermolecular interactions of boron compounds – borohydrides, their derivatives containing organometallic fragments, carboranes, metallocarboranes, aminoboranes with different proton donating and proton accepting centers (hydrogens of B-H, C-H groups in polyhedron, OH, NHR substituents) will be presented in this communication [1-3]. Transition metal coordination compounds containing the borohydride ligand as BH_4 or LBH_3 (L = amine, phosphine) possess many valuable properties and useful applications. Thus, they have been used as selective reducing agents, as building blocks for the synthesis of new organometallic derivatives, as precursors for the production of borides, hydrides and other inorganic materials, as well as in hydrogen production. Herein we report on the reactivity of a variety of metal complexes, *i.e.* $[(R_3P)_2Cu(\eta^2\text{-}BH_4)]$, $[(\text{triphos})Cu(\eta^1\text{-}BH_4)]$, $[(\text{triphos})RuH(\eta^2\text{-}BH_4)]$, $[(PP_3)RuH(\eta^1\text{-}BH_4)]$ ($PP_3 = \kappa^4\text{-}P(CH_2CH_2PPh_2)_3$, triphos = $\kappa^3\text{-}CH_3C(CH_2PPh_2)_3$) and $[Ir(PCy_3)_2(H)_2(\eta^2\text{-}H_2B(H)NR_3)]^+$ $[BAr_4^F]^-$ complexes (R = H, alkyl) as well as of simple boron hydrides (BH_4, BH_3NR_3) towards mono and bidentante XH acids of different strength. It was studied by variable-temperature IR, UV-vis and NMR spectroscopies in low polar solvents (CH_2Cl_2, THF) in combination with DFT calculations. Availability of several types of hydride ligands (MH, BH^{term}, BH^{br}) leads to multiplicity of reaction intermediates (mono-, bi- and trifurcate DHB complexes).The influence of coordination to the metal on the BH proton accepting ability mechanism of the reactions involving proton transfer as a key step will be discussed. Crutial role of additional Lewis acidic centers in the reactivity of transition metals borohydride complexes will be shown.



DHB



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Acknowledgment: This work was supported by Russian Foundation for Basic Research (projects 12-03-33018, 13-03-00604 and 12-03-31176)

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3. O. A. Filippov, N. V. Belkova, L. M. Epstein, E. S. Shubina *J. Organometal Chem*, **2013**

THERMALLY AND LIGHT INDUCED PHASE TRANSITION IN Cu(hfac)$_2$ COMPLEXES WITH *tert*-BUTYLPYRAZOLYLNITROXIDES

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A. Bogomyakov, R. Sagdeev and V. Ovcharenko

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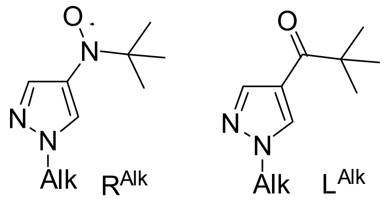

Alk = Me, Et, Pr

We succeeded in the synthesis of Cu(hfac)$_2$ polymer-chain complexes with *tert*-butylpyrazolylnitroxides (R$^{\mathrm{Alk}}$). It was found that temperature variation leads to switching of complexes [Cu(hfac)$_2$R$^{\mathrm{Me}}$]$_n$ and [Cu(hfac)$_2$R$^{\mathrm{Et}}$]·0.5Solv (Solv = C_6H_{14}, C_7H_{16}) between two structural and spin states: (**A**) elongated CuO$_6$ octahedral units with axial Cu1-O1 distances, weakly exchange-coupled heterospin clusters, (**B**) elongated CuO$_6$ octahedra with equatorial Cu1-O1 distances, strongly exchange-coupled heterospin clusters. Illumination of [Cu(hfac)$_2$R$^{\mathrm{Me}}$]$_n$ with light (λ~540 nm) at cryogenic temperatures leads to switching of the clusters from the spin state **B** to **A**, which relax to the ground state on a timescale of hours.

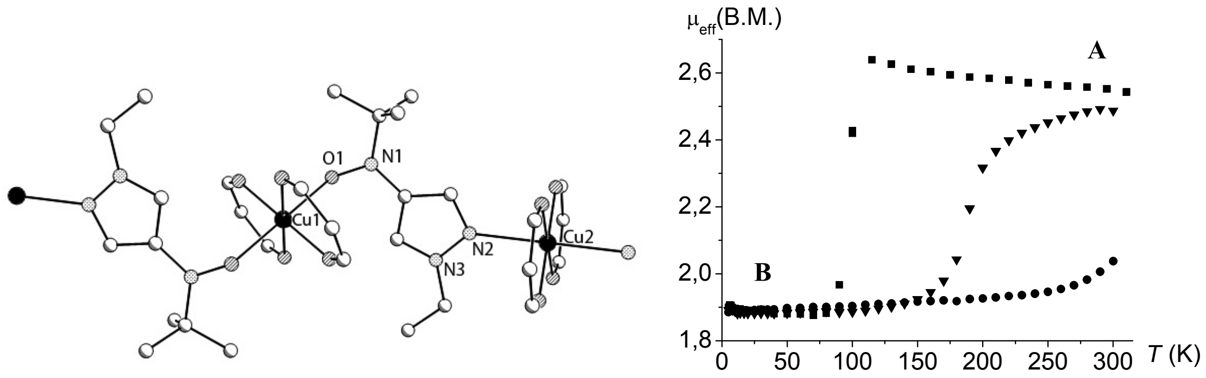

Figure 1. Fragments of the [Cu(hfac)$_2$(R$^{\mathrm{Et}}$)]$_n$ chains and experimental dependences $\mu_{\mathrm{eff}}(T)$ for [Cu(hfac)$_2$(NPz$^{\mathrm{Me}}$)] (■), [Cu(hfac)$_2$(NPz$^{\mathrm{Et}}$)]·0.5C_7H_{16} (▼), [Cu(hfac)$_2$(NPz$^{\mathrm{Pr}}$)] (●) at 1.0 T.

Contrary to the complexes [Cu(hfac)$_2$R$^{\mathrm{Alk}}$]$_n$, their structural analogs with diamagnetic ligands L$^{\mathrm{Alk}}$ do not undergo rearrangements in the copper(II) coordination environments. This confirms experimentally the crucial role of paramagnetic ligands and exchange interactions between them and Cu(II) ions for the origin of magneto-structural anomalies in this family of molecular magnets.

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ORGANIC LIGHT EMITTING DIODES AND INORGANIC QUANTUM DOTS

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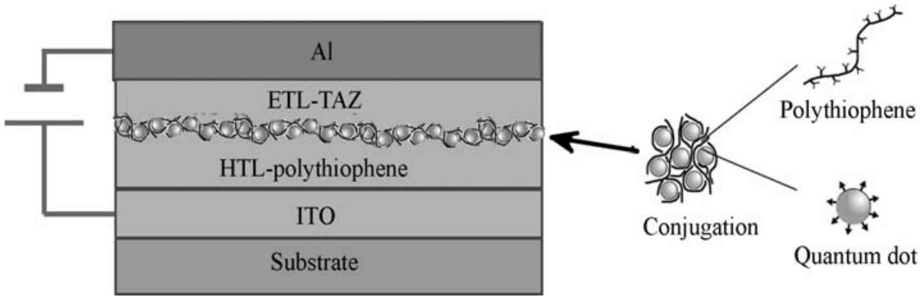
Currently there are intensive studies of new composite nanomaterials, as well as photonic and optoelectronic devices based on hybrid nanostructures [1, 2]. This report presents results of investigations of organic light-emitting diodes (OLED) with colloidal semiconductor quantum dots CdSe / CdS and CdSe / CdS / ZnS used as light emitters. We theoretically demonstrated a strong influence of quantum effects on spectral and electronic properties of device. Namely, there is a strong increase of energy transfer rate from excited state of organic molecules to quantum dots on decrease of either CdSe nanocrystal core diameter or CdS shell thickness. Decreasing of CdS core size from 5 to 3 nm leads to the transfer rate increase by an order of magnitude.

Based on the theory, we fabricated a novel type of hybrid nano-emitters - a mixture of multilayer CdSe / CdS / ZnS quantum dots in conjunction with specially synthesized conductive polymers. The polymers having bithienyl fragment were additionally modified with amino groups. Such a composition provides good complex formation and allows to fabricate highly uniform thin films. Finally, the quantum dots linked with polythiophene derivatives exhibit bright electroluminescence when embedded in organic light emitting diodes. Results of these investigations are presented.



Besides that we investigated bare-core CdS semiconductor nanocrystals with an average diameter 4.5 nm, which were passivated with oleic acid. Photoluminescence spectra measured with 405 nm laser excitation exhibit strong luminescence of surface states. Further investigations to find out an origin of the luminescence are presented and discussed. It is concluded that surface state luminescence offers an opportunity to fabricate white light organic light emitting diodes, where narrow emission of interband recombination in quantum dot is accompanied with broad luminescence of defect states.

The results of our research demonstrate the possibility of effective control the spectral characteristics and energy transfer rates in nanophotonic devices based on semiconductor quantum dots embedded into organic matrix.

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Acknowledgements -
The work was supported by LLC "OPTOGAN - Organic light solutions," contract number 45, and partially supported by RFBR, grant 12-03-00839-a
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Synthesis & Reactivities of Divalent and Trivalent Nickel Complexes Based on Pincer Ligands

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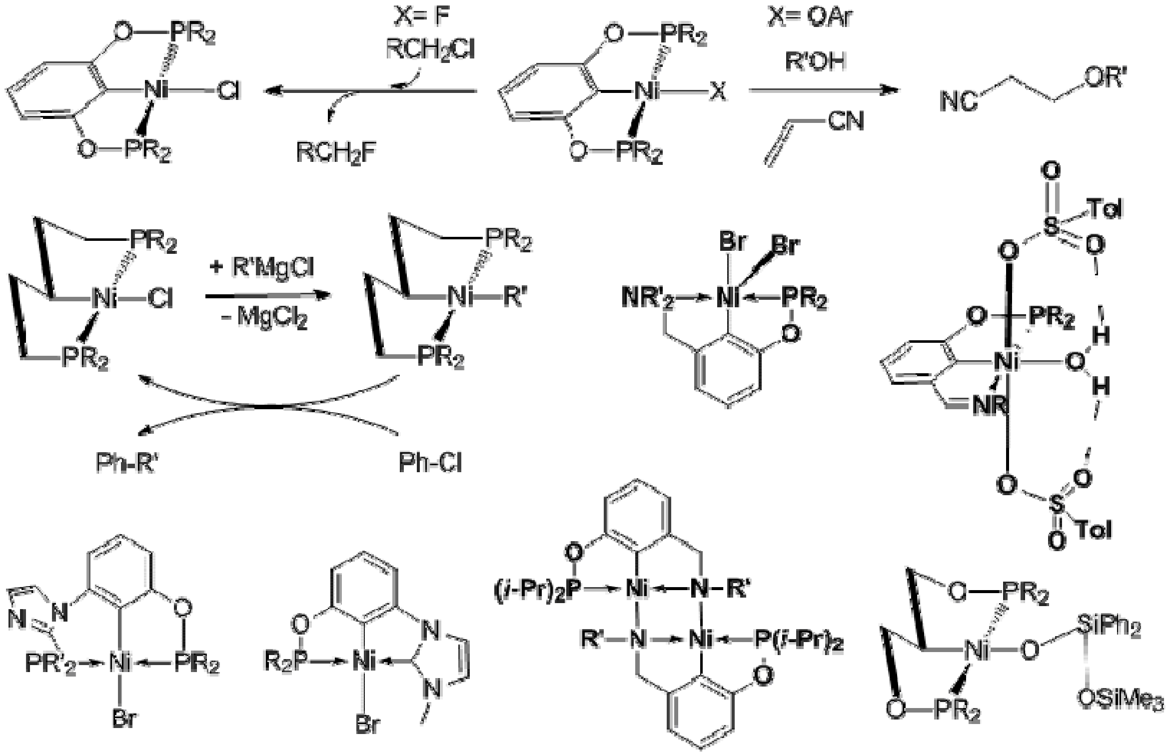
Many pincer complexes have found applications in catalysis thanks to their enhanced thermal stabilities and the novel reactivities they promote. Our group has introduced a variety of pincer-type nickel complexes based on symmetrical or unsymmetrical ligands featuring amine, imine, phosphine, phosphinite, imidazolophosphine, imidazoliophosphine, or NHC-carbene donor moieties. Some of these complexes show good thermal stabilities and promote interesting reactivities, including Kumada coupling, alcoholysis and amination of acrylonitrile, fluorination of alkyl chlorides, and hydrosilylation of olefins, alkynes, and carbonyl substrates. This presentation will describe the synthesis, structures, and reactivities of divalent and trivalent pincer complexes of Ni.



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Oral Presentations

SOME HIGH COORDINATION COMPOUNDS OF LANTHANIDES(III) DERIVED FROM SCHIFF BASES

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Initially coordination chemistry of lanthanides was limited to strongly chelating ligands with oxygen as donor atom. With the development of new complexing compounds, a significant number of lanthanide complexes with various types of ligands were synthesized and characterized. The chemistry of metal complexes with heterocyclic compounds containing nitrogen, sulfur and oxygen as complexing ligands has attracted increasing attention. These compounds are worth attention for many reasons due to their biological activities while many drugs involve heterocycles, sulfur, oxygen, nitrogen, amino-nitrogen, azomethine-nitrogen and alcoholic or phenolic-oxygen are some of the donor atoms of interest. Pyrazolones (N-heterocyclic compounds) is an active moiety as a pharmaceutical ingredient, especially in non-steroidal anti-inflammatory agents used in the treatment of arthiritis and other musculoskeletal and joint disorders. Earlier work reported that some drugs showed increased activity when administered as metal-chelates rather than as simple organic compounds.

Lanthanides constitute an interesting group of 15 elements with similar physico-chemical properties which change periodically with the atomic number. Lanthanide compounds frequently have magnetic, catalytic and optic properties and therefore they are widely used in industries. In recent years new experimental methods have been developed due to which new data on the role of lanthanides in the biochemical processes operating in cellular membranes organelles and cytoplasm have been obtained. The coordination compounds formed by lathanides(III) generally display the coordination number varies from six to twelve with different geometries. In present lecture, the author reports the summary of the work mostly carried out in our laboratory on lanthanide(III) complexes of Schiff bases derived from 4-aminoantipyrine and their properties.

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OXYGEN-FREE CONVERSION OF METHANE

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One of the most intriguing goals of specialists working in catalysis is to convert methane into valuable and transportable chemicals. Aside from oxidative rearrangements some successful attempts to upgrade methane into higher hydrocarbons have been reported in the last few years.

We have employed the metal vapor method (MVM) for design of the novel catalytic materials containing on the support surfaces different combinations of layered transition metals (Ni, Co, Re, Rh, Ru, Pt, and Mo) on their atomically dispersed state. As established in our laboratory, MVM-prepared catalysts possess high C-H and C-C bond insertion ability, which causes the hydroconversion of hydrocarbons under very mild temperatures (400-480K). Here we describe and discuss the results of non-oxidative conversion of methane over MVM-prepared catalysts.

Methane reacts with the most of MVM-prepared catalysts under mild conditions (normal pressure, 450-570K). In the first stage of interaction, methane forms CHx species on the catalyst surface, which can be condensed into C_2-C_6 alkanes at the same temperature range by hydrogen treatment. Combination of Ru with Re and Pt gave best results. Coupling of the accumulated on the catalyst surface CHx species can be promoted also by passing a mixture of $CO+H_2$ through the catalyst. The selectivity of the methane coupling process can be regulated by the reaction temperature and nature of the active metals.

Increasing the reaction temperature up to 973-1073K causes the one stage catalytic conversion of methane. Benzene was the main reaction product (85-95%) along with small amounts of ethylene, ethane, and toluene. Among the studied MVM-prepared catalysts Mo-ZSM-5 systems were the most effective. Methane conversion on these catalysts achieved up to 7-7.5%. Activity and stability could be improved significantly by modification of Mo-ZSM-5 samples by other metals such as Co, Re, Ru, Rh and Pt. This reaction seems to be one of the promising routes for practical utilization of methane.

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SYNTHESIS AND LUMINESCENT PROPERTIES OF IRIDIUM-CONTAINING NORBORNENE-BASED COPOLYMERS

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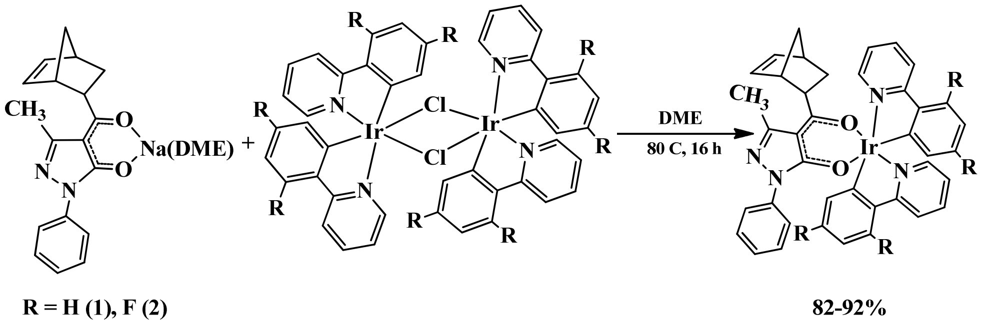
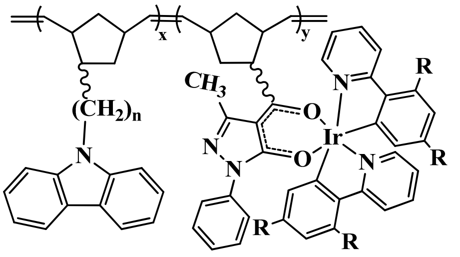
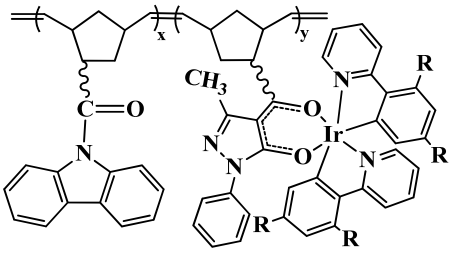
Iridium(III) compounds have attracted considerable attention due to their efficient electroluminescent properties. In the present work novel phenylpyridine Ir(III) complexes with norbornenyl-substituted pyrazolonate ancillary ligands were synthesized and structurally characterized:



Compound **1** and **2** were copolymerized with carbazole-functionalized norbornene by ring-opening metathesis polymerization.



n = 1, 5
x : y = 8 : 1



Photoluminescent spectra of synthesized Ir(III)-containing copolymers consist of broad bands in the region of 483-522 nm assigned to metal to ligand charge transfer transition. The relative quantum yields were found to be in the range of 1.0-8.4 %.

Light-emitting diodes with the configuration of ITO/Ir(III)-copolymer/BATH/Alq_3/Yb produced yellowish-green light. Maximum brightness of 986 cd/m^2 and current efficiency of 2.20 cd/A were reached.

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FINE-TUNING OF CAGE-LIKE METALLASILOXANES SYNTHESIS. PECULIARITIES OF STRUCTURES AND MAGNETIC PROPERTIES.

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The phenomenon of cage-like metallasiloxanes synthesis’ fine tuning was established. It was found that changing of solvents system and/or stoichiometric (“magic”) ratio between interacted polyphenylmetallasiloxane and sodium phenylsiloxanolate gave an opportunity of isolation of cardinally different in their structure cage products. Determination of structural features and stacking’ style of cages in crystal lattice (which is strongly depends on nature of solvates used) were made by the X-ray. Peculiarities of molecular magnetism of synthesized cages (including first observation of single molecular magnet behaviour for cage-like metallasiloxanes) were studied in details.

This work was supported by the Russian Foundation for Basic Research (grant No. 11-03-00646)

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ELECTROLUMINESCENT PLATIMUM-CONTAINING COPOLYMERS ON THE BASE OF FUNCTIONALIZED NORBORNENE MONOMERS

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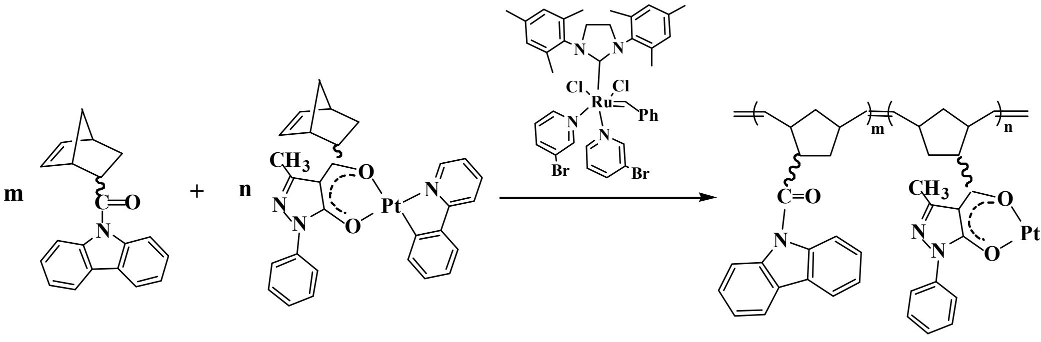
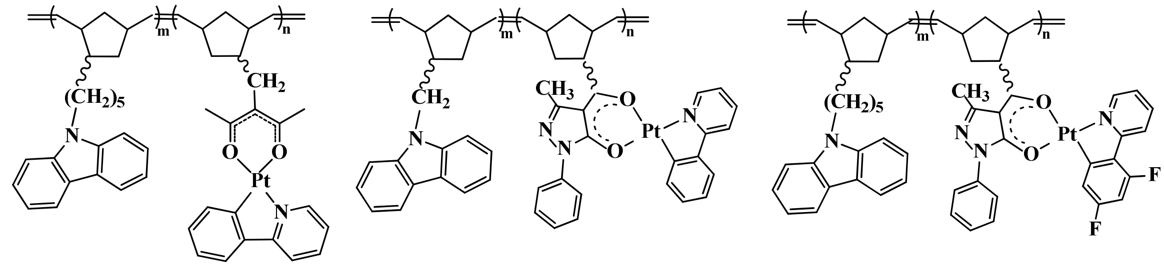
A series of norbornene-based platinum-containing copolymers were synthesized by ring-opening metathesis polymerization and characterized by elemental analysis, NMR, IR, GPC, DSC, TGA. A representative synthesis of Pt-copolymers is shown in the scheme:



The examples of the obtained copolymers are shown in the chart:



All the copolymers are air stable solids well soluble in THF, CH_2Cl_2 and $CHCl_3$.
Photophysical and electroluminescent properties of the synthesised Pt-copolymers were studied. The emission bands in the region of 470-550 nm in photoluminescence and electroluminescence (EL) spectra can be assigned to metal to ligand charge transfer transition. The color of EL was found to depend on the composition of Pt-copolymers and changed from green to orange to white. Maximum brightness of 400 cd/m^2 was reached.

Acknowledgements - This work was supported by the Russian Foundation for Basic Research (Project No. 12-03-00250-a)

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MAGNETO-STRUCTURAL CORRELATIONS IN 3d METAL COMPLEXES WITH SUBSTITUTED IMINONITROXIDES

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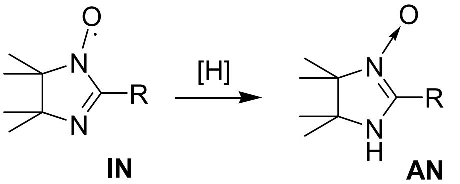
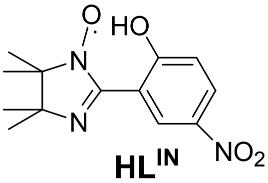
Iminonitroxides (**IN**s) are widely used in design of magnetoactive compounds because of exchange interactions between spins of paramagnetic metal ions and coordinated by N atom **IN** fragments are strongly ferromagnetic. In some cases complex formation reactions are accompanied by a reduction of **IN**s into corresponding aminonitrons (**AN**s), and **AN**s can be involved in complex formation.

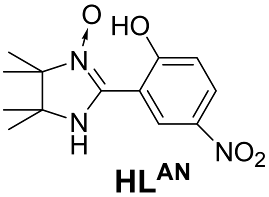


IN **AN**

Structural differences of **IN**s from **AN**s small, but are. Revealing of **AN**s in the complexes by X-ray allowed to avoid a misinterpretation of magnetic properties.

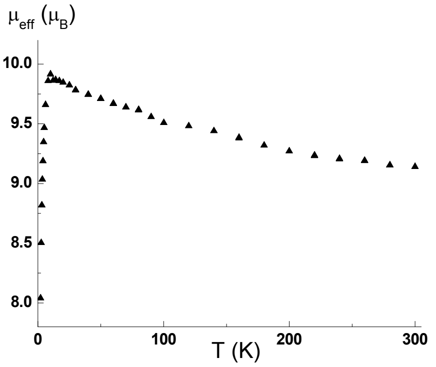


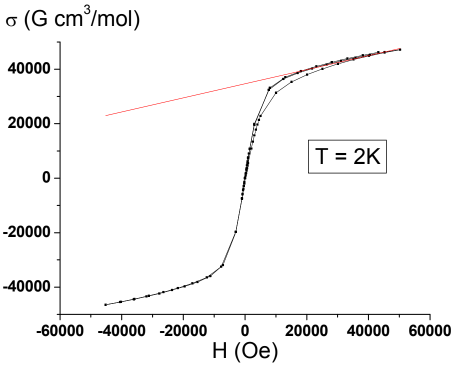
HL^{IN}



HL^{AN}

We found that interaction of 3d metal pivalates with (2-hydroxy-5-nitro-phenyl)-iminonitroxide (HL^{IN}) leads to heterospin complexes with both L^{IN} and L^{AN} as a ligands. The $[Co_3(L^{IN})_2(L^{AN})_2(Piv)_2]•Me_2CO•C_7H_{16}$ complex demonstrates behaviour of a soft magnet at low temperature with spontaneous magnetisation at 2 K is about 36700 G·cm^3/mol.





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REDOX-ISOMERIC TRANSFORMATIONS. ELECTRONIC AND LATTICE CONTRIBUTIONS.

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Redox-isomerism phenomenon in bis-quinonato cobalt compounds is the reversible metal-ligand electron transfer accompanied by spin-crossover of cobalt ion. Redox-isomerism occurring in solid state is extensively studied because of it possible application in microelectronics. The main regularities determining redox-isomeric equilibrium in general are known.

We have already investigated the influence of the nature of quinonato ligand on the redox-isomeric equilibrium [1]. We have shown how the difference between 2,2'-dipyridine and 1,10-phenanthroline (two carbon atoms) change the temperature and steepness of transition [2]. The last two compounds are isostructural which allow to obtain solid solutions of variable composition. Solid solutions also demonstrate phase transitions accompanying redox-isomeric transformations. Thermodynamic parameters of phase transitions correlate with solid solution composition.

Recently we have obtained three binuclear bis-semiquinonato cobalt complexes where the tetradentate neutral N-donor ligand play a role of bridge. Complexes differ one from another by quinonato ligands. Surprisingly that the transition temperature in this case does not depend on the nature of quinonato ligand. The only steepness of transition changes upon coming from one complex to another.

We have successfully produced polycrystalline films of some redox-isomeric complexes by thermal vacuum deposition [3]. It was shown that electric conductivity of polycrystalline films and crystal samples of redox-isomeric complexes nonlinearly depend on a temperature. Temperature dependence of electric conductivity has maximum which temperature interval coincides with interval of redox-isomeric transformation.

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Acknowledgements - We are grateful to the RFBR (grants №№ 13-03-12444, 13-03-97082, 13-03-97070), Russian President Grant supporting Scientific Schools (NSh-1113.2012.3) and Fundamental Research Programm of Presidium of RAS (№ 18) for financial support. We are thankful to O.Kuznetsova and N.Khamaletdinova for NIR-IR spectroscopy experiments, A. Bogom'akov for magnetic measurements.

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DISCOVERY OF CARBON IN "CHELYABINSK" METEORITE BY RAMAN MICRO-MAPPING,

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As it is well-known, on Febr. 15 2013 a meteorite has exploded over Russia near Chelyabinsk, giving many fragments, which were gathered and investigated by several groups of Russian geologists and geochemists. They concluded that it was a stony meteorite— a chondrite of the type LL5S4WO. Based on optical reflection, SEM, X-ray diffraction, and TGA methods as well as chemical analysis, mineral content of the meteorite was established. The «Chelyabinsk» meteorite was also investigated in the Scientific and Technical Center on Raman Spectroscopy RAS, using LabRAM an spectrometer (Horiba-Jobin-Yvon) equipped with a microscope×50x (Olympus BX) with 632.8 nm He-Ne laser line excitation. Applying Raman micro-mapping to the freshly cleaved grey surfaces of the meteorite fragments (Fig 1), more than 750 high-quality Raman spectra were registered. Using Horiba-Jobin-Yvon Raman spectra database, the authors identified in the meteorite several minerals, found by other investigators. However, the authors succeeded in detecting several Raman lines belonging to carbon species [1]. These are micro-particles (less than 3 μm) of cubic diamond (a very narrow Raman line at 1333 cm^{-1}, FWHM=3.5 cm^{-1}, Fig. 2) and of an sp^2-carbon substance (the lines D 1324, G 1598 and 2D 2660 см$^{-1}$, Fig. 3). The latter spectrum nearly coincides with those of natural Karelian shungite and of a sample of industrial glassy carbon. The presence of carbon in the meteorite (0.11%) was confirmed by elemental analysis.

Fig. 1. Photographs of two fragments of "Chelyabinsk" meteorite studied.
(left) a fragment covered with a black flowed crust; (right) a fragment with a freshly cleaved grey surface

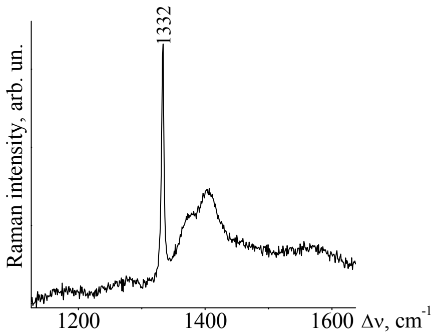

Fig. 2. Raman spectrum, registered from a micro-section inside the freshly cleaved meteorite surface, demonstrating presence of cubic diamond.

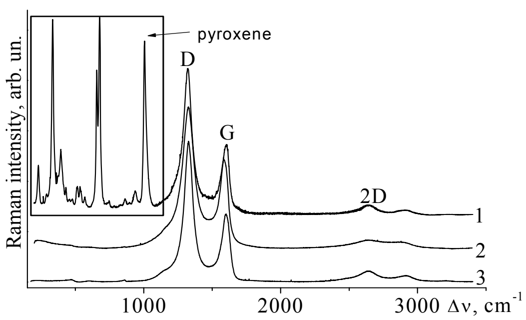

Fig. 3. Comparison of the Raman spectra of (1) a meteorite micro-spot inside the fresh cleavage, (2) a natural Karelian shungite and (3) a sample of a synthetic glassy carbon.

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IRON(II) CLATHROCHELATES WITH LIGAND-CENTRED REDOX ACTIVITY

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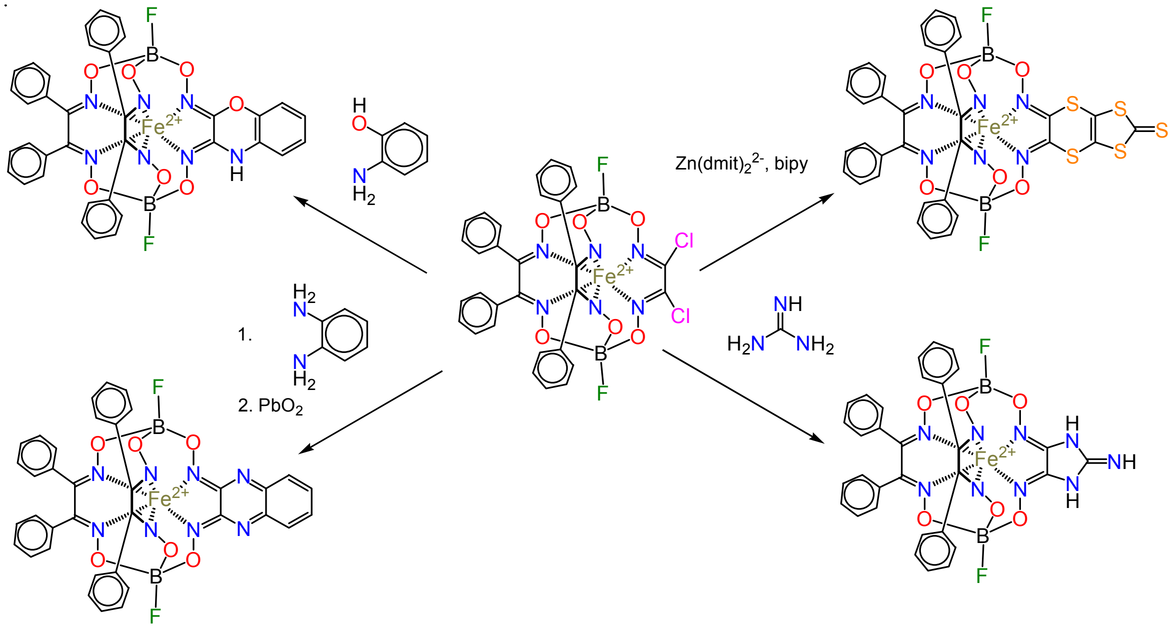
The macrobicyclic metal tris-dioximates (clathrochelates) are the unique type of the cage coordination compounds that have many unusual properties and possible applications [1]. Recently, it was shown that the cobalt clathrochelates are promising electrocatalysts for very efficient hydrogen production [2 – 4]. However, the rigidity of clathrochelate macrobicyclic frameworks imposes severe limitations on the size of the encapsulated metal ion resulting in the strong stabilization of its particular oxidation state. So, the reversible metal-centred redox reactions of the boron-capped tris-dioximate metal clathrochelates are very limited and mainly characteristic of the cobalt complexes. We extended the redox chemistry of these cage complexes on the ligand-centred processes involving their chelate ribbed fragments. The synthesis of the iron(II) cage complexes with non-innocent ribbed-annulated heterocyclic encapsulating ligands and their redox properties will be discussed.



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IRON(II) COMPLEXES WITH PYRAZOLYLPYRIMIDINES: INTERPLAY BETWEEN SPIN CROSSOVER AND POLYMORPHISM

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The spin crossover (SCO) in iron(II) complexes has attracted attention due to its fundamental importance and prospects for applications. The main challenge in this field is the synthesis of complexes undergoing abrupt transition at room or higher temperatures and showing wide bistability domain. Polymorphism in SCO systems is a tool to modulate SCO behavior.

Iron(II) complexes with N,N,N-tridentate 2,6-bis(pyrazolyl)pyridines/pyrazines are one of the flexible groups of SCO compounds [1]. We began to study SCO properties of their analogs, *i.e.*, iron(II) complexes with 2,4-bis(1*H*-pyrazol-1-yl)pyrimidines. A series of high spin complexes have been synthesized. An iron(II) perchlorate complex with 2,4-bis(1*H*-pyrazol-1-yl)-6-methylpyrimidine can be synthesized in the form of two polymorphic modifications. The first one is in the high spin state at room temperature and converts to the low spin state on cooling, while the second modification remains in the high spin state. Thus, 2,4-bis(1*H*-pyrazol-1-yl)pyrimidines feature rather weak ligand field favoring high spin state either low temperature SCO.

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. We expected that introducing of pyridinyl group being a stronger σ-donor and π-acceptor than pyrazole should stabilize the low spin state and shift the transition to higher temperatures. Magnetic data on iron(II) complexes with 2-(pyridin-2-yl)-4-(1*H*-pyrazol-1-yl)pyrimidines confirmed this hypothesis. These compounds are in the low spin state at room temperature and undergo a transition to the high spin state above room temperature.

An iron(II) tetrafluoroborate complex with 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(pyridin-2-yl)-6-methylpyrimidine is of special interest. It shows unusually complicated interplay between spin crossover behavior and polymorphism. Depending on the experimental conditions, the starting low spin complex can be converted into one of three low spin phases showing different spin crossover regimes. Two of them display gradual spin transition centered around 320 K. The third phase show reproducible SCO behavior with abrupt transitions at 490 and 360 K for the heating and cooling modes, respectively. Thus, an unprecedented hysteresis loop of 130 K was observed.

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FIRST EXAMPLE OF COEXISTENCE OF THE MAGNETIC ORDERING, PRESUMABLE MAGNETOELECTRIC EFFECT AND SPIN CROSSOVER IN DENDRIMERIC IRON(III) COMPLEX

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The unusual magnetic behavior of the first dendritic Fe^{3+} complex [1] with general formula $[Fe(L)_2]^+Cl^-\cdot H_2O$ based on a branched Schiff base has been investigated by electron paramagnetic resonance (EPR) and Mössbauer spectroscopy. EPR display that complex consists of the three types of magnetically active iron centers: one $S = 1/2$ low-spin (LS) and two $S = 5/2$ high-spin (HS) centers with strong low-symmetry and weak distorted octahedral crystal fields. Calculation of the g-tensor component ($g_{x,y} = 2.21$, $g_z = 1.935$) of the LS Fe^{3+} centers has shown that $(d_{xz},d_{yz})^4(d_{xy})^1$ state is the ground. Analysis of the magnetic behavior reflected by I versus T (where I is the EPR lines integrated intensity of the whole spectrum which is proportional to the static paramagnetic susceptibility) demonstrates that dendritic Fe^{3+} complex has sufficiently different behavior in three temperature intervals. The first (4.2-50 K) interval corresponds to the intermolecular exchange interactions between LS-LS, LS-HS and HS-HS centers coupled antiferromagnetically by means of water molecules and Cl counterions. The appearance of the presumable magnetoelectric effect is registered in the second (50-200 K) temperature interval, whereas a spin transition process between LS and HS centers occurs in the third (200-330 K) one. Simulation of the EPR spectra allowed us to trace the dynamics of changing the number of HS centers with respect to LS during a spin crossover. It has been shown that spin transition process is characterized by the following enthalpy $\Delta H = 3.46$ kJ/mol and entropy $\Delta S = 58.8$ $J\cdot K^{-1}$/mol values. The simultaneous coexistence of the magnetic ordering, presumable magnetoelectric effect and spin crossover in one and the same material has been revealed for the first time. The Mössbauer spectroscopy data completely confirm the EPR results. DFT calculations demonstrate the coordination sphere structure of the compound.

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UNCONVENTIONAL MECHANISM OF Pd COMPLEXES OXIDATION BY AQUEOUS ACIDIC SOLUTION OF H_2O_2: KINETIC AND DFT STUDY

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Hydrogen peroxide is an environmentally friendly and cheap oxidant suitable for usage in processes catalyzed by transition metal complexes [1]. Its practical application is limited by unproductive H_2O_2 decomposition and by kinetically unfavored oxidation of reduced form of Pd in Wacker-type reactions. It has been stated that in dilute hydrogen chloride both rate and selectivity depend on the acid/H_2O_2 ratio [2]. Acid addition accelerates electrophilic oxidations by H_2O_2 what is representing in a kinetic equation containing a third order term with acid concentration [1]:

$$r = k_2[H_2O_2][Nu] + k_3[H_2O_2][Nu][HA] \qquad (1)$$

This term is explained by protonation of H_2O_2 (2) which leads to highly electrophilic hydroperoxonium ion $H_3O_2^+$ formation [1]:

$$H_2O_2 + H_3O^+ \xrightleftharpoons{K} H_3O_2^+ + H_2O,\ K = 10^{-3} \text{ at } 298\text{ K} \qquad (2)$$

Hydroperoxonium ion $H_3O_2^+$ can act as oxidizing specie under mild conditions and can be regarded as hydrated hydroxyl cation HO^+.

Earlier [3] selective oxidation of terminally substituted allylic complexes into linear allyl derivatives (3) was studied. For complex with R = MeCH(OH) kinetic equation (4) of fourth total order was received.

$$[(R\text{-}\eta^3\text{-}C_3H_4)PdCl_2]^- + H_2O_2 + HCl \rightarrow RCH{=}CHCH_2OH + Cl^- \qquad (3)$$

$$r = k^{obs.}[H_2O_2][H^+][Cl^-][\eta^3] \qquad (4)$$

DFT study (approximation PCM-B3LYP/LANL2DZ(Pd)+6-31+G*) supposed unconventional mechanism of reaction (3). It includes direct addition of $H_3O_2^+$ to the central atom of complex anion $[(R\text{-}\eta^3\text{-}C_3H_4)Pd^{II}Cl_2]^-$ with formation of neutral intermediate $(\eta^3\text{-}RC_3H_4)Pd^{IV}(OH)Cl_2$, which isomerizes into thermodynamically more stable η^1-allylic complex having unconventional disphenoid structure. At the rate-determining step external nucleophilic attack of Cl^- onto carbon atom in $(\eta^1\text{-}RC_3H_4)Pd^{IV}(OH)Cl_2$ to form allylchloride and Pd(II) complex occurs. So the first order in chloride ions agrees with change of hapticity of η^3-allylic complex. The mechanism was proved by IRC calculations and by single imaginary frequency found for each transition state.

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SYNTHESIS OF ANTITUMOR HETEROCYCLE-CONTAINING ALLOCOLCHICINOIDS

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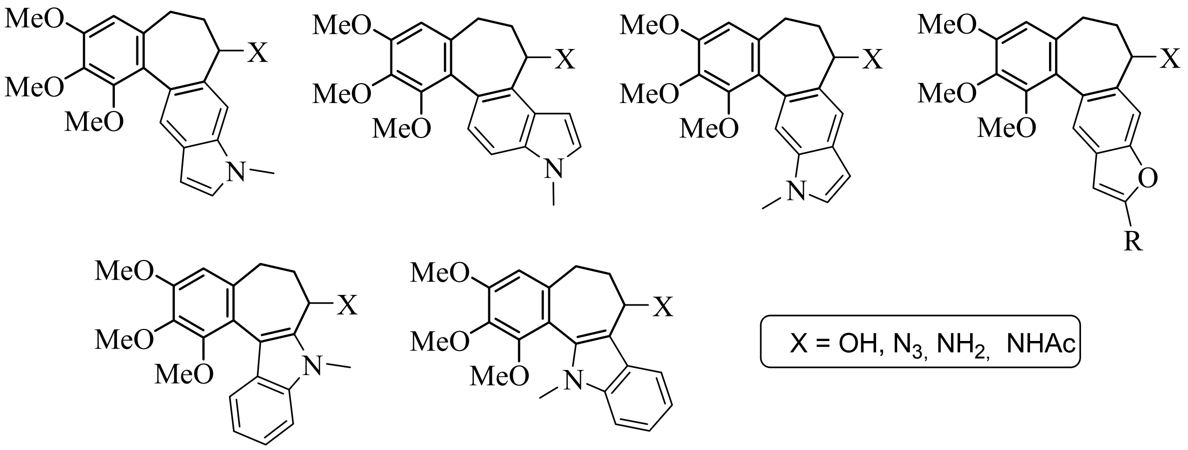
A range of indole- and furane-containing allocolchicinoids was synthesized using the methods of metallocomplex catalysis:



X = OH, N_3, NH_2, NHAc

Several from synthesized compounds manifest antitumor activity at nanomalar or even at subnanomolar concentration range [1], along with particularly low unspecific toxicity.

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REGIO/STEREOSELECTIVE CATALYTIC NORBORNADIENE ALLYLATION BY Ni AND Pd COMPLEXES. NEW SINTHETIC POSSIBILITIES AND MECHANISM.

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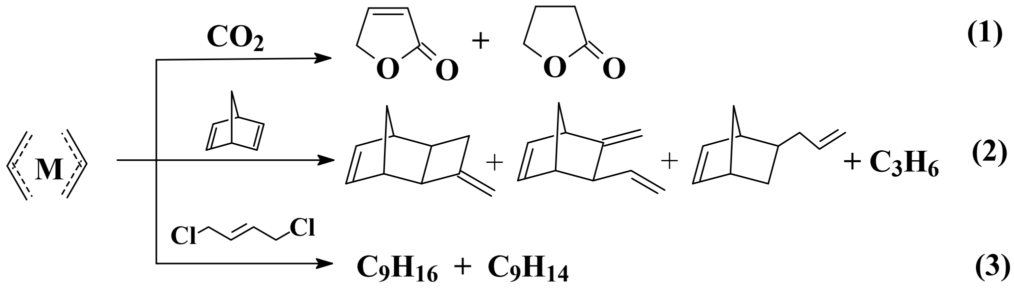
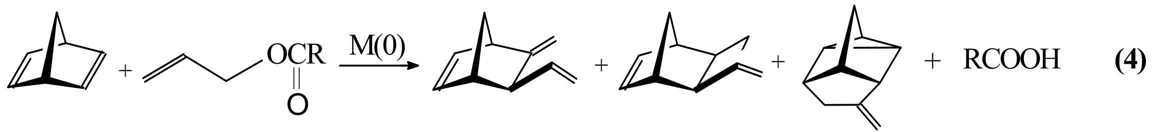
The report comprises results concerning unusual direction of transition metal allyl complexes, that is redox disproportionation of allyl ligands. The share of disproportionation depends on the effective positive charge (from +0,4 up to +0,8) on metal and the substrate nature.



1. M – *Ni, Pd*; ***2.*** M – *Fe, Co, Ni, Rh, Pd, Pt*; ***3.*** M – *Ni*

Nonconventional catalytic allylation of norbornenes and norbornadiene (NBD) by allylacetates and allylcarbonates is the unique synthetic method allowing to introduce in NBD of structure methylen-, vinyl- and methylenecyclobutane fragments.



New catalysts for the unconventional NBD allylation by allyl acetate, allyl formiate, methylallyl carbonate and diallyl carbonate (reaction 4) were investigated based on palladium phosphine systems: $Pd(dba)_2$+2PPh_3, $Pd(OAc)_2$+2PPh_3, $PdCl_2(PPh_3)_2$, $[(C_3H_5)Pd]NO_3$+2PPh_3.

Phosphite nickel complexes show high catalytic activity and also high regio- and stereoselectivity only in the complete absence of oxygen. Phosphine palladium complexes carry out catalytic process with high parameters in normal conditions. On the basis of X-ray photoelectron and ^{1}H-, ^{13}C-, ^{31}P-NMR spectroscopy and kinetic data it was shown, that nickel and palladium have qualitative analogies in this reaction. The ratio of stereoisomers and the number of catalytic cycles depends on the metal – ligands ratio. The mechanism of reaction proceeding with the participation of both metals was offered. β-Hydride transfer with participation different metals, allylic and NBD fragments was confirmed by isotopic methods.

Acknowledgements: RFBR supported this work, grant 11-03-00662.

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NEW CATALYTIC SYSYEMS FOR ORGANOMETALLIC MEDIATED RADICAL POLYMERIZATION OF VINYL MONOMERS

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Organometallic mediated radical polymerization has become one of the most important and effective methods of polymer synthesis in recent years. The use of organometallic compounds for precise polymer synthesis is perspective division in modern polymer chemistry. It allows not only to control the polymerization kinetics and molecular-weight parameters of macromolecules but offers scope for effective solutions of problems of macromolecular design owing to an opportunity to synthesize graft and block copolymers as well as macromolecular nanostructures.

It has been shown in our laboratory that the complexes of ruthenium, nickel, cobalt, iron, tin and some other metals with different ligands does not only initiate radical homo- and copolymerization of styrene, vinyl chloride, acrylonitrile, methyl methacrylate, butyl acrylate and some other vinyl monomers but have a significant impact on the propagation stage of the polymer chain. A particular attention has been paid to the application of complexes of transition metals with variable valence in processes of macromolecule synthesis by Atom Transfer Radical Polymerization as the most effective approach to the carrying out of polymerization under "living" chain conditions. It has been shown that a series of organometallic compounds are able to control the polymer chain growth through the mechanism of Reverse Organometallic Radical Polymerization exerting substantial influence on the molecular-weight characteristics of homo- and copolymers as well as their composition and the microstructure. In such processes metalocomplexes play a role of a reversible spin trap for polymer radicals, regulating their concentration and preventing from the bimolecular termination like stable nitroxyl radicals. New original agents based on sterically hindered quinones and catecholate complexes of IV group elements are offered for the controlled synthesis of macromolecules via the mechanism of Quinone Transfer Radical Polymerization.

The influence of investigated organometallic complexes especially the electronic structure of the metal atom and the ligand environment on the mechanism of polymerization as well as molecular weight parameters, composition and some properties of obtained homo- and copolymers were estimated.

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RADICAL REACTIONS OF RUTHENIUM CARBORANE COMPLEXES: HALOGEN EXCHANGE AND CATALYSIS OF RADICAL POLYMERIZATION

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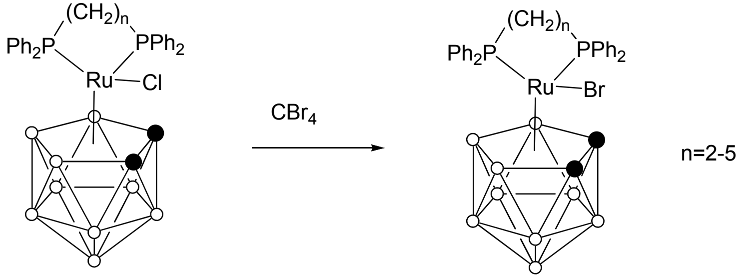
Ruthenium compounds are known as perfect catalysts of radical reactions, such as Kharasch addition and controlled radical polymerization via ATRP mechanism. Among them ruthenium carborane complexes are of a special interest due to their high stability and efficiency. Dicarbollide ligand is capable to stabilize metal centres in high oxidation state due to double negative charge and high degree of electron delocalization. Here we report the radical reactions of ruthenium carborane complexes with chelate diphosphine ligands, namely halogen exchange and catalysis of radical polymerization.

Reactions of chloride-containing paramagnetic ruthenium carborane complexes with excess of carbon tetrabromide in benzene or toluene give corresponding bromine-containing compounds with high yields (60-90%) in 4 hours. The full conversion of initial compounds was confirmed by HPLC and MALDI MS experiments. Halogen exchange reaction is a more convenient way of obtaining of bromine containing ruthenacarboranes in comparison with conventional way through exo-nido -> closo rearrangement and further thermolysis [1-2].



The obtained bromine complexes as well as their chlorine containing precursors were investigated in catalysis or controlled radical polymerization of methacrylates and styrene. The proposed catalysts allow to obtain polymers with low polydispersity (M_w/M_n=1.1-1.4) and desired molecular weight. The linear increase of molecular weight with conversion and successful synthesis ob block-copolymers confirms controlled manner of polymerization. Our investigations show that amine additives significantly accelerate controlled polymerization of MMA in the presence of ruthenacarboranes. Polydispersity of the formed polymers remains very narrow (<1.2) in spite of little decrease of control over polymerization. It was shown, that presence of amine additives allows to decrease catalyst concentration while the process remains controlled.

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RATIONALIZATION OF SOLVATION AND STABILIZATION OF PALLADIUM NANOARTICLES IN IMIDAZOLIUM- AND PHOSPHONIUM-BASED IONIC LIQUIDS

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Metal nanoparticles (M-NPs) attract interest across diverse areas of science. Small M-NPs are only kinetically stable and combine to form thermodynamically favoured larger metal particles via agglomeration. Ionic liquids (ILs) can be used to generate and stabilise metallic NPs *in situ*. The required stabilization is provided through the formation of an ion layer around the M-NPs. The nature of this layer and hence, the mode of stabilization of M-NPs in ILs, is still a matter of debate. We applied the combined DFT-vibrational spectroscopy approach to determine the interactions of ionic components of various ILs based on the 1-alkyl-3-methylimidazolium [$C_n$mim], 1-(2'-hydroxylethyl)-3-methylimidazolium [C_2OHmim] and the tetraalkylphosphonium cations with Pd NPs immersed in the ILs. According to the computations, Pd_n (n=5 - 21) clusters, taken as models of Pd NP, interact more strongly with the anions than with the cations [1,2]. The following order was obtained for interaction energies between a Pd_n cluster and various anions: [TFA] (trifluoroacetate) > [BF_4] > [OTf] > [PF_6] ≅ [Tf_2N]. The IR spectra suggest that both the anions and cations in the ILs interact with the Pd-NP surface. In agreement with the above findings, the influence of both the cationic and anionic components of the ILs on the properties of Pd NPs, formed and stabilized *in situ*, were established experimentally [2]. Indeed the anions, which exhibit the strongest interaction with the Pd_5 cluster, resulted in the lowest extent of Pd NP formation whereas the anions with weakest interactions provided the highest percentage of Pd NPs. A presence of the latter weakly-interacting anions in IL results in the formation of the largest-size NPs, while the smallest-size NPs are formed in ILs containing strongly interacting anions. [C_2OHmim]-based ILs allows the formation of the smaller NPs than [C_2mim]-based ILs. This finding, as well as the formation of the largest NPs in tetraalkylphosphonium-based ILs, agrees with the order of the cluster-cation interactions: [C_2OHmim] > [C_2mim] > tetraalkylphosphonium.

The energy of the interaction of the IL components with Pd_n clusters is shown to be smaller than the energy of addition of a Pd atom to the cluster. Stronger Pd-Pd interactions in comparison to the interactions of the palladium cluster with the IL suggest kinetic stabilisation of Pd-NPs in the ILs rather than thermodynamic stabilisation. This feature could explain why Pd-NP catalyst reservoirs that react to form catalytically active mononuclear palladium species in cross coupling reactions are particularly active in ILs.

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SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF SOME SEVEN AND TEN COORDINATED COMPLEXES OF LANTHANIDES(III) DERIVED FROM SEMICARBAZONE CONTAING HETEROCYCLIC RING

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The structural chemistry of the lanthanide (III) compounds has recently undergone considerable development and a wide variety of coordination numbers and geometries have been observed. The coordination numbers exhibited by the tripositive lanthanide ions usually vary from 6 to 10. However, other examples of lanthanide (III) complexes with more than 10-coordination number have also been reported in the literature. In the present studies the effect of quinoline N-oxide (QNO) on the stereochemistry of the coordination compounds of trivalent lanthanides derived from 4[N-(2’,4’-dimethylbenzalidene)amino]antipyrine semicarbazone (DMBAAPS) is reported. The general composition of these coordination compounds is LnX_3.n (DMBAAPS).QNO (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy or Ho ; X = NO_3, n = 1, X = ClO_4 or NCS, n = 2). All these compounds were characterized by elemental analysis, molar mass, molar conductance, magnetic susceptibility, infrared and electronic spectra. The infrared studies reveal that the DMBBAAPS acts as a neutral tridentate (N,N,O), while QNO is coordinated to the central metal ion *via* its lone oxygen atom. In nitrato complexes, the nitrates ions are bicovalently bonded, while thiocyanate is coordinated through hard N-atom. Perchlorato ions are not participating in coordination and are present outside the coordination sphere. From electronic spectral data, nephelauxetic effect (β), covalence factor ($b^{1/2}$), Sinha parameter (δ %) and the covalence angular overlap parameter (η) has been calculated. Antibacterial properties of these compounds were also studied. Thermal studies of these compounds were studied by thermogravimetric analysis. The present studies reveal that the coordination number of lanthanide(III) in the present compounds is either 7 or 10 depending on the nature of anions.

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REMARKABLE INSERTION OF ELECTROPHILIC PHOSPHINIDENE COMPLEXES INTO CARBON-HALOGEN BONDS

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Phosphinidenes are phosphorus analogue of carbenes. Phosphinidene tungsten pentacarbonyl complexes could be generated in-situ only which are extremely unstable and highly reactive. A remarkable insertion of these phosphinidene complexes into carbon-halogen bonds was observed. These intermediates could be trapped easily in presence of various reagents containing π-systems to afford a number of P-heterocycles1. A number of compounds are known to give phosphinidene intermediates but 2H-azaphosphirene tungsten pentacarbonyl complex (1) is the most stable precursor for the in-situ generation of terminal phosphinidene complexes (2), via thermal decomposition of 1, which can be trapped via [2+1] cycloaddition reactions1 or with C-X bond systems leading to selective insertion reactions2-5 – all reactions and their manipulations were carried out under strict anhydrous conditions and were monitored by 31P NMR spectroscopy. All products were characterized by NMR spectroscopy and by single-crystal X-ray crystallography.

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VIBRATIONAL SPECTRA AND ELECTRONIC STRUCTURE OF 1-GERMATRANOL, 1,1-QUASIGERMATRANEDIOL, AND 1,1,1-HYPOGERMATRANETRIOL $(HO)_{4-n}Ge(OCH_2CH_2)_nNR_{3-n}$ (R=H; n=1-3)

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IR spectra of 1-germatranol, 1,1-quasigermatranol, and 1,1,1-hypogermatranol with general formula $(HO)_{4-n}Ge(OCH_2CH_2)_nNR_{3-n}$ (R=H; n=1-3) are recorded. Equilibrium structures and vibrational spectra of monomeric and centrosymmetric dimeric species of these compounds are predicted by the B3LYP/aug-cc-pVDZ method. The X-ray diffraction study [1] indicates that the crystal structure of 1-germatranol consists of hydrogen-bonded dimers $[HOGe(OCH_2CH_2)_3N]_2$ in which the hydroxyl group proton of one monomer is bound to endocyclic oxygen of another. The crystal structure of 1,1-quasigermatranol is also built from dimers, however the pattern of hydrogen-bonding in these dimers is diffent since only hydroxyl groups are involved in this bonding: one OH group in each molecule acts as a proton donor and another as an acceptor. The analysis of experimental spectra based on theoretical predictions of the vibrational spectra of dimeric species of these compounds confirms the character of hydrogen-bonding in these compounds. The structure of 1,1,1-hypogermatranol is not known and the comparison of experimental and theoretical spectra indicate that the crystal structure of this compound cannot be satisfactorily described in the dimeric model.

The persistent difference between the length of the transannular Ge…N bond length in the gas and solid phases manifests itself in the comparison of theoretical and experimental spectra of all species studied. In this work this difference was compensated by scaling of theoretical GeN force constants.

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DIAZADIPHOSPHAPENTALENE: AROMATIC MOLECULE WITH TWO-COORDINATE AND FORMALLY TWO-VALENT PHOSPHORUS

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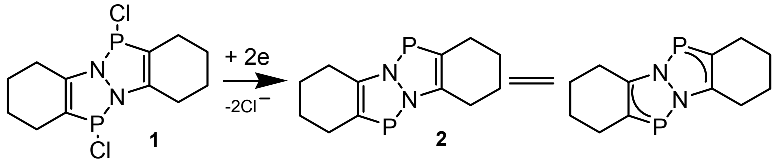
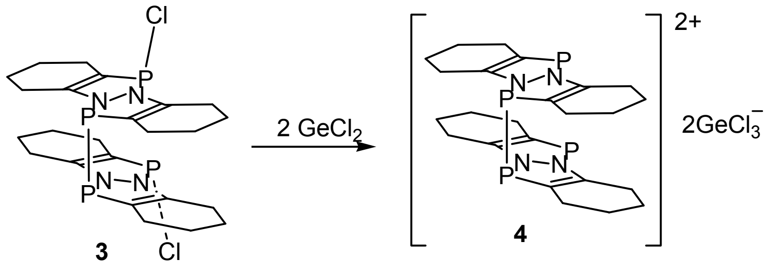
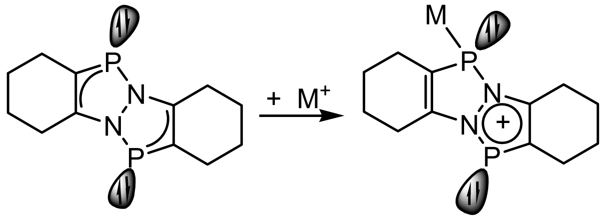
Reduction of dichlorodiazaphosphalene **1** [1] results in formation of diazadiphosphapentalene **2**. This is diamagnetic compound showing single resonance in ^{31}P NMR spectrum at 177.0 ppm. The bond distance between the two carbon atoms in the PCCN fragment (1.335(7) Å) is corresponded to the normal double C=C bond in alkenes. The C–P, P–N, N–N and N–C bond lengths lie in the range, typical for 1,2,3-diazaphospholes. It is important to note that the shortest distances between the phosphorus atoms of adjacent molecules in crystal (4.180 Å) exceed the sum of van der Waals radii (3.60Å). Calculated NICS(0) of −11.44 is compatible with an aromatic character of the cyclic C_2N_2P moieties.



Interestingly, the equimolar mixture of **1** and **2** gives new easily dissociated compound **3** which after reaction with $GeCl_2$ forms structurally characterized complex **4**. It is important to highlight that the positively charged diaza-diphosphapentalene units can effectively bind to each other not only by P-P single bond. Formation of staked 18-e dication may be explained by the concept of stacked-ring aromaticity assuming throughspace delocalization of π-electrons.



Activity of **2** in coordination bond formation is very high that may be explained rather by unusual mechanism of complexation. While the lone pair of sp^2 phosphorus is poor available, the 10e system may submit another two electrons via phosphorus atom, taking away one electron from neighboring phosphorus. Complexes of **2** with $HgCl_2$ and $SnCl_2$ demonstrate supramolecular organization dependent on preparation method.



The molecule **2** possesses reducing activity, converting easily Ph_2PCl to Ph_4P_2 and $PhPCl_2$ to $(PhP)_5$. Reaction with Ph_3CCl gives the P,P’-addition product $\{Ph_3C\text{-}PNNP\text{-}Cl\}$. One equivalent of 3,6-Di-*t*Bu-*o*-quinone interacts to one phosphorus atom of **2** to form hypervalent (four-coordinate) phosphorus(III) compound.

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SYNTHETIC APPLICATION AND CATALYTIC ACTIVITY OF CATIONIC (ARENE)METALLACARBORANES

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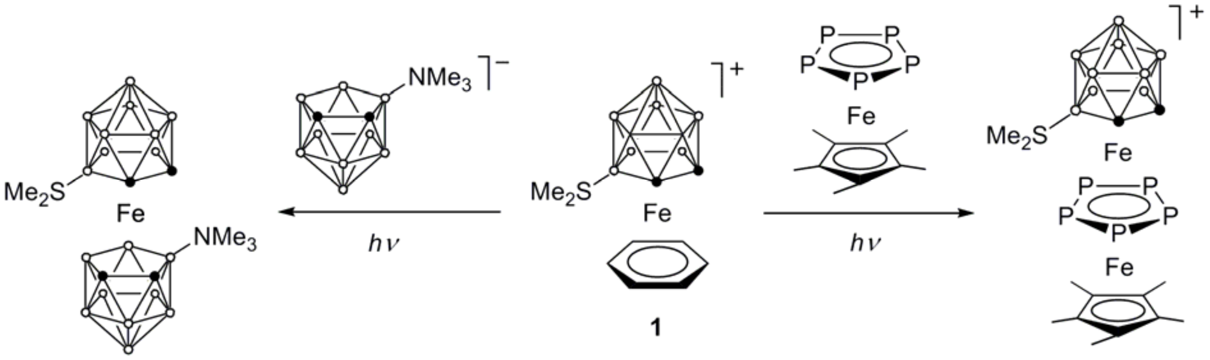
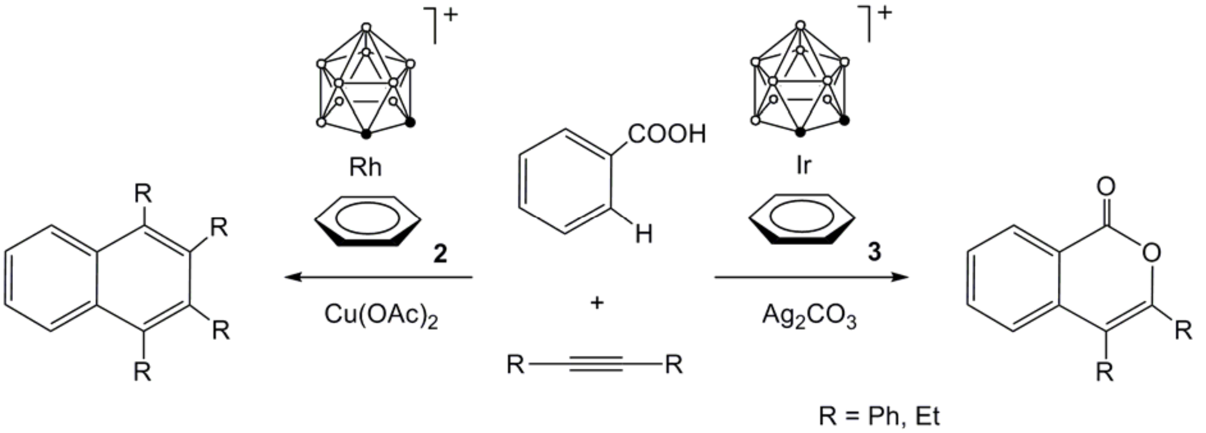
(Arene)metallacarboranes are perspective compounds as a synthons of the CarbM fragments owing to high substitutional lability of the arene ligand. In particular, we shown that photochemical replacement of benzene in the iron complex **1** by other ligands is an effective method for the direct preparation of the hard to get metallacarboranes, namely, unsymmetrical bis(carborane) complexes and triple-decker compounds.



The (benzene)rhoda- and iridacarboranes **2** and **3** catalyze the coupling of benzoic acid with alkynes. In the case of rhodium, naphthalenes were isolated as the major products. In contrast, the coupling catalyzed by iridium complex **3** results in isocoumarin derivatives exclusively.



These and other similar (arene)metallacarboranes will be discussed, along with their reactivity and structures.

Acknowledgements - This work was supported by the Presidium of Russian Academy of Sciences (program P8).

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TARGRTED ELECTROSYNTHESIS IN COORDINATION ENVIRONMENT OF CHIRAL Ni(II) COMPLEXES OF α-AMINO ACID SCHIFF BASE: A CONVINIENT ROUTE TO α-AMINO ACID FUNCTIONALIZATION

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Metal complexes with chiral ligands create an efficient asymmetric environment around the metal center to afford the high-level induction of enantioselectivity. This approach is widely used for various types of stereoselective synthesis. However, an involvement of a substrate in the asymmetric metal coordination environment allows not only providing asymmetric induction but also opens a possibility to perform electrochemically induced stereoselective reactions, thus broadening a scope of available reaction routes.

Aforementioned novel approach was used for developing of practical and highly efficient routes to various types of α-amino acid derivatives. Electrochemically induced reactions in coordination environment of three different chiral Ni(II) complexes of α-amino acid Schiff-base (glycine, alanine, dehydroalanine) were elaborated. Various types of chemical transformations will be considered, including oxidative or reductive activation of starting complexes as well as their *in situ* reactions with electrochemically generated species.
The consideration of possible sites of cathodic and anodic activation in Ni(II) complexes was performed in the context of their electrochemical behavior and quantum-chemical DFT calculations of their frontier orbitals.

Varying the type of activation (anodic or cathodic), different types of Ni(II) binuclear complexes can be obtained. Further electrochemical reduction of new dimers allows obtaining chiral mixed-valence species which might be of interest for catalytic applications.

The reactions of glycine and alanine Ni(II) complexes with electrochemically generated base open a route to various condensation reactions. Since some of them have been performed earlier using common bases [1], the comparison of stereochemical result of chemical and electrochemical transformations might be of interest. The elaborated approach to enantiopure β-hydroxy α-amino-acids using galvanostatic electrolysis of Ni(II) complexes of glycine Schiff-base in alcohols in one-compartment cell in the presence of KOH constitutes a convenient and more practical alternative to common aldol reaction with aldehydes [1].

The relative and absolute configurations of the products isolated using column chromatography were determined from NMR and CD spectra. The modified Ni(II)-Schiff base complexes can be easily decomposed using HCl in methanol yielding various amino acids derivatives.

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COEXISTENCE OF FERROMAGNETIZM AND CONDUCTIVITY IN IRON MIXED-VALENT ANILATO-BRIDGED NETWORKS. FIRST EVIDENCE OF DOUBLE-EXCHANGE INTERACTION

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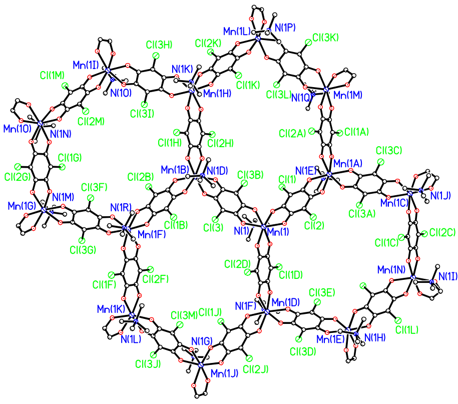
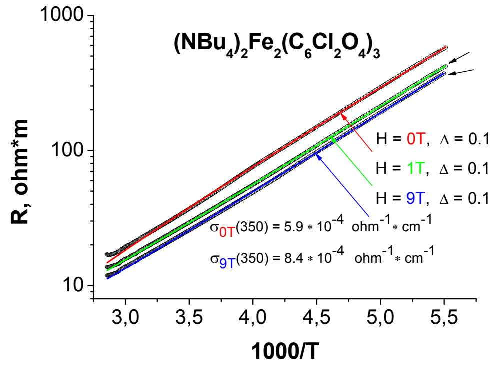
Synthesizing and studying the physical properties of multifunctional molecule-based materials is currently blossoming [1]. Our objective is the systematic study of the effects related to the coexistence within the one material of several physical properties and/or to the resulting cross-effects [2].

Our next pathway consisted in replacing the oxalate ligand by non-innocent bridge. Metal compounds containing $(DHBQ)^{2-}$, choranilate $(CA)^{2-}$ etc., as bis-bidendantate ligands having delocalized π-system are attractive for constracting new molecule-based magnets. Recently, both bimetallic $(NBu_4)_2[MFe(CA)_3]$, M=Mn-Cu, and monometallic $(H_3O)_2(phz)_3[M_2(CA)_3]$, M=Mn, Fe, compounds with extended networks were syntesized [3, 4]. Here we report a characterization of a new family of monometallic compounds with TBA counter cation, $(NBu_4)[M_2(C_6Cl_2O_4)_3]$, M=Mn, Fe, Cu. They possess a stack of layered $[M_2(C_6Cl_2O_4)_3]^{2-}$ anionic networks separated by a double $(NBu_4)^+$ cationic layer. A charge delocalized $Fe^{2.5+}$ state related to the rapid electronic exchange has been evidenced by the Mossbauer spectroscopy leading to a ferromagnetic long-range order of iron magnetic moments following the double exchange mechanism. In contrast to many molecular magnets, usually belonging to the category of insulators, the double-exchange interaction between the metal centers favors a semiconducting behavior with low activation energy. Thus, a functional molecular material combining ferromagnetism and electrical conductivity within the same sub-lattice has been obtained for the first time.





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METALLOCENE AND BIS(ARENE) COMPLEXES OF TRANSITION METALS WITH 1,2,5-CHALCOGENADIAZOLE RADICAL ANIONS — A NEW APPROACH TO HETEROSPIN SYSTEMS

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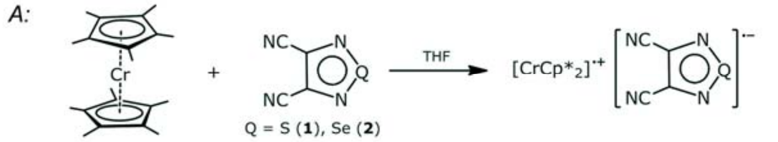
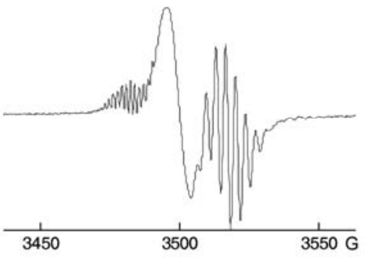
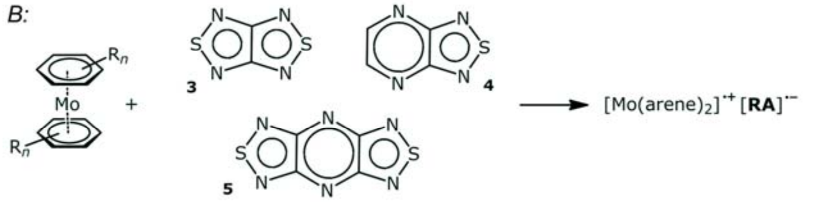
Chalcogenadiazoles represent an important type of main group element compounds, subclass of a large family of chalcogen-nitrogen π-heterocycles. An interesting feature is their positive electronic affinity, which gives them a possibility to turn to stable radical anions (RAs) upon reduction. This property can be efficiently used for the synthesis of crystalline phases based on combinations of the RAs with suitable radical cations; such heterospin salts may possess different types of magnetic ordering. We are investigating an approach of using reductive sandwich metal complexes, such as MCp^*_2 and $M(Arene)_2$, as both the reducing agents and sources of radical cations.

3,4-Dicyano-1,2,5-chalcogenadiazoles (S, Se) were shown to react with $CrCp^*_2$ to give crystalline salts (scheme *A*), which are heterospin, $S_1 = 3/2$ and $S_2 = 1/2$, systems experimentally featuring antiferromagnetic exchange interactions. Their Te congener has a prominent propensity to Te···N interactions to form coordination bonding, which precludes the formation of separate radical anions in the crystalline state.





EPR for [Cr(toluene)2][5]



To achieve ferromagnetic ordering, the spin canting model of interacting spins can be implemented, which requires spin-orbit coupling at heavier metal atoms (the Dzyaloshisky-Morya mechanism). To this end, we involved MAr_2 complexes (Ar = toluene, mesitylene; M = Cr, Mo) as reducing agents. Compounds $CrAr_2$ do not interact with the heterocycles **1** and **2**. Reactions take place with the heterocycles possessing larger electron affinity (**3**—**5**, scheme *B*), to give heterospin radical-ion species. Their EPR spectra show broad signals of radical cations and multiplets corresponding to RA. Heterocycle redox properties depend on the structure; the strongest acceptor **5** can be reduced with decamethylferrocene to give heterospin radical-ion salt.

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CHARACTERIZATION AND ANTIBACTERIAL PROPERTIES OF DIOXOMOLYBDENUM(VI) COMPLEXES WITH SYMMETRICAL TETRADENTATE SCHIFF BASE

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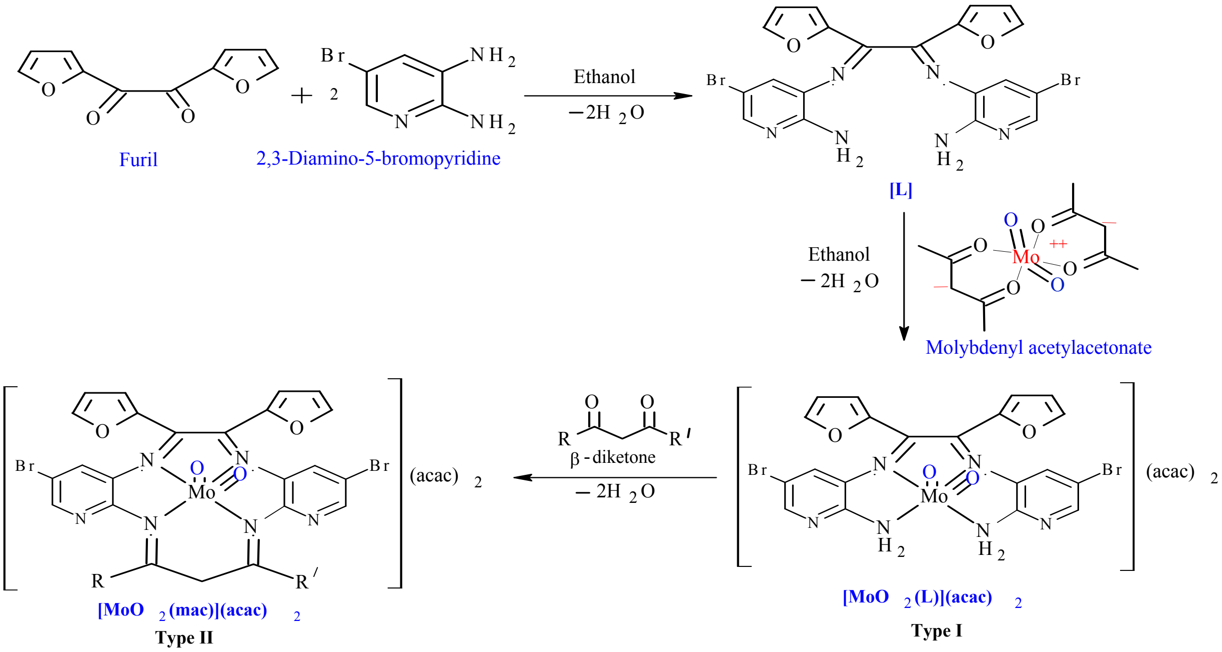
Synthesis of five new dioxomolybdenum(VI) complexes having formula $[MoO_2(mac)](acac)_2$, with a Schiff base , derived from condensation of furil with 2,3-diamino-5-bromopyridine and their cyclization with β-diketones are reported. The dioxomolybdenum(VI) complexes have been characterized by elemental analyses, molar conductance, UV-Vis, IR, mass, nmr spectra and thermal studies,. The probable coordination number of molybdenum is six. All complexes of dioxomolybdenum(VI) have octahedral geometry.



Where, L = furil + 2,3-diamino-5-bromopyridine; mac = macrocyclic ligands carried out from condensation of L with β-diketones in presence of dioxmolybdenum(VI) cation; R = CH_3, C_6H_5, C_4H_3S, C_6H_5; R' = CH_3, CH_3, CF_3, C_6H_5; respective β-diketone = (i) acetylacetone, (ii) benzoylacetone, (iii) thenoyltrifluoroacetone, (iv) dibenzoylmethane.

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Acknowledgements - Gratitude is expressed to the UGC, New Delhi, India [project F. No. 39-740/2010 (SR)] financial support. The authors would like to thank the Secretary, Board of Management, D.A-V. P.G. College, Kanpur, U.P., India for providing laboratory facilities for research work. Analytical facilities provided by SAIF, IIT, Bombay, India and STIC, Kochi, India are gratefully acknowledged.

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FACILE DESIGN OF COORDINATION COMPLEXES AND ORGANOMETALLICS USING ELEMENTOORGANIC LIGAND KIT

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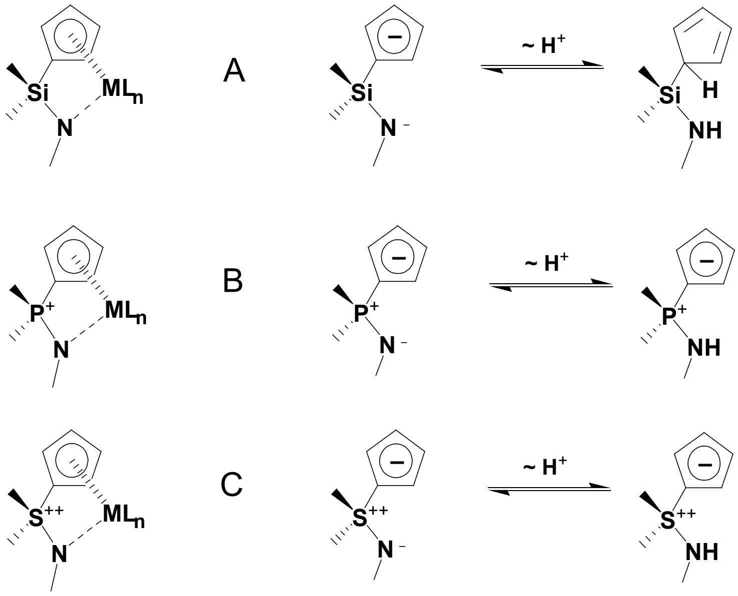
Generalization of synthetic approaches towards coordination and organometallic complexes is a fundamental challenge. Importance of this task can scarcely be exaggerated. Systematic ligand design based on organoelement compounds of a genaral type $R_2E(X)Y$, where E=P, S and X, Y = CHR, Cp(Ind or Flu), NR and O (S or Se) comprises a ligand kit thatr allows facile variation of ligand properties.



Thus, for example, linked cyclopentadienylsilylamido systems **A** become one of the best established and developed class of specially designed ligand precursors.

Bridged cyclopentadienylamido complexes therefrom, better known as "*constrained geometry catalysts*", are analogous to *ansa*-metallocenes. Depending on the nature of the ligand framework these complexes give high molecular weight polyethylene with long chain-branching and effeciently co-polymerize higher α-olefins. Isoelectronic analogues of the **A** systems are linked cyclopentadienyl-phosphazenes (**B**) and cyclopentadienyl-thiazenes (**C**).

Synthesis of a series of organometallics complexes, their catalytic applications and synthetic possibilities of elementoorganic ligand kit for design of new complexes will be discussed.

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RECENT ADVANCES IN BORON CLUSTER NUCLEOSIDE CONJUGATES CHEMISTRY

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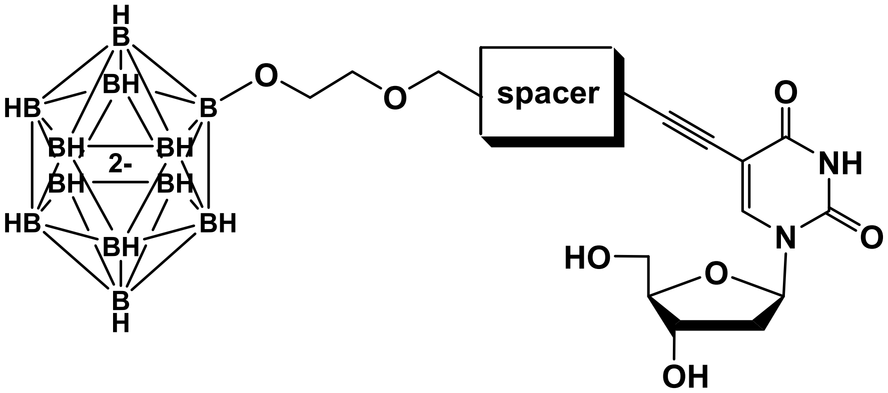
Development of methods for the synthesis of nucleosides bearing boron cages focuses growing attention in recent time. Potential application of these new type of bio-inorganic conjugates in medicine and biology range from their use as potential boron donors for BNCT of tumors and antiviral drugs[1,2].

In this contribution we would like to present our results on the synthesis of a series of cobalt-bis-dicarbollide and *closo*-dodecaborate clusters conjugates with nucleosides. Synthesis of the desired compounds by action of the nucleophile-modified nucleosides with a range of cyclic oxonium adducts of cobalt-bis-dicarbollide and *closo*-dodecaborate clusters and biological investigations of some of them will be discussed.



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THE REDOX TRANSFORMATIONS OF THE DIGALLIUM COMPLEX WITH REDOX-ACTIVE ACENAPHTHENE-1,2-DIIMINE LIGAND

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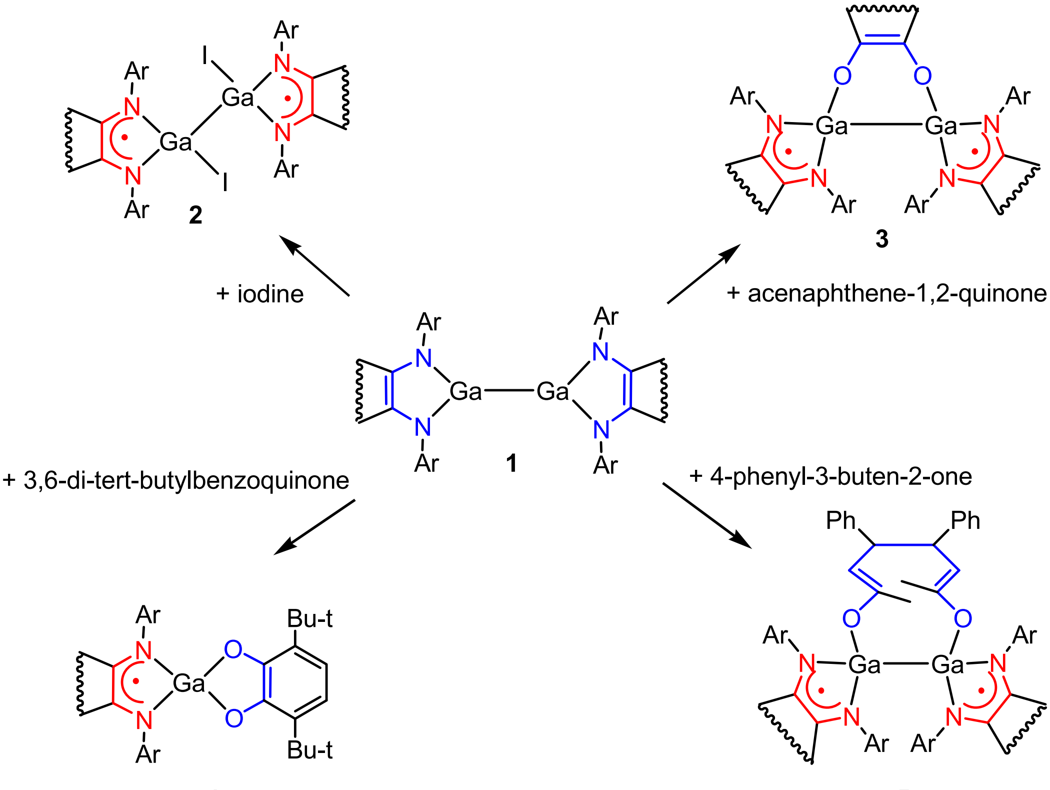
Main group metal complexes of bis(1,2-arylimino)acenaphtene ligands are highly reactive towards different organic substrates and might be useful reagents in organic synthesis. Recently we have established [1] the facile addition of various alkynes to binuclear gallium complex supported with 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN), (dpp-BIAN)Ga–Ga(dpp-BIAN) (**1**) and unusual thermally induced elimination of the alkyne.

Compound **1** contains two redox-active centres – atom Ga(+2) and diimine ligand and therefore exhibits diverse reactivity: the reactions of the digallane may occur with metal-metal bond cleavage or with electron transfer from the ligand to the substrate. Thus reaction of a digallane with one equivalent of iodine or acenaphthene-1,2-quinone leads to the compounds [(dpp-BIAN)GaI]$_2$ (**2**) and (dpp-BIAN)Ga(AcQ)Ga(dpp-BIAN) (**3**), containing gallium–gallium bond, whereas **1** reacts with 3,6-di-tert-butyl-o-benzoquinone (1:2) to give the monogallium catecholate complex (dpp-BIAN)GaCat (**4**), correspondingly. The oxidation of **1** with 2-phenyl-3-buten-2-one resulted in the bisenolate complex **5** containing new carbon–carbon bond. The compound **5** can be converted under heating to the initial digallane or to the monogallium complex.



acenaphthene parts are omitted for clarity

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FERROCENES-BASED ANTICANCER DRUGS. FACTS AND HYPOTHESES

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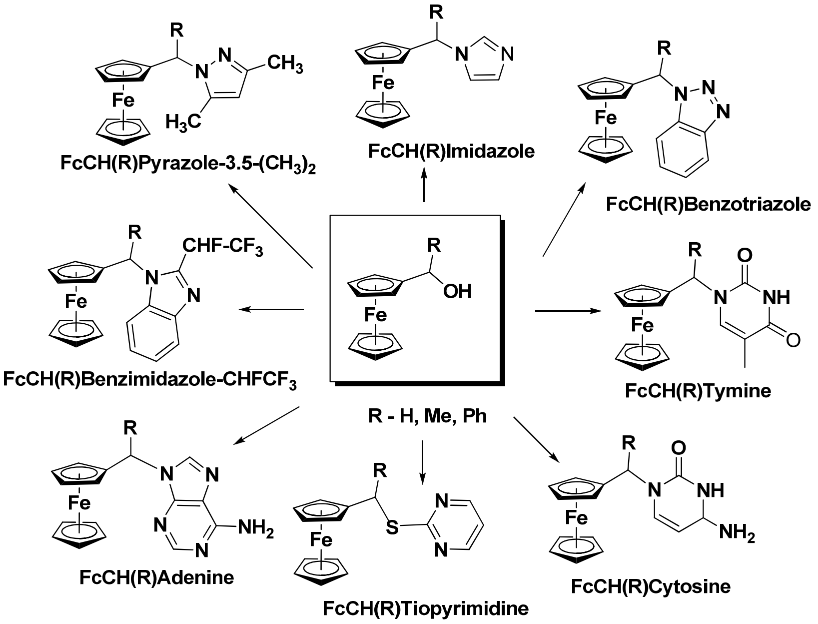
We investigated a large range of ferrocene compounds as anticancer drug candidates (Scheme). Antitumor effects of ferrocene derivatives of nucleobases, pyrimidines, and azoles including fluoroazoles against some murine tumor systems such as carcinoma 755, melanoma B16 and Lewis lung carcinoma were evaluated *in vivo*. Treatment of human ovary cancer cells with 1*N*-(ferrocenylethyl)adenine resulted in inhibition of DNA synthesis.

Authors postulate that the mechanism of antitumor ferrocene compounds consists in the initiation of the tumor cell apoptosis by protection telomere from the action of telomerase and/or by decreasing telomerase activity. These conclusions are supported by unique physical, chemical and biological properties of ferrocene compounds.

Synthetic approaches to ferrocene-modified biomolecules have been developed based on synthetically available hydroxyl(alkyl)ferrocenes (Scheme).



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THE OCTAHEDRAL IODIDE CLUSTERS OF Mo(II). SYNTHESIS AND LUMINESCENCE

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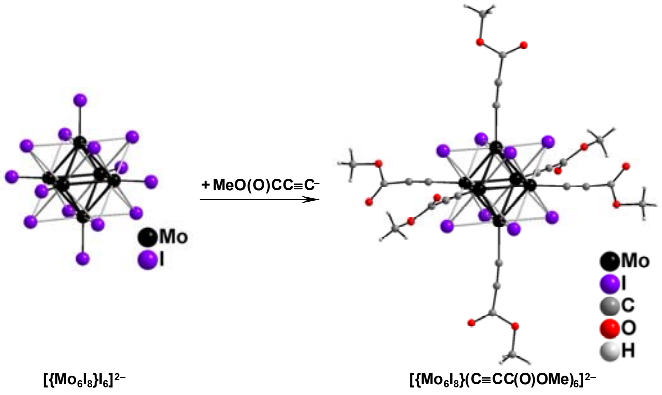
The octahedral halide bridged clusters of Mo(II) possess remarkable photophysical properties which can be used for development of new fluorescent materials. New results on $[Mo_6I_{14}]^{2-}$ chemistry will be presented. The anion $[Mo_6I_{14}]^{2-}$ is hydrolyzed in a solution of borate buffer at pH = 9.7, forming crystalline hydrates $[Mo_6I_8(OH)_4(H_2O)_2]\cdot 14H_2O$, $[Mo_6I_8(OH)_4(H_2O)_2]\cdot 12H_2O$, $[Mo_6I_8(OH)_4(H_2O)_2]\cdot 6H_2O$. X-ray analysis showed that the water molecules and hydroxide ligands are coordinated to the cluster core $\{Mo_6I_8\}^{4+}$; in the first two hydrates the water molecules form three-dimensional frameworks that resemble the structure of different modifications of ice, where cluster core are located in large cavities. Starting from $[Mo_6I_{14}]^{2-}$ several types of new luminescent cluster complexes were obtained: carboxylate complexes with a general formula of $[Mo_6I_8(OOCR)_6]^{2-}$ (R = C_5H_3O (α-furyl) (see **figure 1**), $C_{10}H_7$ (α-naphthyl), C_4SH_3, C_6F_5), nitrophenolate complexes $[Mo_6I_8(OR)_6]^{2-}$ (R = $-C_6H_4NO_2$, $-C_6H_3(NO_2)_2$), thiolate complex $[Mo_6I_8(SR)_6]^{2-}$ (R = C_6F_4H) and acetylenide complex $[Mo_6I_8(CCR)_6]^{2-}$ (R = CO_2CH_3). The complexes were obtained by metathesis reactions between $[Mo_6I_{14}]^{2-}$ and corresponding silver salts, and characterized by X-ray analysis, mass-spectrometry and other methods. The acetylenide complex $(Ph_4P)_2[Mo_6I_8(C_2CO_2CH_3)_6]$ containing six ligands of deprotonated methyl propiolate, is the first example of an homoleptic organometallic complex for octahedral clusters $\{M_6Q_8\}$. Luminescence properties of all new complexes were measured. The quantum yields and phosphorescence lifetimes depend on the external ligands in the following order: carboxylate > phenolate > thiophenolate > acetylenide. Among the carboxylates, introduction of fluorinated or aromatic groups improve the photophysical performance. In particular, perflurobutyrate $(Bu_4N)_2[Mo_6I_8(C_3F_7COO)_6]$ displays extraordinarily bright long-lived red phosphorescence, with the highest emission quantum yields among hexanuclear metal cluster complexes of Mo, both in acetonitrile solution (Φ_{em} = 0.59, λ_{em} = 668 nm) and solid phases (Φ_{em} = 0.36, λ_{em} = 659 nm). To conclude, unusually bright long-lived red luminescence can be expected for iodide cluster complexes of molybdenum with a fluorinated organic ligands, and the presence of conjugated systems in the structure of the ligand can greatly increase the luminescence intensity.



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FERROCENYLTELLURIM HALIDE AND METAL-CARBONYL DERIVATIVES.

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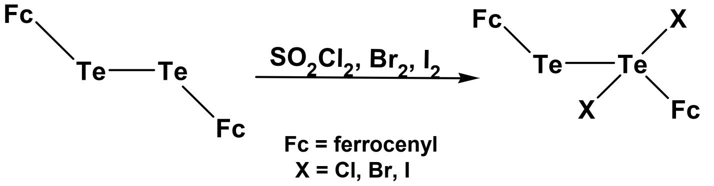
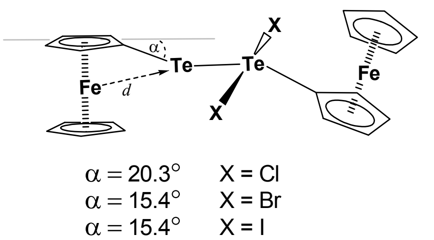
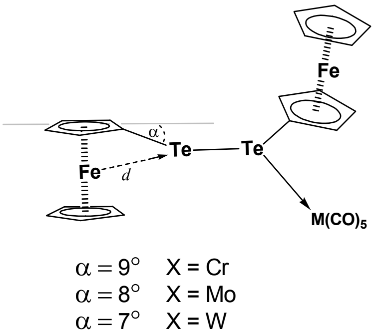
Despite the relative amount of halogenating agent halogenation of diferrocenyl ditelluride (Fc_2Te_2) affords only mixed-valent ferrocenyl-tellurenyls [FcTe-TeX_2Fc] (X=Cl (**1**), X=Br (**2**), X=I (**3**)). Unlike FcTe-TeCl_2Fc (**1**) and FcTe-TeBr_2Fc (**2**) revealing two signals in ^{125}Te NMR spectrum, the single ^{125}Te NMR resonance peak of iodo-(**3**) suggests the monomeric [FcTeI] structure in the solution at room temperature. In all three structures **1** - **3**, non-halogenated atom of Te^{II} bents towards the Fe atom of ferrocenyl so that the deviation of Te(2) atom from the plane of the related Cp ring increases from 15.5° to 20.3° as we move . from the iodo- **3** to the chloro- **1** (the Fe(2)---Te(2) distance decreases from 3.3714(6) Å in the iodo- **3** to 3.293(3) Å in the chloro- **1**). This lays within the range of 14.6° ~ 20.7° observed in α-ferrocenyl carbocations $[C_5H_5FeC_5H_4C(C_6H_5)_2]^+[BF_4]^-$ [1], $[C_5H_5FeC_5H_4($*cyclo*$-C_3(C_6H_5)_2)]^+[BF_4]^-$ [2] for which the interaction of filled nonbonding 3*d* t_2g orbitals of Fe with the LUMO of carbocation moiety was assumed.



Similar, but less pronounced bent of non-coordinated Te atom towards the Fe atom of ferrocene was observed in $M(CO)_5(Fc_2Te_2)$ – products of diferrocenyl ditelluride (Fc_2Te_2) interaction with VIb group metal carbonyls, let us suggest the analogous interaction of filled nonbonding 3*d* t_2g orbitals of Fe with the tellurium localized LUMO. Shortening of M-Te distance and corresponding elongation of Te-Te and Te-C distances in these complexes occurs due to and depends on the back donation of metal *d*-orbitals to Te-Te and Te-C localized LUMO of Fc_2Te_2 ligand.





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OBTAINING OF ANTIREFLECTIVE COATINGS ON THE BASIS OF NANOPOROUS SILICON DIOXIDE AT LOW TEMPERATURE ANNEALING GEL

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The sol-gel process becomes one of the most important ways to obtain various inorganic and composite organic-inorganic film coatings on glass, metals, and polymers. It has been found recently [1–8] that addition of nonsurfactant organic compounds (organic acids, their derivatives, synthetic carbochain polymers, statistical copolymers, and oligomers based on ethylene or propylene oxide) to a silicon dioxide sol makes it possible to obtain film coatings with strong antireflection effect on glass and quartz. However, the film coating deposited from a sol onto silicate glass was annealed at an elevated temperature of 500°C for several hours in order to obtain nanoporous silicon dioxide. The goal of our study was to examine the optical properties of coatings and glass with coatings produced from silicon dioxide sols with addition of poly(propylene glycols) (PPGs) with various molecular masses and a gel annealing temperature of 200°C. The results of present work: 1) Annealing of silicate glass with a film coating deposited from silicon dioxide sols with addition of PPG-425, PPG-725, PPG-1000, PPG-2700, PPG-4000 at a low temperature 200°C yields antireflection coatings composed of nanoporous silicon dioxide with low refractive index 1.26–1.30. 2) The optical transmission of a coated glass depends on the content of an additive in the sol and has the maximum values of 98.2% at 6.0% PPG-425, 97.7% at 6.0% PPG-725, 98.7% at 6.0% PPG-1000, 97.9% at 4.0% PPG-2700, and 97.5% at 4.0% PPG-4000. 3) With increasing content of a PPG in the sol, the peaks in the optical transmission curves for a coated glass shift to longer wavelengths, and this effect becomes more pronounced as the molecular mass of a PPG increases.

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POLYARYLENCARBORANES: FROM C-FUNCTIONALIZED BIPHENYL-*O*- AND *M*-CARBORANES TO LINEAR AND THREE-DIMENSIONAL POLYMERS WITH RECORD HEAT AND THERMO-OXIDATIVE STABILITY

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In Memory of prof., academician V.V. Korshak and prof. V.I. Stanko.

The report describes the history of development of carborane (12) containing monomers by C-functionalization of bis (4-phenyl) *ortho*-, *meta*- and in some cases *para*-carboranes, starting from the corresponding tolanes and decaborane, and also synthesis and properties of linear and three-dimensional polymers - polyarylencarboranes (PCAR).

The properties of PCAR are compared to their aromatic analogs. The essential difference of PCAR is unusual behavior at elevated temperatures in oxidizing medium (air), inert atmosphere or in vacuo: crosslinking at relatively low temperatures, low release of volatile compounds during heating until 1000°C.

It was found that reasons of such unusual thermal and thermo-oxidative behavior of PCAR consist predominantly in reacting generated boron-centered free radicals with aromatic surrounding of polymer matrix. Formation of boron-centered stable radicals has been first described in example of carborane-12. This in turn gave rise to the creation of carborancontaining monomers and polymers based on aromatic B-C and B-C unsaturated compounds. For example, first synthesis of carboranyl-B-(3,6)-p-phenyltrichlorosilanes was done - an important intermediate for producing crosslinked polycarboranylphenylsilanes. With the participation of GNIICHTEOS the appropriate setup was created at the plant "AVIABOR", Dzerzhinsk. The process was terminated due to the privatization of the company and change its technology policy.

The data on the materials (adhesives, hermetics, carbon plastics) with record thermal and thermo-oxidative properties are given. The development of materials based on PCAR was carried out jointly with NIIPLASTMASS, VIAM, GNIIChTEOS and other companies.

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MODIFICATION OF IRON(II) CLATHROCHELATES BY RADICAL REACTIONS

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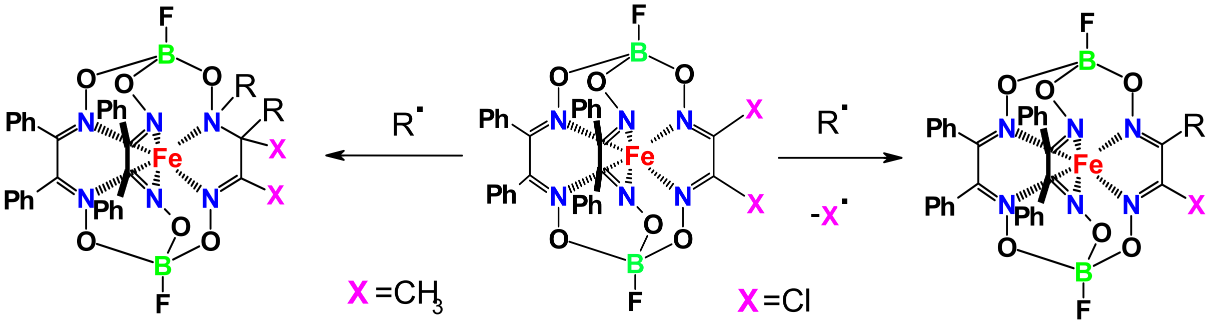
Tris-dioximate transition metal clathrochelates are promising molecular scaffolds for design of the polytopic molecules and polyfunctional materials [1]. Earlier [2], we have reported the functionalization of the dichlorine-containing boron-capped iron(II) macrobicyclic clathrochelate with different substrates using free-radical substitution.

This reaction proceeds as a radical addition-elimination at the azomethine C=N bond of the dioxime fragment (Scheme) and can be extended to cyclic ethers, alcohols, esters and alkanes. In all cases studied we observed chlorine atom elimination and the formation of new C–C bonds at the azomethine fragment. In continuation of this research, we try to use dimethylsubstituted iron(II) clathrochelate in such reactions. In this case clathrochelate reacts similarly to oxime ethers and hydrazones via addition of alkyl fragments to double C=N bond.



The clathrochelate complexes obtained were characterized by single-crystal X-ray crystallography and ^{1}H, ^{13}C-NMR.

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COBALT-INDUCED B-H AND C-H ACTIVATION LEADING TO FACILE B-C COUPLING OF CARBORANEDITHIOLATE AND CYCLOPENTADIENYL

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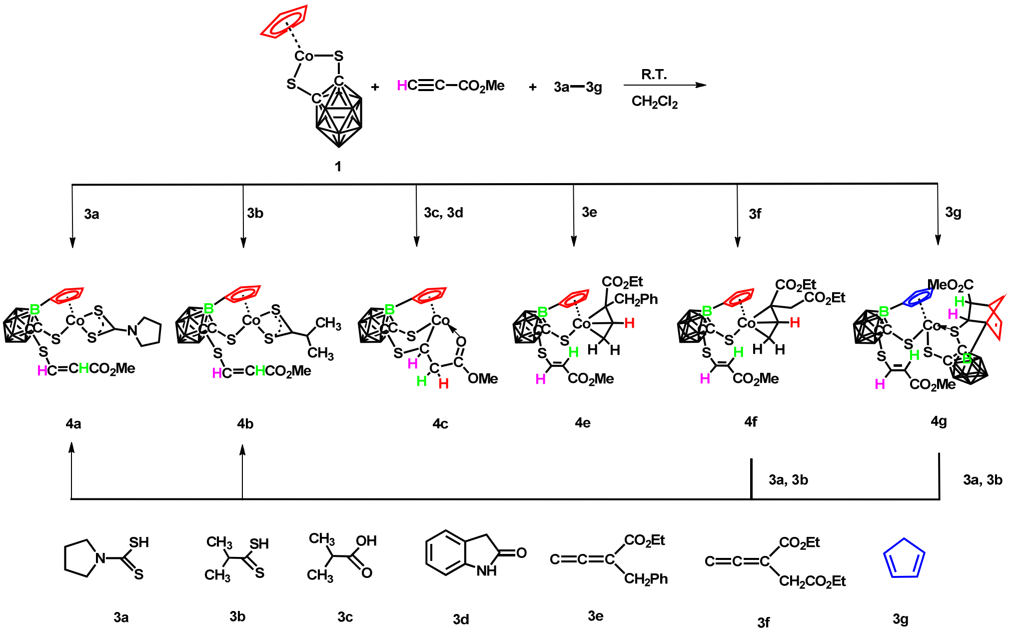
We report the one-pot reactions of the 16e half-sandwich complex CpCoS2C2B10H10 (1), methyl propiolate and 3e-donor ligands which have led to selective B-functionalization at carborane with cyclopentadienyl as a functional group at ambient temperature in good yields. Metal-promoted activations of both B–H bond at carborane and C–H bond at Cp unit have taken place sequentially in the cooperation of organic ligands. The reaction requires a 3e-donor ligand and an activated alkyne, therefore suitable for a broad range of substrates. This investigation provides a simple and efficient synthetic route to B-functionalized carborane derivatives.



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International Youth School-Conference on Organometallic and Coordination Chemistry

NEW HYBRID Nb AND Ta POLYOXOMETALATES FUNCTIONALIZED WITH ORGANOMETALLIC COMPLEXES

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Grafted noble metals on polyoxometalates (POM) can find applications in different catalytic applications [1, 2]. The hottest research area of such complexes is the photocatalytic water splitting [3]. In this case soluble POMs of Nb can be used as analogs of insoluble TiO_2 and POMs of Ta are soluble analogs of $NaTaO_3$. Synthesis of various complexes of $\{(p\text{-}cym)Ru\}^{2+}$ (p-cym = cymene) with $[Nb_6O_{19}]^{8-}$ with Ru/POM stoichiometries 1:1, 2:1, 3:1 and 4:1 was reported in 2007 [4]. We have found that reaction of $[(C_6H_6)RuCl_2]_2$ and $Na_8[Ta_6O_{19}]$ gives, depending on the reagent ratio, two new hybrid organometallic-POM complexes – $Na_{10}[\{(C_6H_6)RuTa_6O_{18}\}_2(\mu\text{-}O)]\cdot 39.4H_2O$ (1:1 ratio, Fig. 1) and $Na_4($*trans*-$[\{(C_6H_6)Ru\}_2Ta_6O_{19}]\cdot 20H_2O$ (2:1 ratio, Fig. 2). In both cases the half-sandwich fragments $\{(C_6H_6)Ru\}^{2+}$ are coordinated as additional vertices to the $\{Ta_3(\mu_2\text{-}O)_3\}$ triangles. The complexes have been characterized with x-ray structural analysis, NMR, IR, EA and CE. In water $[\{(C_6H_6)RuTa_6O_{18}\}_2(\mu\text{-}O)]^{10-}$ yields monomeric $[(C_6H_6)RuTa_6O_{19}]^{6-}$ which forms different protonated species. The *trans*-$[\{(C_6H_6)Ru\}_2Ta_6O_{19}]^{2-}$ in water solution isomerizes into *cis*-form, the isomers ratio being trans:cys 60:40.

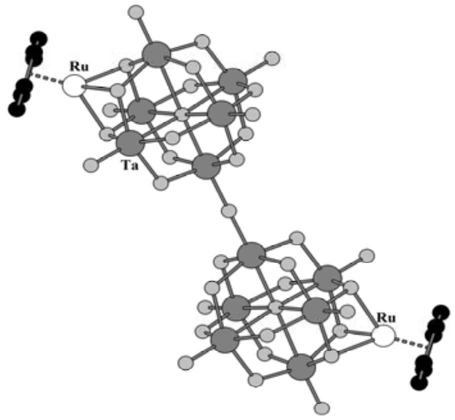

Fig. 1.

Fig. 2.

Reaction between $[M_6O_{19}]^{8-}$ (M = Nb, Ta) and $[Cp^*RhCl_2]_2$ in water gives a mixture of hybrid complexes with $\{Cp^*Rh\}$: $[M_6O_{19}]^{8-}$ ratios of 1:1, 2:1 and 3:1. Crystallization from reaction mixture gives only K^+ and Cs^+ salts of *trans*-$[\{Cp^*Rh\}_2M_6O_{19}]^{4-}$. In the case of $[Cp^*IrCl_2]_2$ the formation of $[\{Cp^*Ir\}_2M_6O_{19}]^{4-}$ also takes place, but according to ESI-MS data, species with Ir(IV) were also detected.

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TRIS(HYDROXYMETHYL)PHOSPHINE TRANSITION METAL COMPLEXES: FROM MONO- TO POLYNUCLEAR COMPOUNDS

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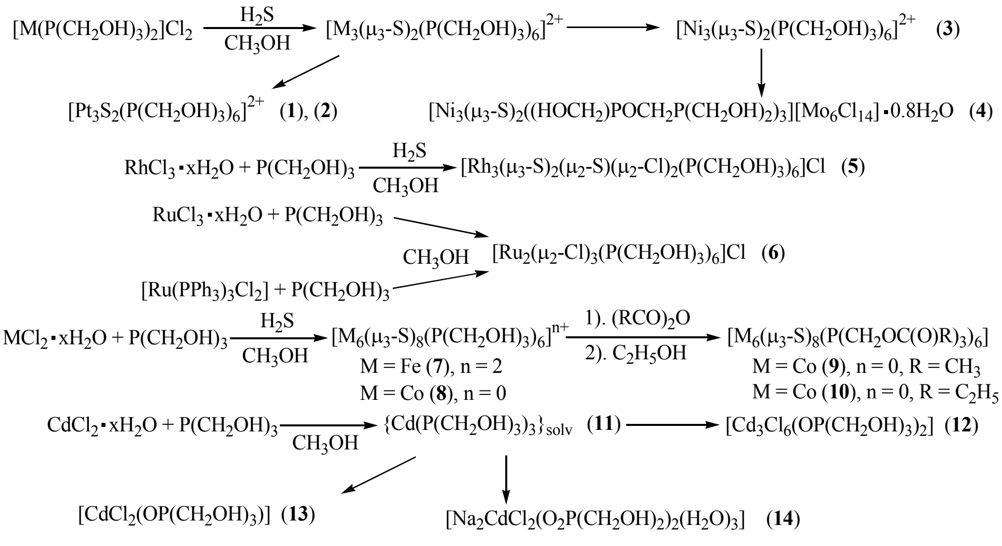
Cluster and polynuclear complexes have a number of properties, such as fluorescence, redox activity etc, which may yield in various application areas, for example, in development of new analytical and diagnostic agents, catalysis etc. However, a major obstacle for the applied use of these compounds is their low solubility in aqueous media/hydrophobicity caused by coordination of hydrophobic organic ligands which are common in this chemistry. This problem can be solved by introduction of special ligands such as tris(hydroxymethyl)phosphine (THP) which belongs to phosphine ligands which are known to stabilize such complexes and, on other hand, is hydrophilic and may be chemically modified. Only a few known examples of metal-sulfide complexes with THP are known, while polynuclear compounds with THP were not known at all. The purpose of this work is to develop a convenient method of obtaining the cluster and polynuclear complexes with THP and further modification of coordinated THP ligands to tune the properties. Synthesis technique was developed for 8-10 groups sulphide-metal clusters with THP.

We, therefore, have obtained 14 new compounds: 11 water-soluble sulfide cluster transition metal complexes with THP and 3 coordination polymers of Cd containing THP oxidation products. It was shown that THP may be involved in condensation to form a bidentate ligand $(HOCH_2)_2PCH_2OP(CH_2OH)_2$ during the synthesis of polynuclear complexes. We have also shown that coordinated THP may be acylated by acetic anhydride to give $P(CH_2OC(O)CH_3)_3$ ligands without destruction of metal-sulfide cluster core. Stoichiometry of THP and Cd^{2+} interaction was defined and the parameters of the transition state complex were determined. Three coordination polymers based on Cd^{2+} and THP oxidation products were synthesized. The donor ability of THP was evaluated in comparison with PMe_3 and PPh_3.



Acknowledgements – RFBR grant No. 13-03-01261 for financial support

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PALLADIUM NANOPARTICLES STABILASED BY STERICALLY HINDERED PHOSPHONIUM SALTS AS AN EFFECTIVE SUZUKI REACTION CATALYST

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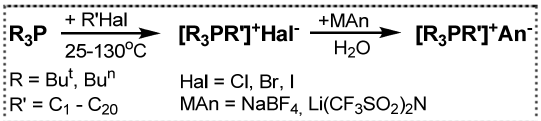
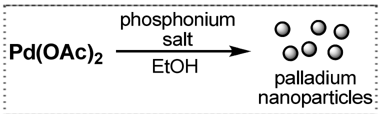
Palladium nanoparticles are effectively used as the catalyst in transition metal catalysed reactions such as Suzuki cross-coupling [1,2]. The problem of nanoparticles aggregation could be solved by using sterically hindered phosphonium salts (Scheme 1) as stabilizers.

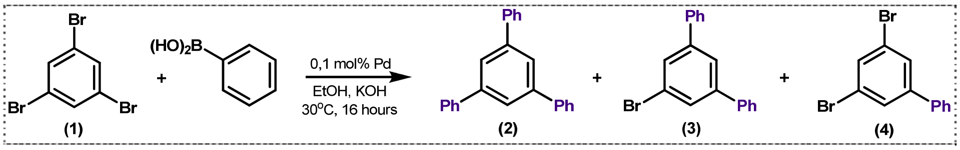


Scheme 1. Synthesis of the phosphonium salts.



Scheme 2. Palladium self-recovery.

Palladium nanoparticles were obtained *in situ* by stirring of palladium acetate in ethanol in the phosphonium salt presence (Scheme 2). The palladium nanoparticles formation has been proved by electron microscopy (Fig. 1).



Scheme 3. The Suzuki reaction.

A number of synthesized phosphonium salts was tested as the stabilizers of palladium nanoparticles in Suzuki cross-coupling of 1,3,5-tribromobenzene **(1)** and phenylboronic acid (Scheme 3). The results of catalysis are shown in Figure 2.

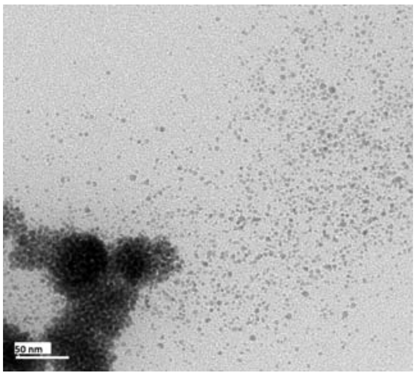


Figure 1. Palladium nanoparticles stabilized by $Bu^tP^+C_{10}H_{21}BF_4^-$.

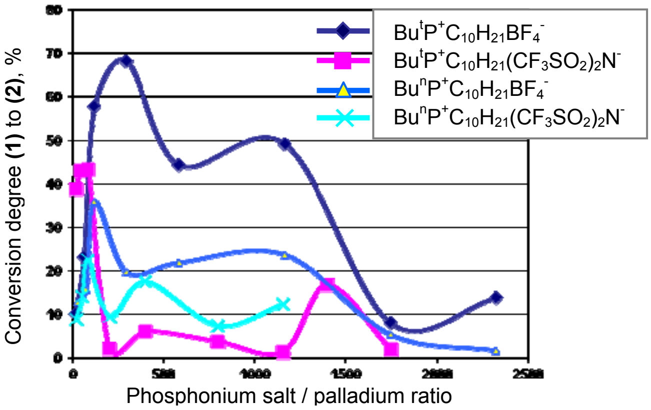


Figure 2. Influence of structure and concentration of the phosphonium salt on conversion degree **(1)** to **(2).**

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COMPLEXES OF YB (II) IN CATALYSIS OF INTERMOLECULAR HYDROAMINATION AND HYDROPHOSPHINATION OF OLEFINS

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Catalytic reactions of hydroelementation of C–C unsaturations attract a great deal of attention due to the 100% atom economy involved in these reactions. Application of this approach could lead to the development of new environmentally friendly green technologies. In addition, the products formed in these processes are used in pharmaceuticals, organic synthesis and materials science. The reaction rates of the hydroelementation reactions are known to increase with increasing ionic radius of the metal center. Therefore, the use of compounds of divalent lanthanides with large ionic radii, is a promising direction in the development of catalytic reactions of intermolecular hydrophosphination and hydroamination of olefins.

In order to investigate the catalytic activity in hydroamination and hydrophosphination reactions a series of amido and hydrido Yb (II) complexes stabilized by various ligand systems were synthesized: $[\{t\mathrm{BuC(NC_6H_3\text{-}2,6\text{-}}i\mathrm{Pr_2)_2}\}\mathrm{YbN(SiMe_3)_2(THF)}]$ (**1**), $[\{t\mathrm{BuC(NC_6H_3\text{-}2,6\text{-}}i\mathrm{Pr_2)_2}\}\mathrm{Yb(\mu\text{-}H)}\}_2]$ (**2**), $[\{t\mathrm{BuC(NC_6H_3\text{-}OMe)(NC_6H_3\text{-}2,6\text{-}}i\mathrm{Pr_2)}\}\mathrm{YbN(SiMe_3)_2(THF)}]$ (**3**), $[\{3,5,10,12\text{-}t\mathrm{Bu_4C_{13}H_4N}\}\mathrm{YbN(SiMe_3)_2(THF)}]$ (**4**), $[\{2\text{-}(\mathrm{N}\text{-}2,6\text{-}i\mathrm{Pr_2C_6H_3})\text{-}6\text{-}(2,6\text{-}\mathrm{Me_2C_6H_3})\text{-}\mathrm{C_5H_3N}\}\mathrm{YbN(SiMe_3)_2(THF)}]$ (**5**), $[\{\mathrm{MeC[(N\text{-}2,6\text{-}Me_2C_6H_3)_2(NC_6H_3)][(NC_6H_3\text{-}2,6\text{-}}i\mathrm{Pr_2)]}\}\mathrm{YbN(SiMe_3)_2(THF)}]$ (**6**), $[\{\mathrm{O\text{-}2,4\text{-}}t\mathrm{Bu_2\text{-}6\text{-}(12\text{-}crown\text{-}5)C_6H_3}\}\mathrm{YbN(SiMe_3)_2}]$(**7**).

It was found that the synthesized compounds exhibit a catalytic activity in intermolecular styrene hydroamination and hydrophosphination reactions. All reactions were found to be regioselective, forming exclusively the Anti-Markovnikov addition product. These catalysts allow carrying out intermolecular hydroamination and hydrophosphination reactions at 60°C with quantitative conversions without using a solvent.

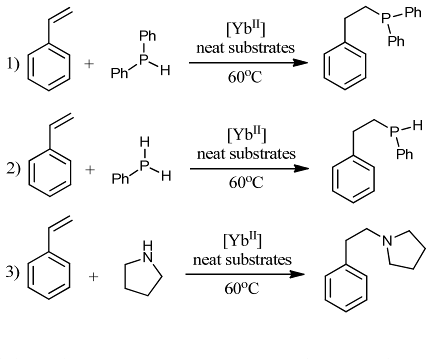

Figure 1. 1) Hydrophosphination of styrene and $\mathrm{HPPh_2}$; 2) hydrophosphination of styrene and $\mathrm{H_2PPh}$; 3) hydroamination of styrene and pyrrolidine catalyzed by Yb(II) complexes.

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SYNTHESES, STRUCTURES AND LUMINESCENT PROPERTIES OF THE TRANSITION METAL COMPLEXES CONTAINING 2,1,3-BENZOTHIADIAZOLE DERIVATIVES

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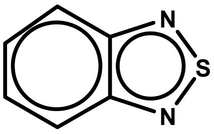
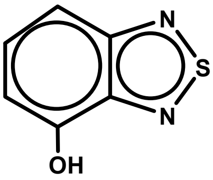
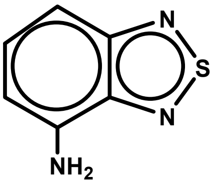
2,1,3-benzothiadiazole derivatives are promising building blocks for design of molecular magnets and conductors. Furthermore, due to their photophysical properties the benzothiadiazoles can be used as components of organic light emitting diodes (OLED). For OLED applications, these heterocycles are interesting not only as structural units of polymers but also as ligands in transition metal complexes [1]. Recently we described the syntheses of the iridium complexes containing 2,1,3-benzothiadiazole (btd) and its 4-hydroxy- (OH-btd) and 4-amino- (NH_2-btd) derivatives [2]. Herein we report about their luminescent properties and about syntheses, structure and some physical properties of the ruthenium, zinc and yttrium complexes of OH-btd and NH_2-btd.



btd



OH-btd



NH_2-btd

Reactions of NH_2-btd with $ZnCl_2$ and $Y(N(SiMe_3)_2)_3$ and OH-btd with $[\{Ru(bpy)_2\}_2(OMe)_2]$ have been investigated. It has been shown that NH_2-btd is a week acid and can react as neutral molecule or deprotonated (NH-btd$^-$) anion. In the first case it coordinates a metal by NH_2-group, in the other one both by NH^- and N atom of heterocycle. Structures of the complexes $[ZnCl_2(NH_2\text{-btd})_2]$, $[Y_2(NH\text{-btd})_6(THF)]$ and $[Ru(bpy)_2(O\text{-btd})](PF_6)$ have been confirmed by single crystal X-Ray diffraction and other routine methods. Furthermore luminescent properties of the iridium and ruthenium complexes have been studied. It has been shown that emission wavelength depend only of the heterocycle nature.

[1] B. A. D. Neto, A. A. M. Lapis, E. N. da Silva Júnior, et al, *Eur. J. Org. Chem.* **2013**, 228–255
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STRUCTURAL FEATURES OF THE HETEROMETALLIC COMPLEXES $V^{IV}O$-M^{II} (M^{II} = Mn^{II}, Co^{II}, Cd^{II}) BASED ON SUBSTITUTED MALONIC ACID ANIONS

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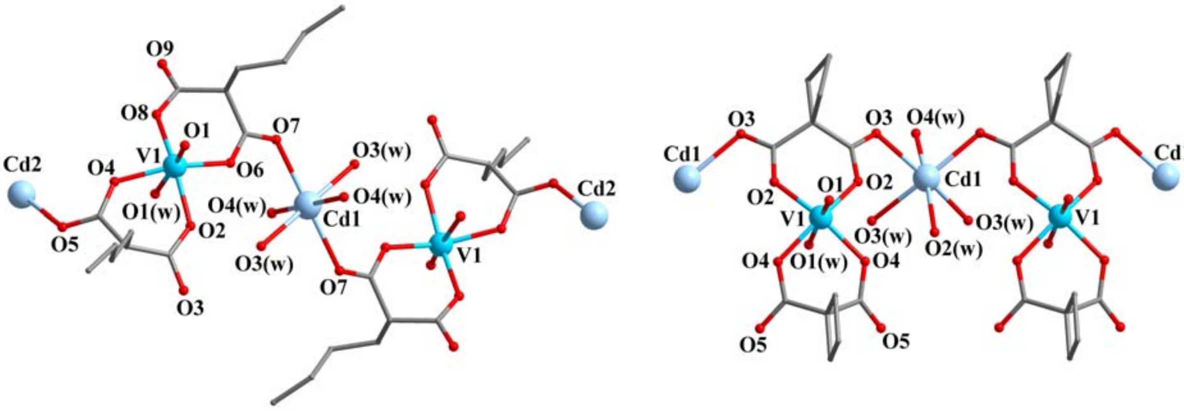
In present work we have studied the possibility of formation of the new heterometallic complex compounds with combination of metals V^{IV}-Mn^{II}, V^{IV}-Co^{II}, V^{IV}-Cd^{II} and dimethylmalonic, (H_2Me_2mal), butylmalonic (H_2Bumal) and cyclobutane-1,1-dicarboxylic (H_2Cbdc) acid anions. Compounds **1**-**5** of general formula $\{[M^{II}(V^{IV}O)L_2(H_2O)_5]\cdot H_2O\}_n$, where **1**: M^{II} = Mn^{II}, L = Me_2mal; **2**: M^{II} = Co^{II}, L = Me_2mal; **3**: M^{II} = Mn^{II}, L = Bumal; **4**: M^{II} = Cd^{II}, L = Bumal; **5**: M^{II} = Cd^{II}, L = Cbdc were obtained in crystalline form and characterized by X-ray diffraction analysis.

Complexes **1**-**5** crystallize from water solutions, obtained by interaction of vanadyl sulfate $VOSO_4\cdot 3H_2O$ solution, d-metal M^{II} sulfate and barium salt of the corresponding dicarboxylic acid BaL in the ratio 1:1:2. Compounds are built on the base of dianionic metal fragments $\{VOL_2(H_2O)\}^{2-}$, in which the vanadium(IV) atom chelates two substituted malonic acid dianions, one water molecule and the oxygen atom of the vanadyl group {V=O} forming distorted octahedral oxygen environment. In structures **1**-**5** bis-chelate fragments linked with Mn^{II}, Co^{II} and Cd^{II} atoms through the acid dianion carboxylate oxygen atoms, which are not coordinated by vanadium(IV) atoms, forming polymeric chains. Heteroatoms complete octahedral coordination environment with four O atoms of water molecules.



a *b*

Fig. 1. Fragments of polymeric chains of compounds **4** (*a*) and **5** (*b*).

In binding vanadium(IV) and d-metal atoms in complexes **1**-**4** both malonate anions of bis-chelate fragment $\{VOL_2(H_2O)\}^{2-}$ take part, and each anion binds vanadium-containing fragment with one d-metal atom. Unlike them in compound **5** only one of the ligand anions takes part in binding $\{VOL_2(H_2O)\}^{2-}$ fragments with Cd atoms, linking together three metal atoms at once; the second anion of the bis-chelate dianionic fragment performs only chelate function (Fig. 1).

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STUDY OF THE FISCHER- TROPSCH SYNTHESIS IN THE PRESENCE OF A NANOSTRUCTURED IRON OXIDE-POLYMER CATALYST

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The Fischer-Tropsch process is a catalytic reaction between carbon monooxide and hydrogen yielding a mixture of liquid hydrocarbons. Catalyst used for the process normally contain iron or cobalt. The key application of the process is production of synthetic lubricants and oil.

Iron oxide (Fe_2O_3, FeO, Fe_3O_4) nanoparticles catalyse reactions which involve allylic chloroolefins, such as isomerisation with the double bond and chlorine atom migration or alkylation of aromatic hydrocarbons. The catalysis efficiency and dominating reactions depend on the presence of oxygen, oxidation state of iron atoms and the immediate environment of the nanoparticles in the catalyst.

Composites consisting of low density polyethylene (LDPE) impregnated with iron-containing nanoparticles were prepared by thermal decomposition of iron nitrate in a solution-melt of LDPE in oil at 240–260 °C in inert atmosphere; the prepared samples were consequently stored in air. The size of the nanoparticles did not exceed 2–4 nm.

The catalyst was mixed with the P-2 paraffin before the Fischer-Tropsch synthesis; the catalyst completely dissolved in the paraffin and formed a stable suspension. The reaction was carried out under vigorous stirring (400 rpm) in an autoclave flow-through reactor. The catalyst was subject to preliminary activation in a carbon mooxide flow (14 nl/g(Fe)·h) at 300 °C and 20 atm for 20 hours.

The catalyst was found to be inactive at low temperatures, but its activity rises during conditioning resulting in higher CO conversion ratios at higher temperatures. The CO conversion ratio at 300 °C is 80%, and the liquid products yield becomes as high as 138 g/m^3. On the other hand, liquid product selectivity decreases from 84% at 240 °C to 54% at 300 °C. The selectivity decrease is mainly due to the water-gas side reaction. The catalyst exhibits high throughput (2228 g/kg(Fe)·h at 300 °C).

The liquid product formed on the catalyst consists of two layers: the aqueous layer with oxigenate compounds and hydrocarbon layer. Hydrocarbon products formed during the synthesis include both saturated and unsaturated hydrocarbons (the content of the latter does not exceed 39% wt.) An important parameter of the Fischer-Tropsch process is the chain growth probability α which can be used as an indicator of the polymerization activity; the tested catalyst has $\alpha = 0.58$. The composition of the hydrocarbon product is: 77% wt. gasoline fraction, 22% wt. diesel fraction, < 1% wt. solid aliphatic hydrocarbons.

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NEW BIFUNCTIONAL QUINONE WITH TETRATHIAFULVALENE BRIDGE. SYNTHESIS, STRUCTURE AND PROPERTIES.

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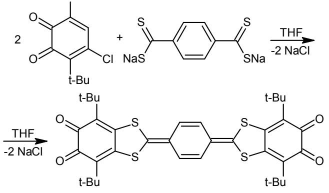
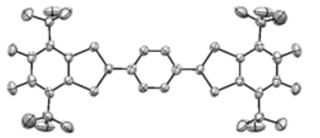
Organic redox-amphoteric compounds have great scientific interest because of their ability to oxidize and reduce reversibly relatively neutral state. Combination in one molecule acceptor and donor units leads to organic redox-amphoteric compounds. Nowadays acceptor-donor-acceptor (A-D-A) triads are extensively studied systems. Here we present a new bifunctional quinone with p-extended tetrathiafulvalene moiety as example of A-D-A triad. Synthesis of novel compound was carried out through three steps. First of all, dichloro-p-xylylene was prepared. Then it was converted into sodium tetrathioterephtalate. Final stage is stoichiometrical interaction between two equivalents of 4-chloro-3,6-di.tert.butyl-o-benzoquinone and one equiv sodium tetrathioterephtalate (scheme 1). Product was isolated as rectangle shaped black needle crystals and characterized with physicochemical analysis methods. Taking into account IR -, NMR-spectroscopy and X-ray data, we have supposed that charge transfer process is proceeded in bifunctional quinone molecule.

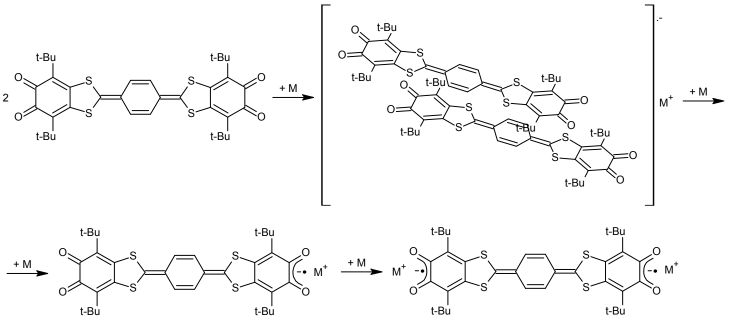


Scheme 1.



Picture 1. Structure of bifunctional quinone with tetratiafulvalene bridge.

Chemical reduction of bis-o-quinone as ligand has been studied (scheme 2). Bifunctional quinone contains four hydrogen atoms at the central phenylene ring. This fact substantially gains an amount of information which can be obtained from EPR spectroscopy data. EPR and UV spectroscopy simultaneous study reveals a sequential formation of two different paramagnetic species during chemical reduction of quinone with metal sodium. On the first stage dimeric radical anion particle with formal oxidation state -1/2 was generated (Robin-Dei III-rd class). Second compound is o-semiquinone metal complex. These two intermediate compounds have different signals in EPR spectra.



Scheme 2.

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FIRST EXAMPLE OF CAGE-LIKE METALLASILOXANES USED AS CATALYSTS IN HOMOGENEOUS OXIDATION OF C–H COMPOUNDS

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Oxidation of hydrocarbons, alcohols and other C–H compounds with peroxides is an important field of contemporary metal-complex catalysis. We revealed a significant potential of cage-like Cu(II)-silsesquioxanes for the homogeneous (acetonitrile solution) oxidation of several C-H substrates by aqueous hydrogen peroxide under mild conditions (temperature <70°C). Such observation is very attractive due to convenient synthesis of catalysts, their low cost and stability. It has been also revealed that the course of the reaction is highly influenced by cage geometry and nature of co-catalysts.

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SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF HIGH-SPIN MANGANESE CARBOXYLATES

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High-spin polynuclear complexes and coordination polymers of 3d metals, especially of manganese(II), attract attention due to their magnetic properties. Such compounds can reveal magnetic ordering, magnetic hysteresis, etc. In this work new results in the field of new manganese compounds synthesis, investigation of their structure and magnetic properties are presented.

Destruction of the polymer $[Mn(Piv)_2(EtOH)]_n$ (Piv = pivalate) by chelating and bridging N-donor ligands (pyrimidine (prm), pyrazine (prz), 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen)) was studied. Reaction of $[Mn(Piv)_2(EtOH)]_n$ with pyrimidine in inert atmosphere resulted in formation of hexanuclear complex $Mn^{II}_6(OH)_2(Piv)_{10}(prm)_4$ (**1**), which consists of two Mn_3 triangular connected by carboxylate bridges. The oxidation of **1** by air led to formation of mixed-valence 1D coordination polymer $[Mn^{II}_2Mn^{III}_4(\mu_4\text{-}O)_2(Piv)_{10}(\mu\text{-}prm)(prm)]_n$ (**2**).

The 2D polymer $[Mn_4(OH)(Piv)_7(prz)_2{\cdot}2MeCN]_n$ (**3**) was formed in reaction between $[Mn(Piv)_2(EtOH)]_n$ and pyrazine.

Two complexes $Mn_2(Piv)_4(\eta^2\text{-}L)_2$ (L = bpy (**4**), phen (**5**)) have been synthesized via the reaction of $[Mn(Piv)_2(EtOH)]_n$ with stoichiometric amounts of 2,2'-bipyridine or 1,10-phenanthroline, respectively, in inert atmosphere. The oxidation of **4** and **5** by air produced tetranuclear mixed-valence complexes $Mn^{II}_2Mn^{III}_2(O)_2(Piv)_6(L)_2$ (L = bpy (**6**), phen (**7**)).

The structures of all complexes were determined by single-crystal X-ray diffraction, magnetic properties of complexes **1**, **3**-**5** were studied.

Exchange coupling parameters for **3** were calculated by fitting of temperature dependence of magnetic susceptibility and independently estimated by DFT.

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NOVEL COORDINATION COMPOUNDS BASED ON OCTAHEDRAL RHENIUM(III) CHALCOCYANIDE CLUSTERS AND COPPER IONS

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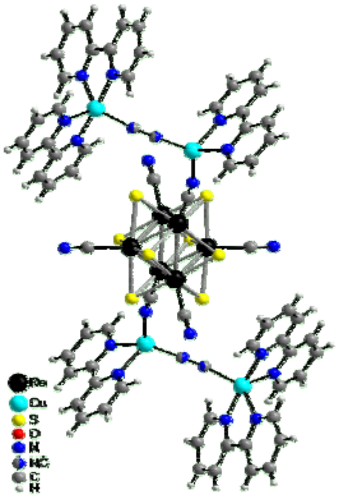
Compounds containing hexanuclear rhenium(III) cluster anions of the type $[Re_6(\mu_3\text{-}Q)_8L_6]^{n-}$ (Q = S, Se, Te; L = CN, OH and other) have been intensively investigated over the past decade [1]. The long-term interest in hexanuclear rhenium(III) cluster compounds is due to a wide variety of their chemical and physical properties, such as the ability to form many organic-inorganic polymeric structures, redox formations, and luminescence both in solution and in the solid state. Particularly, chalcocyanide anions, containing CN groups as terminal ligands are known as building blocks suitable for the creation of extended arrays of clusters constructed *via* CN–M–CN bridging, where M is transition 3d-metal. In these compounds, the coordination sphere of the metal centers are often completed by additional ligands such as water or/and ammonia molecules. The addition of chelating ligands can be used to modify the structure dimensionality of the resulting compounds.



In this work we present the synthesis and characterization of four compounds containing the $[Re_6Q_8(CN)_6]^{4-}$ cluster anions, CuCN and bpy as chelating ligand (bpy – 2,2'bipyridyl). The novel compounds are the discrete molecular complex $[\{Cu(bpy)_2(\mu\text{-}CN)\}\{Cu(bpy)\}_2Re_6S_8(CN)_6]\cdot bpy\cdot H_2O$, 3D polymeric complex $[Cu_2(bpy)_2(CN)][\{Cu(bpy)\}_3Re_6S_8(CN)_6]$ and 1D polymeric complexes $[\{Cu_2CN(bpy)_2\}_2\{Cu(bpy)\}_4Re_6Se_8(CN)_6]$ and $[\{Cu_2CN(bpy)_2\}_2\{Cu(bpy)\}_4Re_6Te_8(CN)_6]$. All of them were hydrothermally synthesized under autogenous pressure starting from corresponding octahedral rhenium(III) chalcocyanide cluster complexes, CuCN and bpy. It is interesting to note that in the case of $[Re_6S_8(CN)_6]^{4-}$ anion, the variation of reaction conditions leads to the formation of molecular complex (depicted in figure) or 3D coordination polymer. The molecular complex features the presence of differently charged copper ions, Cu^+ and Cu^{2+}, possessing tetrahedral and trigonal bipyramidal coordination geometries, respectively. In addition, the compounds were characterized by a set of physical-chemical methods.

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Acknowledgements - This research was supported by Russian Foundation for Basic Research (Grant No. 11–03–00157 and Grant No. 12–03–31670–мол_а).

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BIPYRIDINE AND PHENANTHROLINE IR-SPECTRAL BANDS AS “PROBES” OF METAL SPIN STATE IN HEXACOORDINATED COMPLEXES OF Fe(II), Ni(II) AND Co(II)

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Vibrational spectroscopy is often used to observe the influence of the spin state of transition metals on the binding properties of their complexes. A change of the metal spin state affects mostly the bands of metal-ligand stretching vibrations, which are sometimes weak, or overlaid by intra-ligand vibrational modes, or are not unambiguously assignable. The reported applications of **mid**-IR spectroscopy to analysis of the spin transition behavior are mainly limited to monitoring frequency shifts of easily assignable group characteristic bands, e.g., stretchings of NCS or N_3 moieties. Differences in the bands of aromatic ligands occurring with changes of metal spin state are not so pronounced and are therefore difficult to indicate and to interpret. Recently we have demonstrated on the examples of Fe(II) complexes with cyclopentadienyl [1] and tris(pyrazol-1-yl)methane [2] ligands that quantum chemistry is convenient tool for solving this problem and found several bands of the ligands’ vibrations, which are sensitive to the metal spin state. The main limitation of the above approach is the need in rather time-consuming quantum-chemical computations for revealing the mid-IR spectroscopic markers suitable for spin-state diagnostics of every new type of complexes. The analytical power of the method would grow essentially if the markers found for complexes of one transition metal could be applied to studies of similar complexes of other metals. To study such a possibility we simulated quantum-chemically the IR spectra of a series of 2.2’-bipyridine (bpy) and 1,10-phenanthroline (phen) complexes of Fe(II), Ni(II) and Co(II) for various spin states of the metals, and compared the computed spectra with the experimental IR spectra of the compounds. Spectral changes caused by variation of metal spin state were found not only for metal-ligand vibrations, but also for the ligands’ modes. Differences between the spectra of bpy and phen complexes with populated and non-populated high-lying 3d-orbitals of the metal were practically independent on the metal nature. This fact allows applying IR markers found for the studied compounds to IR spectroscopic analysis of other complexes of 3d-metals. In particular, the markers revealed were demonstrated to be valid for the bpy and phen complexes of Zn(II) and Cu(II) [3]. This suggests that such widely used ligands as bpy and/or phen can be employed as a sort of versatile IR-spectroscopic “probes” for studies of spin/electronic state of the metal centre in the corresponding complexes. It has been demonstrated very recently by the example of newly synthesized dinuclear complex $[Co_2(\mu\text{-}O_2P(H)Mes)_2(bpy)_4]Br_2$, where Mes = 2,4,6-trimethylphenyl [4].

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TRANSITION METAL HETEROMETALLIC COMPLEXES WITH SUBSTETUTED MALONATE ANIONS WITH DIFFERENT METAL RATIO. ASPECTS OF SYNTHESIS AND STRUCTURE FEATURES

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Malonic acid is an efficient bridging ligand for transition metal complexes construction. In literature transition metal heterometallic malonates $[MM'(mal)_2(H_2O)_x]$ are known only with molar ratio M:M'=1:1 and most of that are ionic [1]. In this work we had shown how the complexes packing and metal ratio could be changed.

The reaction of $CuSO_4{\cdot}5H_2O$ with barium cyclobutane-1,1-dicarboxylate ($cbdc^{2-}$) and $MSO_4{\cdot}6H_2O$ led to crystallization of ionic complexes $[Cu(cbdc)_2(H_2O)][M(H_2O)_6]$(M=$Co^{2+}$(**1**) or Ni^{2+} (**2**)) (Fig. 1, *a*). With Mn ion complex $4[Cu(cbdc)_2(H_2O)][Mn(H_2O)_6][Mn(H_2O)_8]{\cdot}15(H_2O){\cdot}3(H_3O)$ (**3**) with ratio Cu:Mn=2:1 was crystallized. But when the starting compound was $[Cu_4K_4(Me_2mal)_8(H_2O)_8]_n$ (Me_2mal^{2-} is dimethylmalonic acid anion) the interaction with $M(NO_3)_2$ gave polymers $[(H_2O)_9K_2NiCu_2(Me_2mal)_4]_n$ (**4**) and $[(H_2O)_{16}K_4Co_3Cu_4(OH)_2(Me_2mal)_8]_n$ (**5**) (Fig. 1, *b*) with total Cu:M ratio 2:1 and 4:3 respectively.

The another way to change the metal ratio is isomorphic substitution of one transition metal to another. This phenomenon takes place in complex $[Co_{0.6}Cu_{0.4}(Me_2mal)(H_2O)_5]_n$ (**6**), that was obtained in reaction of $BaMe_2mal$ with the mixture of Co^{II} and Cu^{II} sulfates.

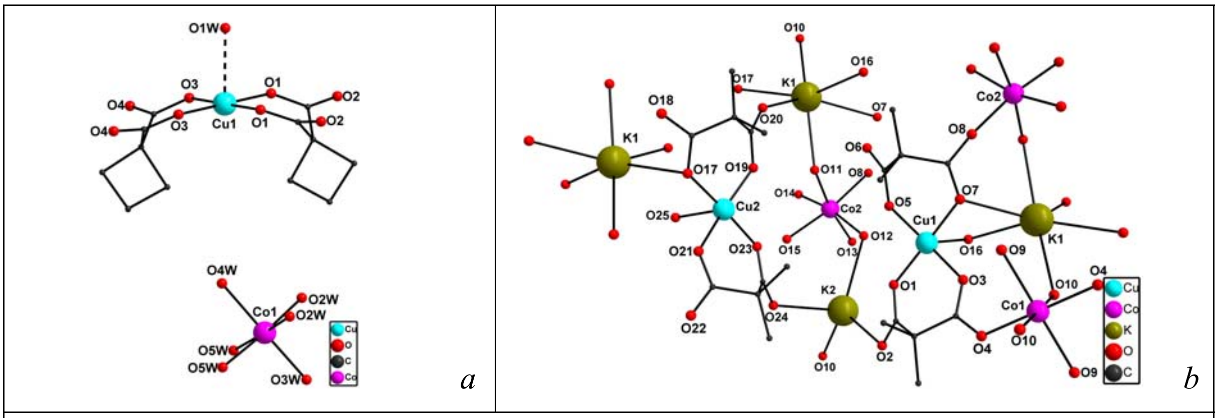

Fig. 1. Structure of complexes **1** (*a*), **5** (*b*).

Crystal packing of complexes and the reasons of some or other special features are discussed.

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Acknowledgements - this study was supported by Russian Foundation of Basic Research (11-03-00735, 12-03-31151), The Council on Grants of the President of the Russian Federation (NSh-2357.2012.3), the Russian Academy of Science.

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ACID-BASE PROPERTIES OF DIMETHYLAMINE-BORANE AND ITS COMPLEXES OF TRANSITION METALLS

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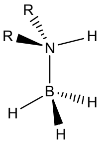
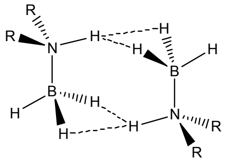
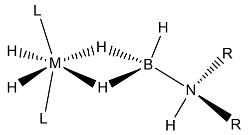
As hydrogenated amine-boranes $R^1R^2NH–BH_3$ as well dehydrogenated aminoboranes $R^1R^2N=BH_2$ – both are of great interest for researchers because of their variety of uses as selective reducing agents and hydroboration reagents in thin organic synthesis, hydrogen source and reversible hydrogen storage material, catalyst of polymerization and building blocks for polymeric materials. The amine-boranes are a neutral equivalent of tetrahydroborate ion (BH_4^-) and isoelectronic to alkanes, so it can be structural models of activation C–H bonds on metal centers.

The dimethylamine-borane (DMAB) and its transition metal complexes was thoroughly studied by means of combination of experimental (IR, UV, NMR and X-ray 190-300 K) and computational (DFT/M06, DFT/BP86) methods.







DMAB contain as acidic center (NH-group) as well as basic center (BH_3-group) – so it capable to form a dimer stabilized by dihydrogen bond (DHB). Acid-base interactions are competing with self-association of DMAB depending on the solvent polarity. So it was determined experimentally that in non-polar media (hexane, CCl_4) the dominant form is associated with the energy of DHB $\Delta H_{H\cdots H}$= 2.06 kcal/mol, at low-polar media the associated form is 15–30% (with respect to integral intensity of ν_{OH}^{free} at 270–290 K) with energy $\Delta H_{H\cdots H}$= 1.47 kcal/mol.

From experimental data of interaction organic bases on acidic center and proton donors on basic centers the acidity and basecity factors were determined by Iogansen's rule of factors and equal to $P_i = 0.51 \pm 0.06$ and $E_j = 0.41 \pm 0.08$ correspondingly. The active intermediates of acid mediated solvolysis were characterized by spectral methods. The crystal products was isolated from reaction mixture and characterized by X-ray. The influence of solvent polarity and its role in ion-pair stabilization was determined by kinetic experiments. On the basis of experimental data by means of quantum-chemical calculations reaction the mechanism was determined and peculiarities of TS structure were revealed.

The amine-borane complexes $[(PCy_3)_2IrH_2(\eta^2\text{-}H_2B(H)NRMe_2)]^+[BAr_4^F]^-$ (R=H,Me) was synthesized and characterized experimentally. The DHB complexes are revealed by experimental and calculation methods. The thermodynamic characteristic of DHB complexes was determined and active intermediates of proton transfer reaction were identified.

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o-BENZOSEMIQUINONATO TIN(IV) COMPLEXES AS THE AGENTS IN THE ELECTRON-TRANSFER REACTIONS

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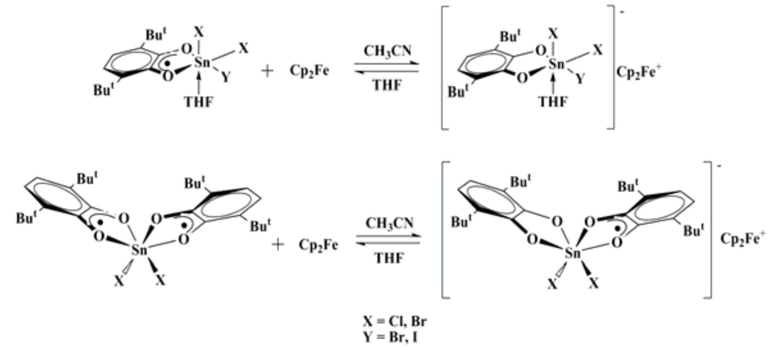
Electron-transfer reactions play an important role in a variety of chemical and biological processes [1]. Dyads based on the complexes with redox-active ligands and ferrocene are proven as a promising system in terms of electron-transfer interactions. However, nontransition metal complexes based on redox-active ligands have never been noticed in such types of processes.

Herein we report on the synthesis and characterization of *o*-benzosemiquinonato halogen-containing tin(IV) complexes and investigation of their electron-transfer reactions with ferrocenes.

Mono-*o*-benzosemiquinonato halogen-containing tin(IV) complexes were synthesized by the oxidative addition of bromine or iodine to the initial tin(IV) catecholates [2]. The more convenient method of synthesis of bis-*o*-benzosemiquinonato tin(VI) complexes is the addition of *o*-benzoquinone to tin(II) halides in acetonitrile [3]. In accordance with electrochemical investigations, *o*-benzosemiquinonato halogen-containing tin(IV) complexes possess unusually high redox potentials (vs. Cp_2Fe/Cp_2Fe^+, acetonitrile) for such type complexes. This fact indicates that these complexes are able to demonstrate oxidative abilities toward ferrocenes producing ferrocenium salts (Scheme 1). It should be noted that formation of electron-transfer (ET) complexes with ferrocene depends on solvent media. ET complexes obtained in these reactions were characterized by a variety of physicochemical methods including IR-, EPR-, UV-vis. spectroscopy, X-ray analysis and magnetic measurements.



Scheme 1

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PROTON TRANSFER REACTIONS IN DONOR-ACCEPTOR COMPLEXES OF GROUP 13 METALS TRIHALIDES WITH 2-AMINOPYRIDINE

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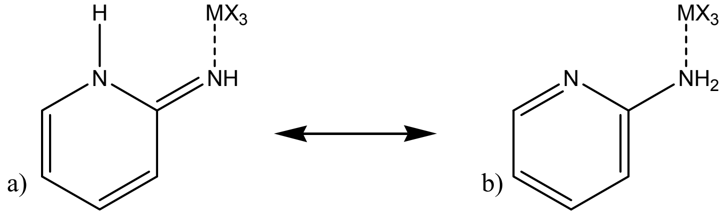
2-aminopyridine (aPy) is bidentate nitrogen-donor ligand. It interesting as novel donor for donor-acceptor complexes with group 13 metal trihalides. Potentially this complexes can be a good single-source precursors for chemical vapor depositions of $A^{III}B^{V}$ semiconductors and nanomaterials. Useability of this complexes depends of structure and vaporisation processes.

The work presented describes synthesis and crystal structures of donor-acceptor complexes with group 13 metal trihalides MX_3aPy (M=Al, Ga, In; X=Cl, Br). All synthetic procedures was performed in sealed vacuum systems. X-ray analysis of single crystal was performed for several complexes. In $AlCl_3$aPy, $GaCl_3$aPy, $GaBr_3$aPy found a first example of unusual pyridone-imine (a) structure of 2-aminopyridine, stabilized in crystal structure.



As the result, during complexation of 2-aminopyridine with AlX_3 and GaX_3 proton-transfer reaction from aminogroup to pyridine ring occurs giving piridone-imine structure. Same ligand structure was proposed in work of Dinkov [1] for 2-aminopyridine complexes with Pd (II) found by IR measurements. Metal - nitrogen donor-acceptor bond in $AlCl_3$aPy (1.852Å), $GaCl_3$aPy(1.878Å), $GaBr_3$aPy(1.888Å) is shorter than in typical complexes with nitrogen-donor ligands of aluminium trihalides (1.900 - 2.014Å) and gallium trihalides (1.937-2.011Å) [2]. However, 2-aminopyridine in $InBr_3$aPy crystal structure coordinate via nitrogen of pyridine ring with In-N distance 2.182Å.

Investigations of vaporization process of $GaCl_3$aPy and $InBr_3$aPy was performed by mass-spectrometric method. Complexes sublimated at low temperatures (373K) and stable in vapour.

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A. Timoshkin, I. Kazakov thanks the Saint-Petersburg State University for financial support (12.37.139.2011).

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SOLUTION-DEPOSITED BIAXIALLY TEXTURED LANTHANUM ZIRCONATE AND LANTHANUM HAFNATE FILMS AS BUFFER LAYERS FOR 2G HTS WIRE

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Oxide compounds with pyrochlore structure, $La_2Zr_2O_7$ and $La_2Hf_2O_7$, are promising materials for catalytic, optical and electrical applications. Moreover, due to their low lattice mismatch with the $YBa_2Cu_3O_{7-x}$ high temperature superconductor (~1%) they can be good buffer layers in the architecture of high temperature superconducting tapes [1]. The aim of this work was to develop chemical solution deposition processes to grow $La_2Zr_2O_7$ and $La_2Hf_2O_7$ thin films on biaxially textured <001>(001) metal alloy substrates.

The coating solutions consisted of a stoichiometric mixture of lanthanum oxide and zirconium or hafnium acetylacetonates dissolved in propionic acid. The advantages of those solutions were their stability at high concentrations and excellent wetting behaviour at metal substrate surfaces. The chemistry of the precursor solutions was studied using thermogravimetric analysis and infrared and NMR spectroscopy. The formation of heteroligand metal carboxylates was found in these complex solutions.

The next step was to study the dip coating process of the oxide precursor layer onto continuously moving 80 micron thick Ni-W alloy tapes. There are several important parameters influencing the oxide films thickness and uniformity, namely the solution concentration, viscosity, temperature and speed of tape motion through the solution bath. We quantitatively studied the dependence of the film thickness on the solution concentration and the tape motion rate and found it to correlate well with the predictions of the Landau-Levich theory [2].

Crystalline oxide films of $La_2Zr_2O_7$ and $La_2Hf_2O_7$ on the Ni-W tapes up to 10 m long were obtained via high temperature treatment (1000-1150^{o}C) of the precursor-coated tapes under reducing atmosphere in the reel-to reel tape motion mode. X-ray diffraction (θ-2θ, ω- and φ-scanning), scanning electron microscopy and electron backscattering diffraction were used for characterization of oxide films. Using the solution deposition approach described we succeeded in preparing biaxially textured $La_2Zr_2O_7$ and $La_2Hf_2O_7$ films. The tapes with the $La_2Zr_2O_7$ films were subsequently used as single buffer layers to make coated conductor tapes with simplified architecture $YBa_2Cu_3O_{7-x}/La_2Zr_2O_7$/Ni-5W. The superconducting critical current of over 100 A/cm was measured in the coated conductors obtained.

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COMPLEXES OF YTTRIUM AND LUTETIUM SUPPORTED BY BULKY AMIDO–IMINO LIGAND. SYNTHESIS, STRUCTURE, REACTIVITY AND CATALYTIC ACTIVITY IN ISOPRENE POLYMERIZATION

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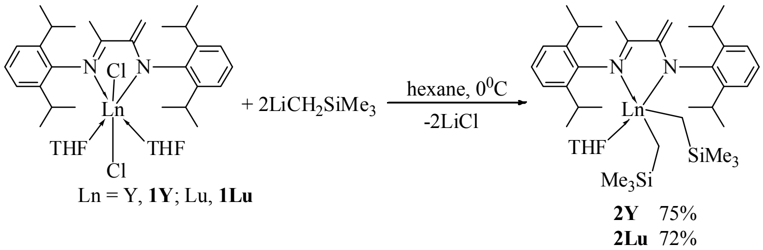
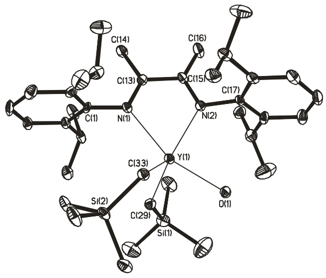
1,4-Disubstituted diazabutadienes attract considerable attention due to their inherent diversity of coordination and redox properties. This ligand system is capable to form five-membered metallacycles with rigid geometry - promising catalysts for polymerization of lactides, dienes and olefins.

A monoanionic amido–imino ligand system $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{-N=C(Me)C(=CH}_2\text{)N(C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2)]^-$ was successfully employed for the synthesis of monomeric dichloro $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N=C(Me)C(=CH}_2\text{)N(C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2)]\text{LnCl}_2(\text{THF})_2$ (Ln = Y, **1Y**; Lu, **1Lu**) and bis(alkyl) $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N=C(Me)C(=CH}_2\text{)N(C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2)]\text{Ln-}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ (Ln = Y, **2Y**; Lu, **2Lu**) species of yttrium and lutetium.





Bis(alkyl) yttrium and lutetium complexes **2Ln** activated by $\text{Al}i\text{Bu}_3$ and borate (borate = $[\text{HNMe}_2\text{Ph}][\text{B(C}_6\text{F}_5)_4]$ and $[\text{CPh}_3][\text{B(C}_6\text{F}_5)_4]$; molar ratio 1 : 10 : 1) performed high catalytic activity in isoprene polymerization affording polyisoprenes with predominant 3,4-selectivity (up to 78%) and moderate polydispersities (2.14–3.52). The nature of borate was found to affect polyisoprene molecular weight and the 3,4-selectivity of the polymerization reaction, but not the catalytic activity of the ternary catalytic systems.

In order to obtain hydride complexes, which are also of interest as a catalyst for the conversion of unsaturated substrates the reaction of dialkyl yttrium complex (**2Y**) with molecular hydrogen and phenylsilane were investigated. It was established that at the first stage the corresponding hydrido complexes form and undergo further transformations. We found that in the case of reaction of **2Y** with H_2 Y-C, C-C and C=N bonds of amido-imine ligand undergo hydrogenolysis. This process is accompanied by the redistribution of nitrogen-containing ligands, resulting in the formation of bisligand complex, wherein yttrium atom is coordinated by one diamide ligand with single C-N and C-C bonds and by amido-amine ligand coordinated to the yttrium atom via unusual η^3-type due to the amide nitrogen atom and double C=C bond.

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COORDINATION CHEMISTRY OF KEPLERATES: LIGANDS EXCHANGE INSIDE THE $\{W_{72}Mo_{60}\}$-CORE

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Porous spherical oxide-based clusters of the type $\{(M^{VI})M^{VI}_5\}_{12}(\text{linker})_{30}$, called keplerates [1], are notable not only for their unique structural features but also because of their properties: they can act as artificial cell membranes exhibiting gated pores while interacting specifically with their environments; they are also of interest for materials science [2-4]. It has been shown that internal surfaces of the keplerates can be used for coordination of different cations and anions. Even encapsulation of a cluster complex inside the cavity based on non-covalent interactions has been achieved, leading to a new type of supramolecular compound.

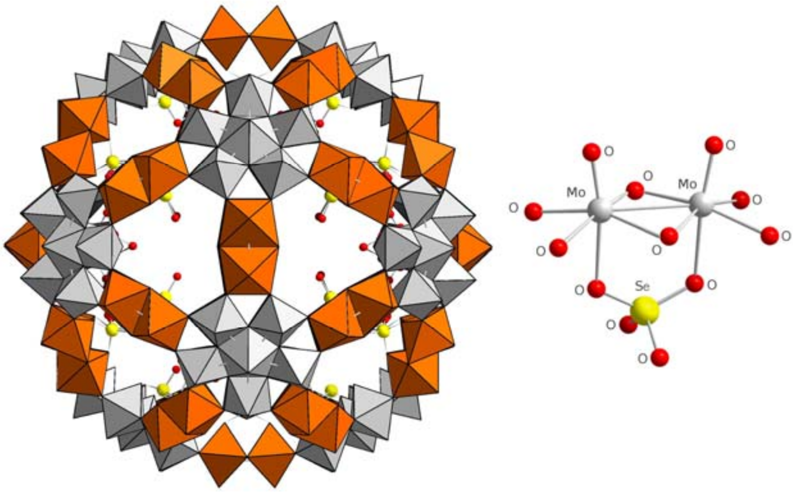

Fig.1. *Left.* Polyhedral representation of $[\{W_6O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SeO_4)\}_{30}]^{72-}$.
Right. Coordination of selenate-anion to $\{Mo_2O_4\}^{2+}$ bridging fragment.

Recently, the mixed-metal keplerate core, $\{W_{72}Mo_{60}\}$, containing 12 pentagonal $\{W_6O_{21}(H_2O)_6\}$ building blocks with 30 internal acetate ligands has been obtained [5]. Herein we report the preparation of three novel keplerate-type structures based on the $\{W_{72}Mo_{60}\}$-core containing sulfate, hypophosphite and selenate (Fig.1) anions as internal ligands. All new compounds are characterized by X-ray diffraction method, IR, Raman and NMR spectroscopy. It's notable that compound $\{W_{72}Mo_{60}(SeO_4)_{30}\}$ represents the first example of the introducing of selenate anion into the keplerate's cavity.

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ACTIVATION OF A (DIENE)RHODIUM(I) COMPLEX SUPPORTED BY A FERROCENYL PHOSPHINE THIOETHER LIGAND FOR HYDROGENATION CATALYSIS : A COMBINED *PARA*HYDROGEN NMR, UV AND DFT STUDY

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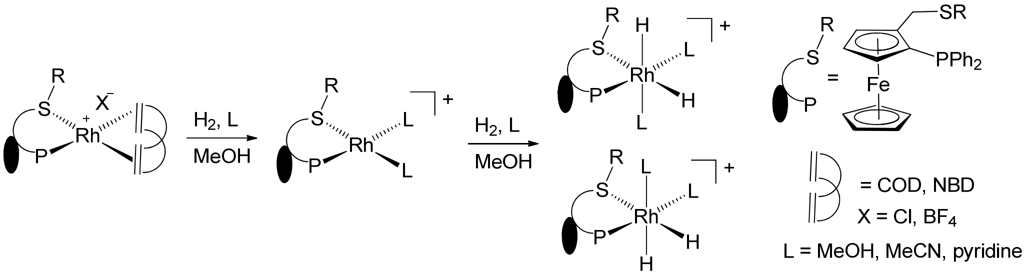
Chiral ferrocene-based phosphine thioether ligands (P,SR) were shown to be particularly efficient for the hydrogenation of aromatic ketones when combined with $[Ir(COD)Cl]_2$ [1]. Since the iridium complexes are too active to generate and characterize the catalytically active species, our attention has turned to the analogous (P,SR)-based rhodium complexes [2], inspired by reports of the isolation and characterization of related diphosphine-based complexes at the pre-catalyst activation stage [3]. These complexes were demonstrated to act as both structural and functional mimics of the analogous Ir systems, although they show lower catalytic activity and selectivity [4].



Scheme 1

Activation of a (diene)rhodium(I) complex with an investigation of the stoichiometric reactivity of these systems towards H_2 was studied by *para*hydrogen NMR, UV and DFT. The addition of H_2 to methanol solutions of [Rh(P,SR)(diene)X] (X = Cl or BF_4) results in diene hydrogenation with a rate that depends on the structure of the complexes (S atom substituent, nature of the diene ligand and anion). Fast H_2/CD_3OD exchange on the NMR time scale does not allow the observation of hydride species. However, addition of L (pyridine, acetonitryle) slows down this exchange and allows dihydride products to be observed (Scheme 1).

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COORDINATION POLYMERS BASED ON ARYL- AND GETEROARYL(POLI)PHOSPHINIC ACID. SYNTHESIS, STRUCTURE AND PROPERTIES

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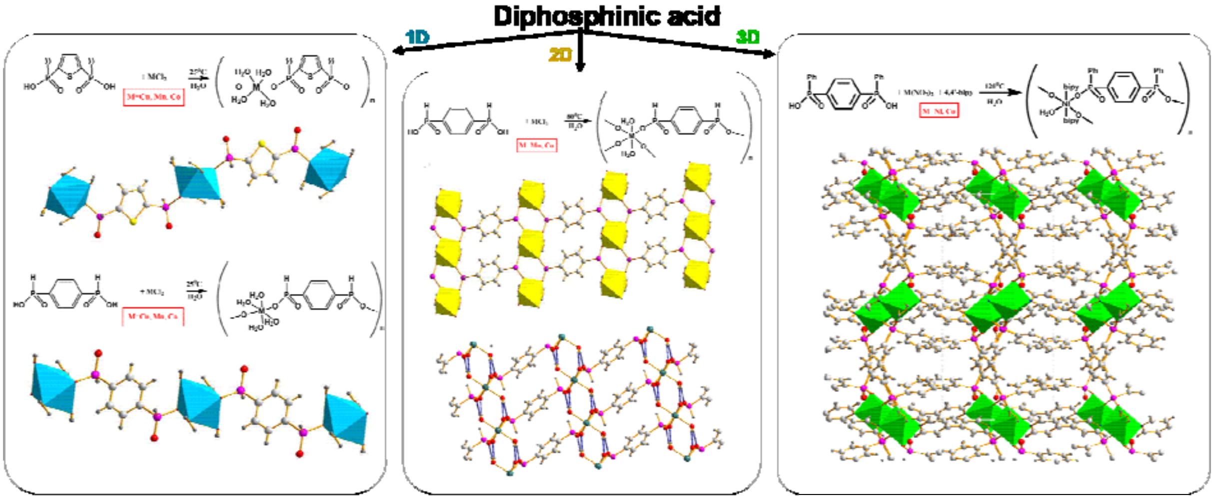
A series of new diphosphinic acids containing aromatic benzene, biphenyl, thiophene bridges between the phosphorus atoms was synthesized and used for the design of coordination polymers of transition metals. Such coordination polymers are of considerable interest in terms of construction new promising materials for storage, purification, separation gas and catalysis.

The self-assembly of transition metal ions, which act as coordination centres, linked together with a variety of multidentantny organic ligands (anions of diphosphinic acids above mentioned), has resulted in coordination polymers of different dimensionalities. We studied the effect reaction conditions, and the addition of the bridging ligand on the architecture of the obtained coordination polymers. 1D polymeric chains, 2D polymeric networks and 3D porous coordination polymers of the second generation were prepared.



An antiferromagnetic interactions in 1D polymeric chains based on copper, manganese phosphinates were observed. Sorption of 3D porous coordination polymer containing 1,4-phenylenebis(phenylphosphinic acid) was measured.

[1] S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem. Int. E,* **2004**, *43*, 2334 –2375.
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SYNTHESIS, STRUCTURE AND PROPERTIES OF NEW COMPLEXES OF 3D-METAL WITH PYRAZOLE-BASED LIGANDS

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The aim of this work is the synthesis and study of complexes of 3d-transition elements with N-donor ligands containing pyrazole moiety. 2,6-Bis(pyrazolyl)pyridine and derivatives of 3,6-bis(pyrazolyl)-1,2,4,5-tetrazine are used as ligands. The advantage of these ligands is a possibility of synthesis of large libraries of ligands with different substituents in the pyrazole ring. All used ligands contain at least two heterocyclic rings: relatively easily modifiable pyrazole ring and six-membered heterocyclic ring (pyridine, tetrazine). For the synthesis of ligands may use different methods: synthesis of bisheterocyclic system from a pyrazole derivative, from the derivative of another heterocyclic ring (thiophene, pyridine, tetrazine), or cross-coupling of two heterocyclic rings.

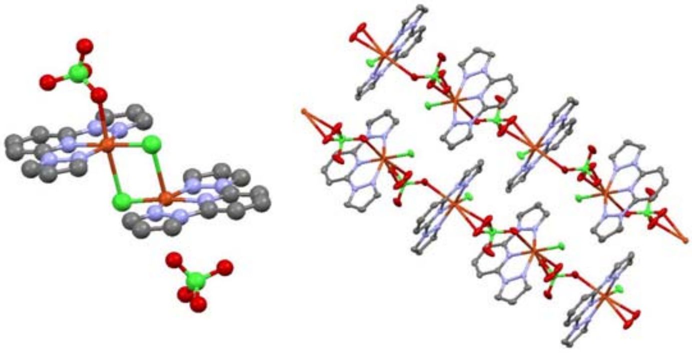

Fig. 1. Structures of **$[Cu(Cl)(bPzPy)]_2(ClO_4)_2$** (left) and **$[Cu(Cl)(bPzPy)(ClO_4)]$** (right).

Various symmetric and non-symmetric 2,6-bis(pyrazolyl)pyridines were obtained in a high yield, the yield was highly dependent on the size of the substituents in the pyrazole ring. Synthesized ligands was used for the synthesis of iron, cobalt, nickel and copper complexes. In the case of iron and cobalt complexes of 2,6-bis(pyrazolyl)pyridines have a monomeric structure regardless of counterions and the introduction of additional ligands capable of acting as bridging ligands – halide- and azide- anions. Dimeric complexes with bridging ligands could be obtained for copper and nickel. There is a weak ferromagnetic interaction for dimeric copper complexes with the structure **$[Cu(Cl)(bPzPy)]_2(ClO_4)_2$** (**Fig 1.**), calculated coupling constant for which is in agreement with the experimental data. Then the introduction of bulky substituents in the pyrazole ring causes distortion of square-planar unit **$[Cu(Cl)(bPzPy)]^{2+}$** and the copper-copper distance increases. For non-substituted pyrazole one-dimensional chain with perchlorate-bridging was obtained in the first time (**Fig 1.**).

Iron and cobalt complexes containing two metal centers were obtained only when using 3,6-bis(pyrazolyl)tetrazine as a bridging ligand. As for copper bis(pyrazolyl)tetrazine undergoes hydrolysis and the hydrolysis products form complexes.

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COMPLEXES OF COPPER(II) WITH ISOTHIAZOLE DERIVATIVES AND THEIR BIOLOGICAL ACTIVITY

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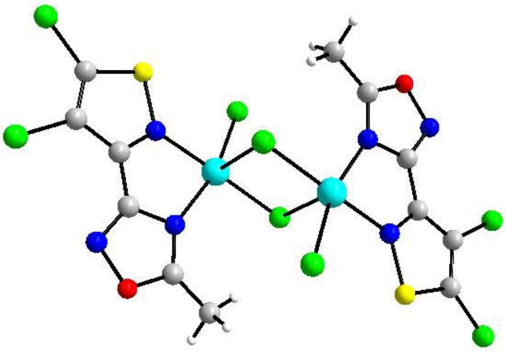
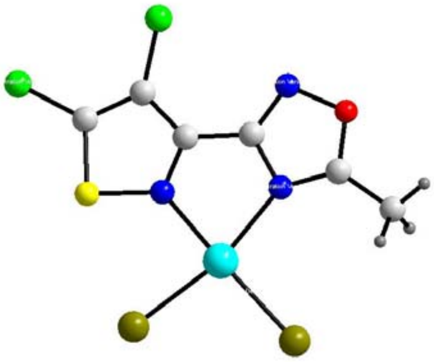
Complexes of copper(II) with isothiazoles are interesting in view of biological activity of the ligands, which is now under investigation. These azole derivatives may intensify pyrethroid insecticide action against the Colorado potato beetle, and they are known to be very effective. We expect the effect increasing if their copper(II) complexes are used. This work is devoted to new coordination compounds of copper(II) with isothiazole derivatives, their X-ray crystal structure and study of their fungicidal and insecticidal properties.

4,5-Dichloro-*N*-hydroxy-isothiazole-3-carboxamidine (L^1), 4,5-dichloroisothiazole-3-carboxylic acid (HL^2), its amide (L^3) and 3-(4,5-dihlorizotiazol-3-yl)-5-methyl-1,2,4-oxadiazole (L^4) were chosen as biologically active ligands. Various copper salts with L^1 form the following complexes: $[Cu(L^1)Cl_2]$ (**1**) and $[Cu(L^1)Br_2]$ (**2**). HL^2 reacts with copper(II) chloride to form complexes $[Cu(H_2O)(L^2)Cl]\cdot 0{,}5H_2O$ (**3**), and $[Cu(H_2O)(L^2)_2]$ (**4**) depending on the ratio metal – ligand. The reaction of different copper(II) salts with L^3 and L^4 yields in complexes $[Cu(L^3)Cl_2]_n$ (**5**), $[Cu(L^3)Br_2]$ (**6**), $[Cu(L^3)_2(H_2O)_2](ClO_4)_2$ (**7**), $[Cu(L^3)_2(H_2O)_2](BF_4)_2$ (**8**), $[Cu_2(L^4)_2Cl_4]$ (**9**) (left fig.) and $[Cu(L^4)Br_2]$ (**10**) (right fig.). All complexes are investigated by the single-crystal X-ray diffraction. It is shown that all ligands are coordinated in a bidentate-cyclic mode through nitrogen atom of isothiazole ring and one of the oxygen or nitrogen atoms of the substitutes.





Fungicidal properties of complexes **3** – **6** in the case of plant pathogenic fungi *Botrytis cinerea* and *Fusarium sp.* were investigated. It was shown that all complexes have fungicidal activity and some of them completely suppress fungi pathogenic process. The complexes **4** and **5** were shown to have the highest fungicide activity.

Insecticidal properties of the complexes **3** – **6** and **9** – **10** against the Colorado potato beetle larvae (*Leptinotarsa decemlineata*) as synergist of insecticide “Kerber” were investigated *in vitro*. It is shown that individual complexes did not cause the death of Colorado potato beetle larvae. A hybrid products Kerber + **6** and Kerber + **10** showed the most effective in the fight against the Colorado potato beetle larvae.

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REACTIONS OF ACENAPHTHENE-1,2-DIIMINE GALLIUM COMPLEXES WITH UNSATURATED COMPOUNDS

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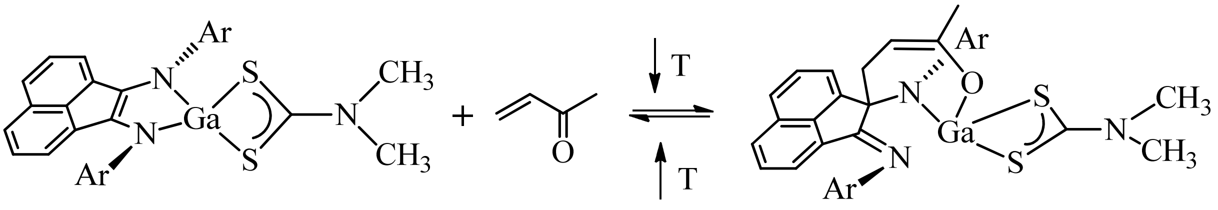
Main group metal complexes with redox-active α-diimine ligands attract attention in the last several years. These complexes can reversibly accept and give up electrons thus changing «oxidation state» of the ligands. This feature can be useful in catalytic reactions. Recently we have reported that the binuclear bisamide of gallium complex (dpp-bian)Ga–Ga(dpp-bian) (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene) may reversibly bind some alkynes and shows a high catalytic activity in reactions of the phenylacetylene with aromatic amines [1]. But we have got no information on addition of unsaturated compounds to mononuclear gallium complexes based on dpp-bian. Here, we report the reactions of (dpp-bian)GaS(S)CNMe$_2$ (**1**) with organic molecules containing multiple carbon-carbon and carbon-oxygen bonds (Scheme 1).



1 **3** Ar = $2,6\text{-}i\text{-}Pr_2C_6H_3$

Scheme 1

Reactions of complex **1** with phenylacetylene and 3-buten-2-one afford two complexes [dpp-bian(PhC=CH)]GaS(S)CNMe$_2$ (**2**) and [dpp-bian(CH$_2$–CH=C(Me)–O)]GaS(S)CNMe$_2$ (**3**) respectively. In both cases the addition is reversible and starting compound **1** is regenerated by heating the solutions of compounds **2** and **3**. Addition of metyl-2-butynoate to **1** proceeds in irreversible manner resulting complex [dpp-bian(CH$_3$–C=C–C(O)–OCH$_3$)]GaS(S)CNMe$_2$ (**4**).

[1] I. L. Fedushkin, A. S. Nikipelov, A. G. Morozov, A. A. Skatova, A. V. Cherkasov, G. A. Abakumov, *Chem. Eur. J.,* **2012**, *18*, 255-266.

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MAGNETO/OPTICAL CORE-SHELL GOLD/PRUSSIAN BLUES ANALOGUES NANOPARTICLES

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Comparatively to the metal/oxides nanoparticles, the synthesis and the study of Prussian Blue analogues are a relatively recent field in coordination chemistry. These nanoparticles present an interest as on fundamental level for their properties (magnetism, conductivity, selective adsorption).

On the other hand, gold nanoparticles present remarkable optical properties because of the plasmon surface phenomena. These nanoparticles are used for a large range of applications, especially in biomedical field (drug delivery vehicles, phototherma therapy, imaging,..). [1]

A new concept consists in taking advantage of both optical properties of gold nanoparticles and magnetic properties of Prussian Blue analogues to obtain multifunctional magneto-optical nano-objects.
In this regard, hybrid core-shell nanoparticles of Au@KNi[Fe(CN)$_6$] have been synthesized (**fig. 1**), and show optical properties resulting from plasmon surface band. The formation of a new shell with KNi[Cr(CN)$_6$] by a subsequent growing has permitted to implement successfully magnetic properties.

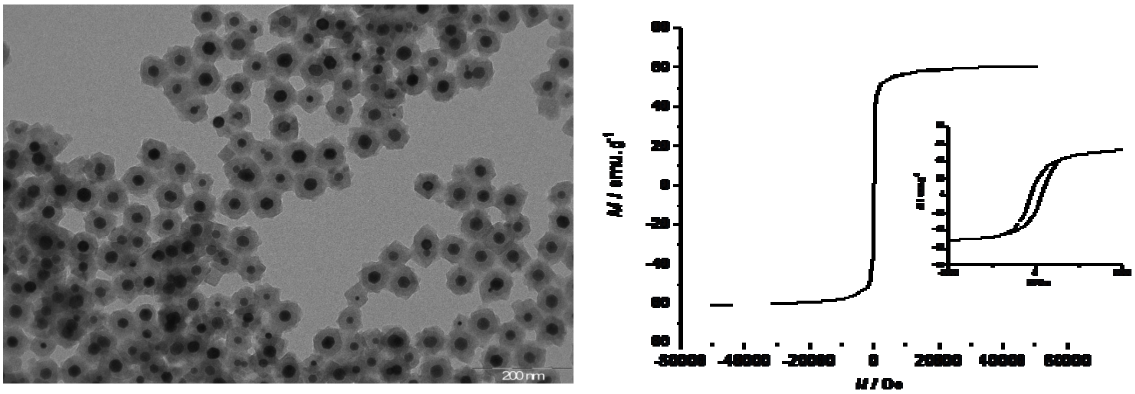

Figure 1: TEM Image TEM of Au@KNi[Fe(CN)$_6$] nanoparticles, on left.
On right, Hysteresis cycle of Au@KNi[Fe(CN)$_6$]@ KNi[Fe(CN)$_6$] nanoparticles.

[1] Erik C. Dreaden, Alaaldin M. Alkilany, Xiaohua Huang, Catherine J. Murphy et Mostafa A. El-Sayed, *Chem. Soc. Rev.*, **2012**, *41*, 2740–27

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GENUINE REDOX ISOMERISM IN A RARE-EARTH-METAL COMPLEX

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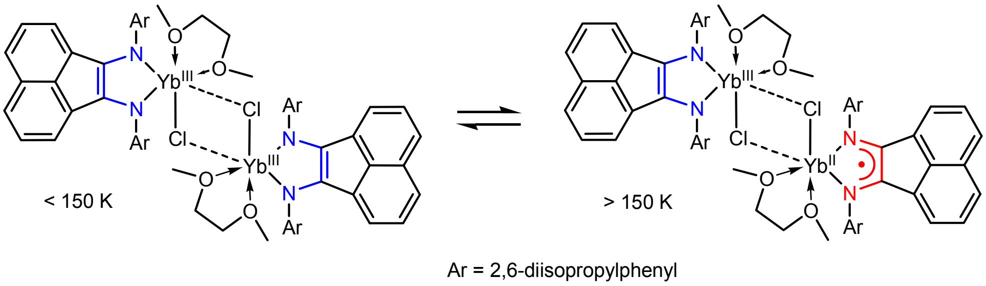
Redox-isomerism – also called valence tautomerism – in solution and in the solid state is known for various *d*-elements [1], including Co, Ru, Cr, Ni, Mn, Fe, Rh, Cu, and Ir. Here we report the synthesis and a combined X-ray crystallography plus SQUID study of the new complex [(dpp-bian)Yb(μ-Cl)(dme)]$_2$ (**1**) (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]-acenaphthene), which turns out to be the first rare earth metal complex that exhibits genuine thermally induced redox-isomerism in the solid state.

Numerous X-ray diffraction studies of single crystals of **1** isolated from a series of experiments show the presence in every crop of three different modifications, i.e. **1-A** (monoclinic *P*2$_1$/n), **1-B** (triclinic *P*-1) and **1-C** (triclinic *P*-1). Unit cell parameters of one of three modifications, namely **1-B**, were found to vary significantly with temperature.



Scheme 1. Redox-isomerism in [(dpp-bian)Yb(μ-Cl)(dme)]$_2$ (**1-B**).

SQUID measurements of the magnetic susceptibility of a single crystal of modification **1-B** showed abrupt increasing of the magnetic moment from 5.2 μ_B at 147 K to 6.6 μ_B at 140 K in cooling mode in the range from 270 to 2 K. Backward scans in heating mode reveal a pronounced thermal hysteresis loop for μ_{eff} ($\Delta T = 7$ K), until μ_{eff} returns to the initial value of 5.3 μ_B at 153 K. At the same time modification **1-C** demonstrates monotonous decreasing of the magnetic moment with the lowering of the temperature from 295 to 25 K.

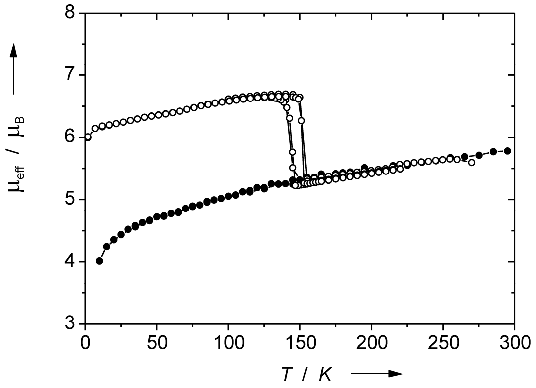


Figure 1. Plot of μ_{eff} vs. *T* for a single crystal of **1-C** (solid dots) in comparison to **1-B** (open dots).

[1] C. G. Pierpont, *Coord. Chem. Rev.* **2001**, *221*, 415-433

Acknowledgements – This work was supported by the RFBR (Grant № 13-03-00713)

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THE ADDITION OF ALKYNES TO FUNCTIONAL-LABILE BISAMIDES OF ALUMINUM

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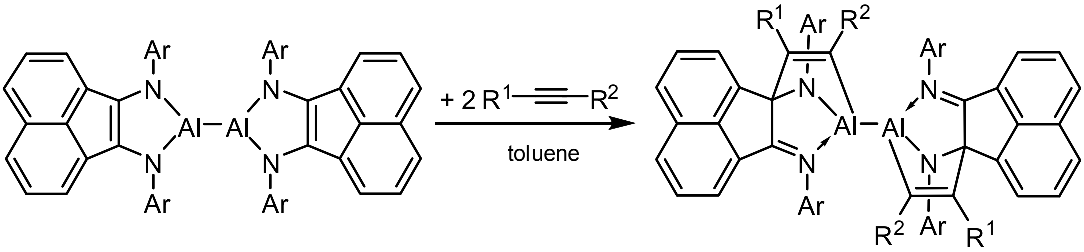
Complexes of main group metals with redox-active ligands based on α-diimines have attracted rising in last years. A major reason for the popularity of these complexes is the idea of the catalytic activation of multiple bonds of organic compounds on these systems. Recently, it was demonstrated that the binuclear bisamide of gallium (dpp-bian)Ga–Ga(dpp-bian), (dpp-bian = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene), may reversibly bind some alkynes [1, 2], and shows the high catalytic activity in reactions of the phenylacetylene with anilines [2]. Here, we report the reactions of binuclear dialane (dpp-bian)Al–Al(dpp-bian) (**1**) with various alkynes. Acetylene, phenylacetylene and methylphenylacetylene react with **1** to give cycloaddition products **2**, **3** and **4** respectively (Scheme 1).



1

Ar = 2,6-diisopropylphenyl

2: $R^1 = R^2 = H$
3: $R^1 = H$, $R^2 = Ph$
4: $R^1 = CH_3$, $R^2 = Ph$

Scheme 1. Reaction of **1** with alkynes.

The reactivity of mononuclear ethyl-aluminum derivative (dpp-bian)AlEt(Et_2O) (**5**) towards unsaturated organic molecules also has been investigated. Reactions of complex **5** with diphenylacetylene and methylvinylketone lead to cycloaddition products [dpp-bian(PhC=CPh)]AlEt (**6**) and [dpp-bian(CH_2–CH=C(Me)–O)]AlEt (**7**). For each case the organic substrate is added across the Al–N–C fragment of metallacycle of starting complex **5**. Addition of diphenylacetylene is accomplished with the formation of new C–C and C–Al bonds. The reaction of complex **5** with methylvinylketone (1,3-π-conjugate) results besides new C–C bond also O–Al bond. Whereas with the methylvinylketone complex **5** readily reacts in toluene at ambient temperature the reaction of **5** with PhC≡CPh does not proceed in solution even at elevated temperatures, for example, in toluene at reflux. However, a placement of **5** in melted diphenylacetylene (110-130 °C) allows elimination of the coordinated diethylether molecules and formation of cycloadduct **6**.

[1] I. L. Fedushkin, A. S. Nikipelov, K. A. Lyssenko, *J. Am. Chem. Soc.*, **2010**, *132*, 7874–7875.
[2] I. L. Fedushkin, A. S. Nikipelov, A. G. Morozov, A. A. Skatova, A. V. Cherkasov, G. A. Abakumov, *Chem. Eur. J.*, **2012**, *18*, 255-266.

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EXPANDED RING N-HETEROCYCLIC CARBENES AS SUPER-DONOR LIGANDS. SYNTHESIS, STRUCTURE, APPLICATIONS IN CATALYSIS.

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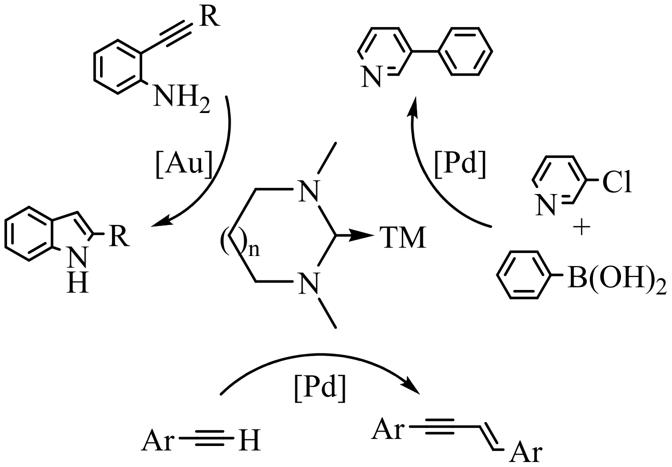
N-heterocyclic carbenes (NHCs) became widely used as powerful ligands for stabilization of reactive species, as organocatalysts, and as spectator ligands in transition metal catalysis. Most of NHC-metal complexes known to date are derived from five-membered ring imidazol-2-ylidene and imidazolin-2-ylidene type carbenes. In recent years our group develops chemistry of 6- and 7-membered ring carbenes. Expanded ring carbenes (er-NHCs) exhibit superior stereoelectronic properties in comparison with five-membered ring counterparts. Expansion of the ring leads to significant increase in donor strength and sterical hindrance.

In this contribution we report our recent results on theoretical calculations of electronic structure and ligand properties of er-NHCs; efficient methods of synthesis of precursors and generation of free carbenes; synthesis of late transition metal (Cu, Ag, Au, Pd) complexes. It was found that er-NHC complexes of palladium are highly active in Suzuki-Miyaura coupling in water, and dimerization of terminal alkynes with formation of E-enynes. Cationic gold complexes are active catalysts of indole synthesis in mild conditions.



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METAL-CONTAINING CHLORINS: THE NOVEL TYPE OF PDT-SELECTIVE DELIVERY AGENTS CONJUGATES.

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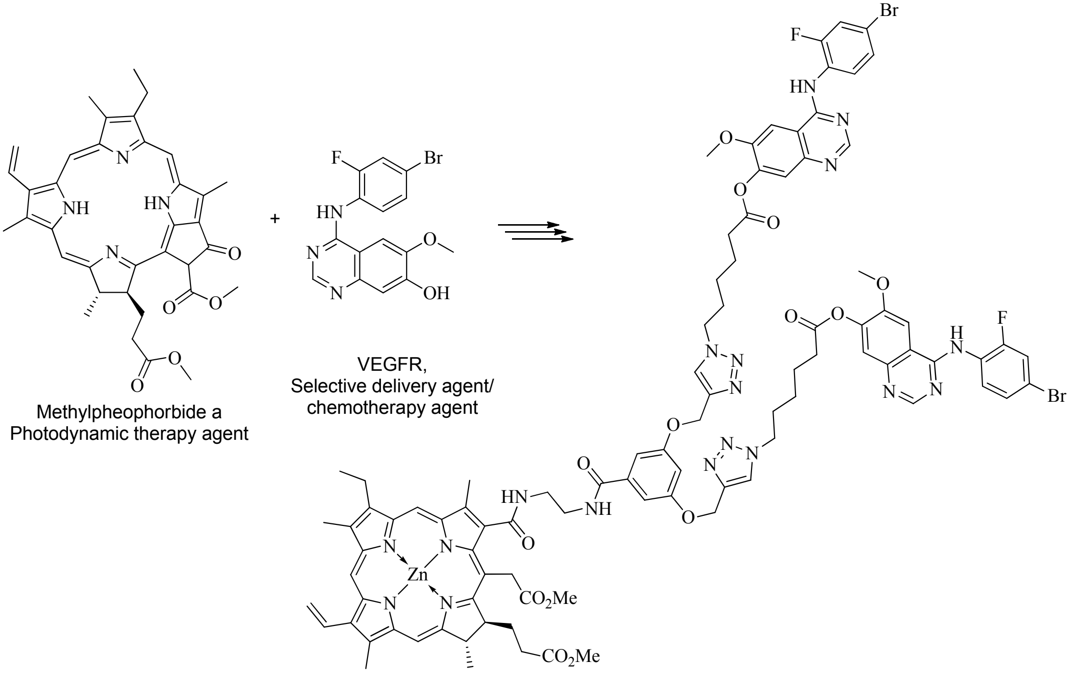
The novel type of anticancer conjugates for combined photodynamic/chemotherapy and selective delivery to cancer cells was developed. Zn-containing chlorin-type compounds [1, 2] were used as PDT agents due to its ability for producing singlet oxygen and fluorescent properties (for bioimaging). 4-Arylaminoquinazolines display properties as vascular endothelial growth factor receptor ligands/epidermal growth factor receptor ligands and tyrosine kinase inhibitor [3, 4], were used as selective delivery agent.



Synthesized compounds display fluorescence in red and infra-red area.

[1] E.S. Nyman and P. H. Hynninen, *J. Photochem. Photobiol. B: Biology*, **2004**, 73, 1-28.
[2] A.E. O'Connor, W.M. Gallagher and A.T. Byrne, *Photochemistry and Photobiology*, **2009**, 85, 1053-1074.
[3] K. Matsuno, J. Ushiki, T. Seishi, M. Ichimura, N. A. Giese, J.-C. Yu, S. Takahashi, S. Oda and Y. Nomoto, *J. Med. Chem.*, **2003**, 46, 4910-4925.
[4] A. Pandey, D.L. Volkots, J. M. Seroogy, J. W. Rose, J.-C. Yu, J. L. Lambing, A. Hutchaleelaha, S.J. Hollenbach, K.Abe, N.A. Giese and R.M. Scarborough, *J. Med. Chem.*, **2002**, 45, 3772-3793.

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SYNTHESIS OF HETEROMETALLIC CLUSTERS WITH {Fe_2S_2} CORE

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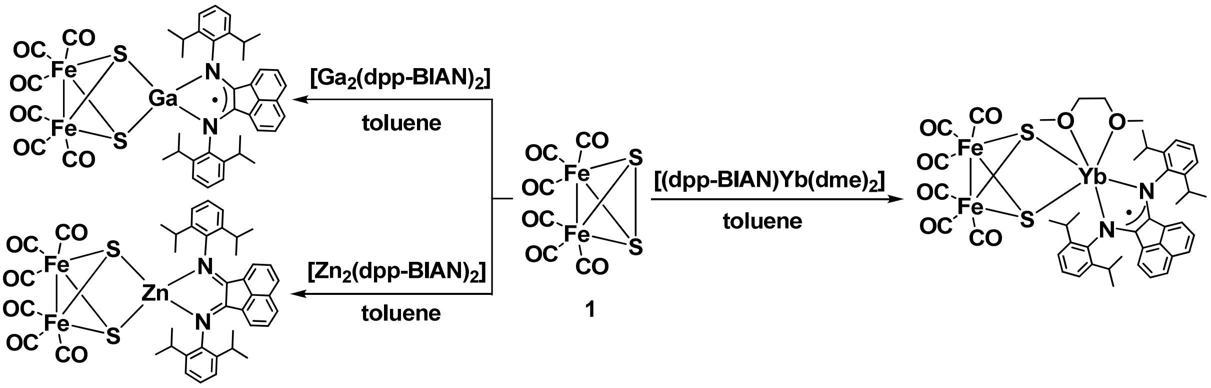
During the last years, the FeS-clusters attract a great attention because of their unique structures and interesting chemical reactivity, and particularly their widespread uses as biomimetic models for the active site of Fe-only hydrogenases.

The [$Fe_2S_2(CO)_6$] (**1**) cluster is a versatile precursor for synthesis of various heterometallic clusters containing the {Fe_2S_2} core. This work is focused on the interaction between cluster **1** and diimine complexes of few different metals.

The reactions of cluster **1** with [Zn_2(dpp-BIAN)$_2$], [Ga_2(dpp-BIAN)$_2$] and [Yb(dpp-BIAN)(dme)$_2$] complexes have been observed to lead to reductive cleavage of S–S bond and insertion of corresponding metal into it. The process is accompanying by oxidation of (dpp-BIAN)$^{\bullet-}$ to (dpp-BIAN)^0 and Zn^+ to Zn^{2+}, or (dpp-BIAN)$^{2-}$ to (dpp-BIAN)$^{\bullet-}$ and M^{2+} to M^{3+} (M = Ga, Yb) (Scheme 1).



Scheme 1

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NOVEL PARAMAGNETIC TRIANGULAR CLUSTERS OF MOLYBDENUM AND RHENIUM

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Previously, we have found that electron-precise clusters $[M_3Q_4(diphos)_3Hal_3]^+$ (M = Mo, W; Q = S, Se; Hal = Cl, Br) bearing bulky diphosphane ligands can be easily converted by treatment with gallium metal to paramagnetic clusters with M_3Q_4, Mo_3Q_5 or Mo_3S_4Ga cores [1]. Recently we have found that the reaction of $[Mo_3S_4(dppe)_3Br_3]Br$ with GaCp* gives cubane-like cluster $[Mo_3S_4(GaBr)(dppe)_3Hal_3]$ with improved yield. The reaction of $[Mo_3S_4(dppe)_3Br_3]Br$ with $[GaBian]_2$ leads to a mixture of $[Mo_3S_4(dppe)_3Br_3]$ and $[Mo_3S_4(dppe)_3Br]Br$ (Fig. 1; phenyl rings omitted for clarity), i.e., the products of 1- and 2-electron reduction of the initial cluster core.

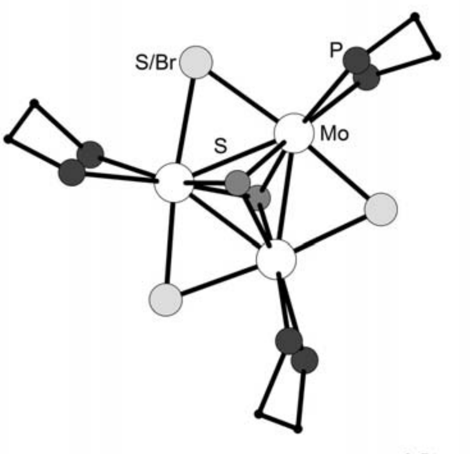

Fig. 1. Structure of $[Mo_3S_4Br(dppe)_3]^+$

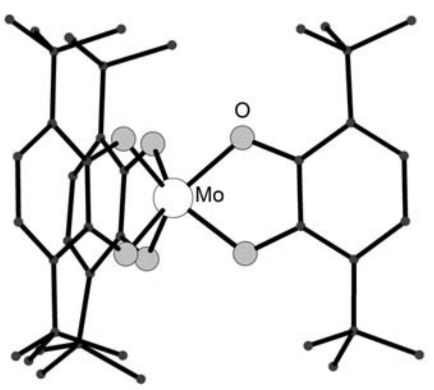

Fig. 2. Structure of $[Mo(cat)_3]^-$

In an attempt to obtain the triangular cluster bearing the redox active ligands the reaction of $(Et_4N)_2[Mo_3S_7Hal_6]$ (Hal = Cl, Br) with potassium 3,6-bis(*tert*-butyl)catecholate (K_2cat) was carried out. The reaction leads to the cluster core destruction, and the mononuclear complex $(Et_4N)[Mo(cat)_3]$ or the product of its oxidation $(Et_4N)[Mo(O)(cat)_2(Hcat)]$ were obtained and characterized by means of XRD. The main feature of $[Mo(cat)_3]^-$ anion (Fig. 2) is the slightly distorted prismatic coordination sphere of Mo(V) ion.

Triangular clusters of Re coordinated with diphosphanes were unknown before our work. $[Re_3S_4(dppe)_3Br_3]^+$ [2] and $[Re_3S_4(dppe)_3(NCS)_3]^+$, in contrast to analogous electron-precise clusters of Mo or W, were found to be paramagnetic with the quartet ground state ($S = 3/2$). High spin value makes $[Re_3S_4(dppe)_3(NCS)_3]^+$ attracting precursor of heterospin arrays or single-molecule magnets.

[1] P.A. Petrov, D.Yu. Naumov, R. Llusar *et al.*, Dalton Trans., **2012**, *41*, 14031-14034.
[2] P.A. Petrov, A.V. Virovets, A.S. Bogomyakov *et al.*, Chem. Commun., **2012**, *48*, 2713–2715.

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The first non-bent lanthanoidocenes (II) (Ln = Sm, Yb), containing bulky cyclopentadienyl-type ligands. Synthesis, structure and reactivity

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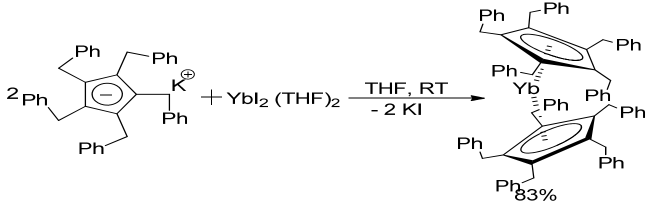
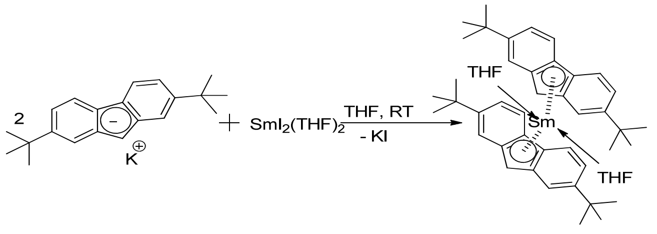
Structures of sandwich complexes of divalent lanthanides markedly differ from those of metallocene complexes of d-transition metals. Unlike the complexes of d-metals featuring a parallel arrangement of ciclopentadienyl ligands, in the analogues containing Ln(II) the Cp-M-Cp bond angles are significantly less than 180^0, due to the peculiarities of their electronic structure. The purpose of this work is the synthesis of novel complexes of Ln(II) (Ln = Sm, Yb) containing bulky aromatic cyclopentadienyl-type ligands, studies of their structure and reactivity. We investigated the influence of bulkiness of cyclopentadienyl-type ligand on their mutual arrangement in the coordination sphere of Ln(II) ions. Another objective of this research was the synthesis of low-coordinated Ln(II) complexes and investigation of their reactions with ligands non-common for organolathanide chemistry (H_2, CO, ethylene, butadiene, SiH_4).

New biscyclopentadienyl (**1**) and bisfluorenyl (**2**) complexes Ln(II) were synthesized by the metathesis reactions of potassium derivatives of corresponding ligands with LnI_2 (Ln = Sm, Yb), biscarbazolyl complex of ytterbium was synthesized through reaction of naphthaleneytterbium with 1,3,6,8-tetra-tert-butylcarbazol:



1



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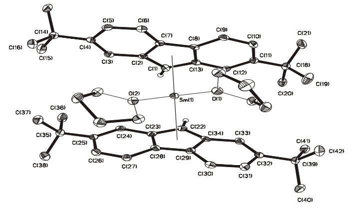

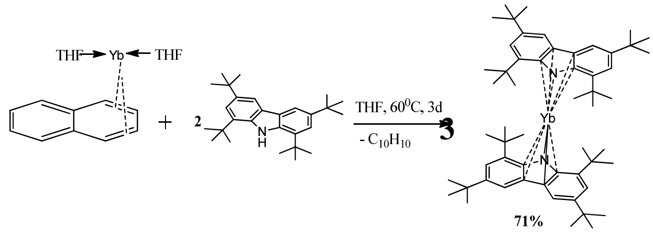

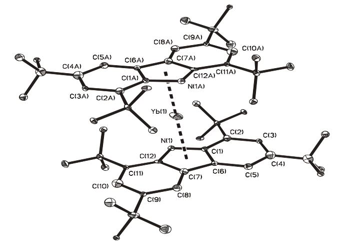

The X-ray diffraction studies revealed that Ln(II) (Ln = Sm, Yb) biscarbazolyl complexes are the first examples of non-bent lanthanoidocenes.

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NOVEL HETEROSPIN RADICAL-ION SALTS OF CHALCOGEN-NITROGEN π-HETEROCYCLES WITH SANDWICH CHROMIUM CATIONS

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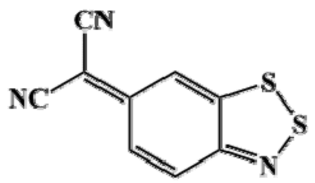
Despite fast progress in the design, synthesis and structural and functional characterization of molecule-based magnetic and conductive materials for electronics and spintronics, there is a permanent demand on new building blocks in the field. A big number of candidate building blocks came from chalcogen-nitrogen chemistry especially in the form of neutral and positively charged π-heterocyclic radicals. Investigation of negatively charged chalcogen-nitrogen π-heterocyclic radicals (*i.e.* radical anions – RAs) begins only recently.

In the present work, compounds **1-3** were reduced with either decamethylchromocene ($Cr(\eta^5\text{-}C_5(CH_3)_5)_2$, compound **1**) or bis(toluene)chromium ($Cr(\eta^6\text{-}C_7H_8)_2$, compounds **1-3**) into corresponding RAs, which were isolated in the form of heterospin $S_1 = 3/2$, $S_2 = 1/2$ (**4**) and $S_1 = S_2 = 1/2$ (**5-7**) radical-ion salts, respectively.


1


2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Structures of **4**, **5** and **6** were elucidated with single-crystal XRD, and a composition of bulk samples was confirmed by elemental analysis. At room temperature, salt **4** is ESR-silent in both the solid state and a MeCN solution. This can be explained by the huge zero-field splitting and fast relaxation of the cation provoking fast relaxation of the anion. ESR spectra of **5-7** in the solid state and DMF solutions confirm their paramagnetic heterospin nature. Magnetic properties (effective magnetic moment μ_{eff} and magnetic susceptibility χ) for salts **4-7** were measured in temperature range 2-300 K. In all cases magnetic curves are characteristic for anti-ferromagnetic (AF) coupling of the spins. Approximation of temperature dependencies gives negative values of exchange interactions (J_i) and Weiss constants (Θ) for all salts, with the exception of **6** for which J_i of both signs and small positive Θ are obtained. The latter may be due to contribution of ferromagnetic (FM) interaction in macroscopic properties of **6**. Value of μ_{eff} for the salt **7** at 300 K is characteristic for homospin system with $S = 1/2$ thus implying diamagnetic π-dimerization of RAs in the solid state. Theoretical values of J_i were calculated on the basis of the XRD structures by a number of quantum-chemical methods to be in a good agreement with the experimental results.

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SINTHESYS, STRUCTURE AND PROPERTIES OF IRON-PHENYLTELLURIUM COMPLEXES

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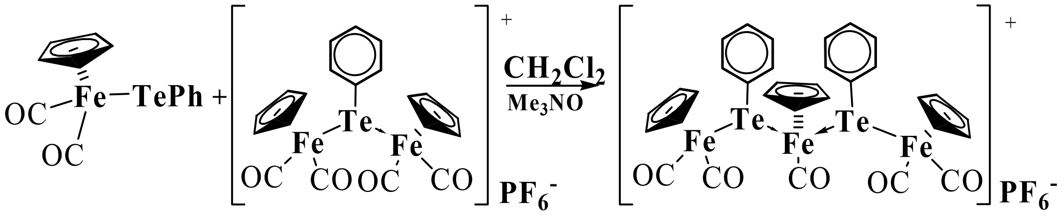
The ability to combine in a single cluster different transitive and intransitive elements in strict predetermined ratio is important in the use of heterometallic complexes as precursors of inorganic and magnetic materials.

Heating an equimolar amount of $[(\eta^5\text{-}C_5H_4(CH_3))Fe(CO)_2]_2$ with Te_2Ph_2 in benzene without boiling affords desired complex $(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2TePh$ (**I**a), which reaction with $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(NO)]PF_6$ leads to the formation of the new compound $[(\eta^5\text{-}C_5H_4CH_3)Fe(CO)_2TePh(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]PF_6$ (**II**a). If the reaction of $(\eta^5\text{-}C_5H_5))Fe(CO)_2TePh$ (**Ib**) with PPh_3 is carried out in refluxing toluene, formation of the complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)TePh$ (**III**) take place, which is in the processing of $[(\eta^5\text{-}C_5H_5)Mn(CO)_2\,(NO)]PF_6$ in MeCN gives brown crystals of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)TePh(\eta^5\text{-}C_5H_5)Mn(CO)(NO)]PF_6$ (**IV**). We find that $(\eta^5\text{-}C_5H_5)Fe(CO)_2TePh$ (**IIb**) is rapidly oxidized by $FcBF_4$ or $FcBPF_6$ (Fc – ferrocenium) in CH_2Cl_2 and complexes $[[(\eta5\text{-}C5H5)Fe(CO)2]2TePh]^+X^-$ (X = BF_4 or BPF_6, **Va,b**) are isolated.

If the prolonged boiling **IIa** and **IIb** is carried out in heptane, formation of the compounds $[(\eta^5\text{-}C_5H_4CH_3)Fe(CO)TePh]_2$ (**VIa**) and $[(\eta^5\text{-}C_5H_5)Fe(CO)TePh]_2$ (**VIb**) take place. Oxidation of **VIa** and **VIb** and by $FcBPF_6$ result in dimeric paramagnetic complexes formation $[(\eta^5\text{-}C_5H_4CH_3)Fe(CO)TePh]_2PF_6$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)TePh]_2PF_6$. In case of oxidation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2TePh$ by $FcBPF_6$ phenyltelluride-bridged complex $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2TePh]PF_6$ (**VII**) can be formed. Treatment of Me_3NO to the CH_2Cl_2 solution of **VII** followed by addition of on equivalent of $(\eta^5\text{-}C_5H_5))Fe(CO)_2TePh$ result in three-nuclear complex $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_3\{TePh\}_2]PF_6$ **VIII** with two phenyltelluride bridging ligands.



νCO = 2044, 2022, 1983, 1972 cm^{-1} **νCO = 2026, 2012, 1980, 1969, 1931 cm^{-1}**

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QUANTUM CHEMICAL MODELING OF ADDUCTS OF CO(II) BIS-CHELATES WITH *O*-BENZOQUINONE LIGANDS: IN SEARCH OF REDOX ISOMERISM

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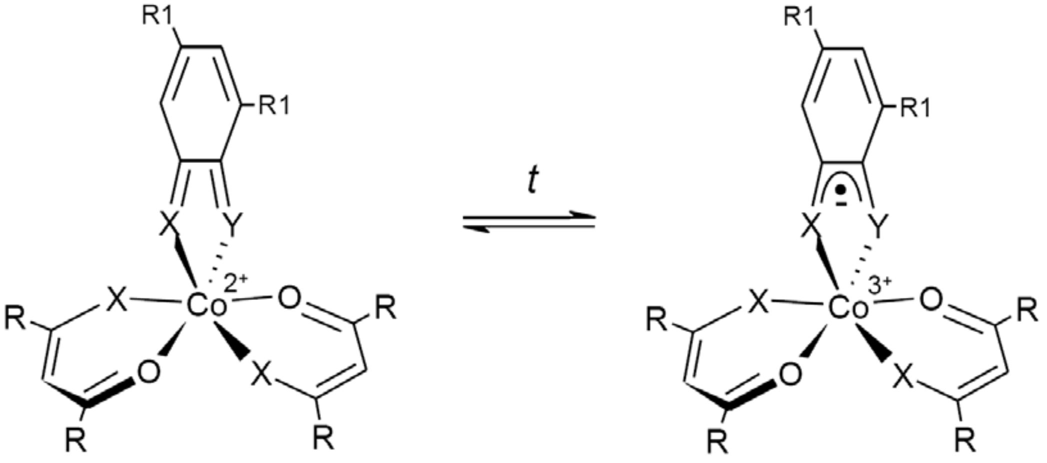
Redox isomerism of coordination compounds (valence tautomerism) is a unique process which consists in reversible intramolecular electron transfer between the ligand and the metal atom excited by external stimuli (temperature, pressure, irradiation and others) [1]. As a rule, valence tautomeric systems contain two redox-active o-benzoquinone ligands with the coordination environment of metal being completed to octahedron by auxiliary ligands. The observed redox-processes in such compounds are associated with transitions between semiquinone and catecholate forms of the ligands. Recently the principal possibility of modeling of another type of valence tautomeric systems has been shown on the example of adducts of bis(N-p-tolylsalycylaldiminato)cobalt(II) with 2,4,6,8-tetra-tret-butylphenoxazin-1-one [2]. In this case neutral and radical anion forms of ligand were involved in redox-processes.



X=O, NH; R=H, CH_3, CF_3; R1=H, t-Bu

With the aim of extension of the compounds capable of valence tautomerism manifestation the structure and properties of adducts of cobalt ketonates and aminovinylketonates with *o*-benzoquinone and its derivatives, *o*-benzoquinone imine and *o*-benzoquinone diimine have been studied using DFT B3LYP*/6-311++G(d,p) method. The influence of substituents on the possibility of occurrence of redox-processes has been studied and valence tautomerism has been predicted for some compounds [3].

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SYNTHESES, STRUCTURES AND LUMINESCENT PROPERTIES OF THE LANTHANIDE COMPLEXES CONTAINING 4-HYDROXY-2,1,3-BENZOTHIADIAZOLE

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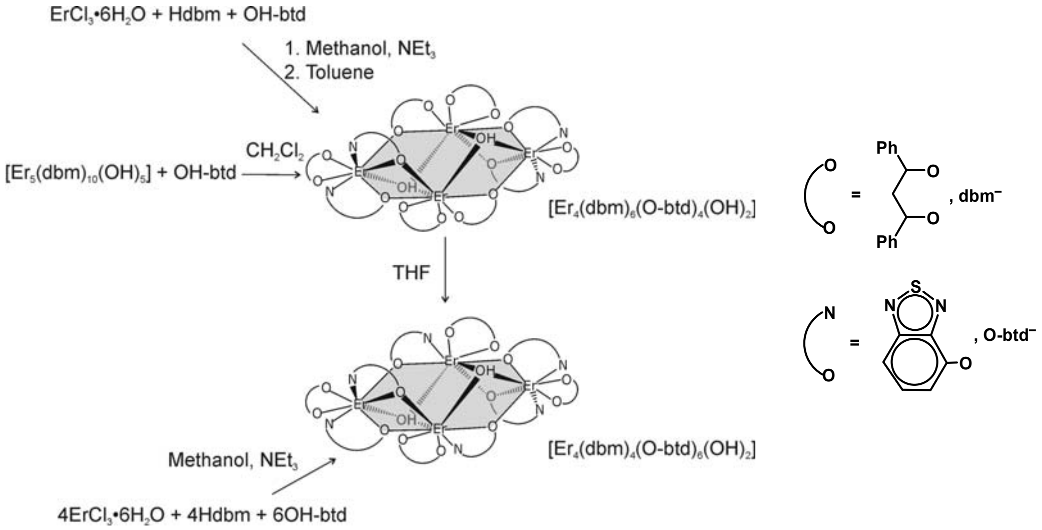
Lanthanide polynuclear complexes have been attracted increasing interest over last years because they can be used in designing of organic light-emitted diodes (OLEDs), in biomedicine and telecommunication applications [1, 2]. Among them lanthanide complexes containing chalcogen-nitrogen heterocycles and β-diketonates are of especial interest. Herein, we report the syntheses, structures and luminescent properties of the lanthanide complexes containing 4-hydroxy-2,1,3-benzothiadiazole.



The europium, samarium, erbium and ytterbium complexes of 4-hydroxy-2,1,3-benzothiadiazole (OH-btd) and dibenzoylmethane (Hdbm) have been synthesized. It has been shown that the tri- and tetranuclear complexes are formed: $[Ln_3(dbm)_4(O\text{-}btd)_5]$ (Ln = Eu, Sm), and $[Ln_4(dbm)_6(O\text{-}btd)_4(OH)_2]$ (Ln = Er, Yb), $[Er_4(dbm)_4(O\text{-}btd)_6(OH)_2]$. Structures of the complexes have been established by single crystal X-Ray diffraction and other routine methods. Furthermore the near infrared luminescence of the compounds has been studied. The emission intensity of $[Ln_4(dbm)_4(O\text{-}btd)_6(OH)_2]$ having 6 $(O\text{-}btd)^-$ ligands appears to be higher than those of $[Ln_4(dbm)_6(O\text{-}btd)_4(OH)_2]$ that have only 4 $(O\text{-}btd)^-$ ligands.

Acknowledgements – The authors are grateful to the Russian Foundation for basic research (grants No. 12-03-31530, 12-03-31759, 13-01-01088), and Federal target program "Kadry" (Contract No. 8631) for financial support.

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THE COMPLEXES OF TRINUCLEAR MACROCYCLIC COPPER(I) AND SILVER(I) PYRAZOLATES WITH CARBONYL COMPOUNDS

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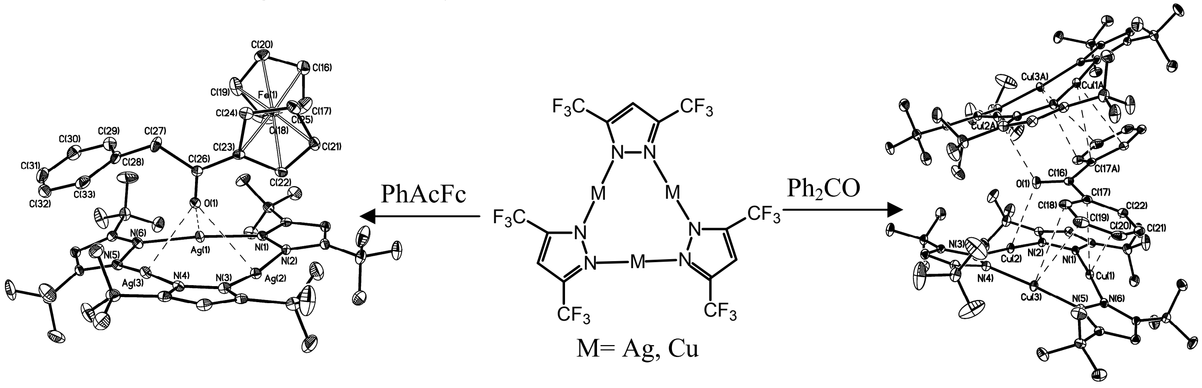
There is constant interest in the chemistry of coinage metal (group 11 metal) pyrazolate adducts. Cyclic trinuclear complexes of d^{10} transition metal represent an important class of coordination compounds whose significance spans multiple fundamental areas, such as including acid-base chemistry, metalloaromaticity, metallophilic bonding, supramolecular assemblies, and host/guest chemistry [1, 2].



The complexation of the copper (I) and silver (I) cyclic trinuclear pyrazolates $[ML]_3$ (M=Cu, Ag; L=3,5-bis(trifluoromethyl)pyrazolate) with acetylferrocene, (phenylacetyl)ferrocene, benzophenone and butanone-2 was studied by means of IR, NMR, UV-vis spectroscopy (230-290K) in low-polar solvents (CH_2Cl_2, hexane) and X-ray diffraction in solid state.

The complexation were observed at all temperature and one type of complexes with coordination of the oxygen atom of CO group to metal atom of $[ML]_3$ were found in solution and solid state. Their spectral features, structure, formation constants and thermodynamic characteristics were determined. Influence of substitutient in pyrazole ring to acid-base properties of macrocycles and complexation will be discussed.

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COPPER COMPLEXES WITH NEW PYRIDYL-SUBSTITUTED NITROXIDES

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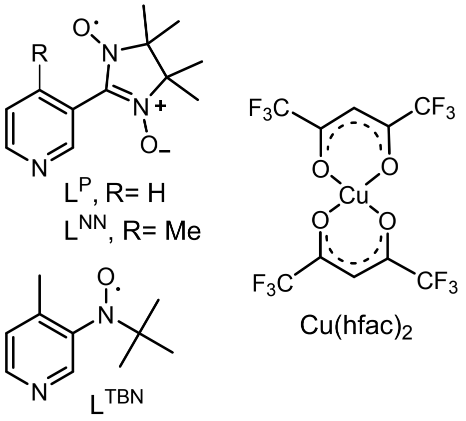
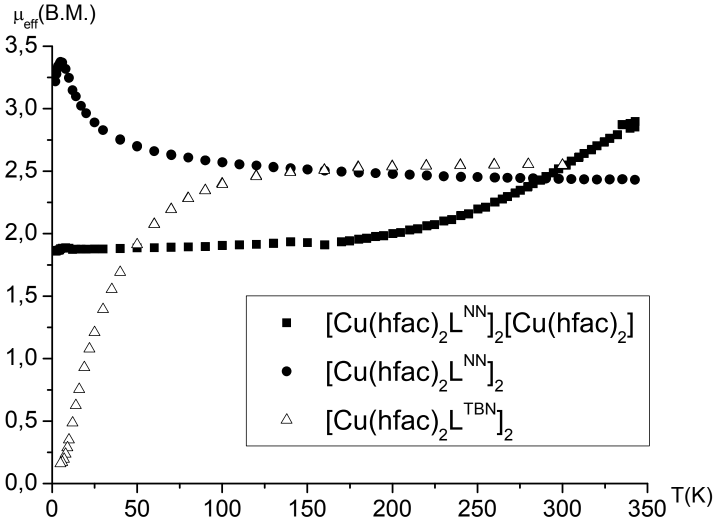
Copper-nitroxide complexes exhibiting thermally-induced magnetic anomalies attract significant attention in the field of molecular magnetism. One of the first of such complexes was tetranuclear complex $[(Cu(hfac)_2)_4L^P{}_2]$. Its magnetic behavior, similar to spin crossover in the temperature interval 70–140 K, was associated with a transition of the coordinated O atom of the nitroxyl fragment from axial to equatorial position [1].
We synthesized new ligands: L^{NN} bearing, as compared to L^P, methyl group in position 4 of the pyridine cycle and L^{TBN} with modified paramagnetic fragment.





We succeed in preparation of new $Cu(hfac)_2$ complexes with L^{NN} and L^{TBN}: dimeric complexes $[Cu(hfac)_2L^{NN}]_2$ and $[Cu(hfac)_2L^{TBN}]_2$, and complex $[Cu(hfac)_2L^{NN}]_2[Cu(hfac)_2]$ with polymer-chain structure. In solid $[Cu(hfac)_2L^{TBN}]_2$ antiferromagnetic exchange interactions are realized between paramagnetic centers, while in the complex $[Cu(hfac)_2L^{NN}]_2$ in 5–350 K temperature range dominates ferromagnetic exchange. In case of complex $[Cu(hfac)_2L^{NN}]_2[Cu(hfac)_2]$, where cyclic fragments $\{Cu(hfac)_2L^{NN}\}_2$ are linked by $Cu(hfac)_2$ matrixes in chains, there is a drastic increase of μ_{eff} at higher temperatures due to the expanded phase transition accompanied by thermochromic effect.

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MIXED-LIGAND BETA-DIKETONATES OF ALKALINE- AND ALKALINE-EARTH ELEMENTS: STRUCTURAL FEATURES AND PROPERTIES

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Interest in the coordination chemistry of alkaline (AE) and alkaline-earth (AEE) elements has increased in the last 20 years. The one of the driving force is the development of new AE and AEE containing materials (superconductiors, ferroelectrics, high-K materials, multiferroics etc.) The metal beta-diketonates and mixed ligand complexes with ancillary donor ligands are the most promising precursors for manufacturing of thin films of these materials.

The present work is devoted to novel mixed-ligand complexes of AE and AEE hexafluoroacetylacetonates with polyglymes ($CH_3O(CH_2\text{-}CH_2O)_nCH_3$, n = 2 – diglyme, 3 – triglyme, 4 – tetraglyme) or trigmo ($CH_3O(CH_2\text{-}CH_2O)_3OH$).

The DFT calculations predict the formation of M(hfa)(glyme) molecules (M = Na, K; glyme = diglyme, triglyme, tetraglyme) with energy gains of ΔE=110-130 and 75-100 kJ/mol for M=Na and K respectively. The certain compounds were synthesized and their X-ray crystal structures were determined. It was shown that the increasing of the number of donor atoms in polyglyme significantly changes the structure motif and thermal behavior: from 1D polymers $[[Na(diglyme)_2^+][Na_7(hfa)_8^-]]_\infty$ and $[[K(diglyme)_3^+][K_2(hfa)_3^-]]_\infty$ to polynuclear $[Na_3(hfa)_3(triglyme)]_2$, $[Na_3(hfa)_3(trigmo)_2]$, $[Na(hfa)(triglyme)]_2$, $[K_4(hfa)_4(trigmo)_2]$ and to mononuclear [Na(hfa)(tetraglyme)] и [K(hfa)(tetraglyme)] complexes at last.

The synthesis of AEE mixed-ligand complexes shows the dependence on synthetic conditions. So, the compounds $[Sr(hfa)_2(triglyme)]$ and $[Ba_2(hfa)_4(triglyme)_3]$ could be obtained in anhydrous conditions, while $[Ca(hfa)_2(diglyme)(H_2O)]$, $[Sr(hfa)_2(diglyme)(H_2O)]$, $[Ba(hfa)_2(diglyme)_2]$, $[Ca(hfa)_2(triglyme)]$, $[Sr(hfa)_2(triglyme)(H_2O)]$, $[Ba(hfa)_2(triglyme)(H_2O)]$ are formed in the presence of water. In contrast to AE compounds the AEE complexes have similar structure motif which does not significantly changes with the increasing the length of polyglyme. However, the intermolecular interactions and thermal behavior correlate with the composition of compounds.

The obtained novel complexes of AE and AEE demonstrate high volatility in vacuum and could be recommended as precursors for MOCVD of thin films.

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COORDINATION CHEMISTRY APPROACHES TO DESIGN OF NEW LUMINESCENT LANTHANIDE CONTAINING MATERIALS

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Thanks to the variable and versatile co-ordination behavior of lanthanide metal ions (Ln^{III}) wide possibilities of the molecular design, by means of combination of different ligands and metal ions in one molecule, are opened. It allows to achieve materials with the required functional properties, including luminescence, varying their composition and structure. Both fundamental and applied tasks of organic luminescent materials can be solved using the coordination chemistry approaches. Understanding of fundamental correlations between luminescent properties, composition and structure of luminescent metal-organic coordination compounds helps to find new highly luminescent materials for common and even special applications.

Ten year research in this area, carried out in Laboratory of Coordination Chemistry, Chemistry Department, Lomonosov Moscow State University, resulted in the formation of the Luminescence group, which activity has been aimed on the synthesis along with both structural and luminescent studies and valuation as luminescent materials of coordination compounds of lanthanide ions. Both optically active (Eu, Tb, Dy, Sm, Tm) and optically inactive (Gd, Lu) have been chosen for investigation. In the first group the main task is to find the suitable organic sensitizers of lanthanide luminescence, which will form stable complexes. While in the second group an appropriate metal has to be selected to increase luminescence efficiency or to change luminescent characteristics of emissive organic ligand. Search of the new luminescent materials is carried out among the compounds which are easy to handle and thus can be used for practical applications. Thus great attention has been paid to the methods of compound transformation into luminescent materials and, first of all, into thin films.

Among the topics under investigation is a search for the new *vis*-luminescent materials among lanthanide coordination compounds and their validation as emitting layer materials in OLEDs. To solve the problem of low UV stability of the luminescent lanthanide-organic compounds, the highly stable, but non-volatile and insoluble aromatic carboxylates were suggested, and two new chemical methods of their thin film deposition were proposed and developed. The features of the quenching mechanism of lanthanide coordination compounds is another topic under investigation, aimed on the search of “smart” luminescent sensor materials with temperature-dependent luminescence. Recently the research activity is focused on the quenching mechanism of NIR-emitting lanthanide ions and search for the new higher luminescent compounds.

The results of these investigations, the same as the further development in the field of luminescence of coordination compounds, are to be discussed in the presentation.

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EASY WAYS TO FORMATIONS OF THE HOMO- AND HETEROMETALLIC COMPLEXES WITH SEMI-LATERN FRAGMETS

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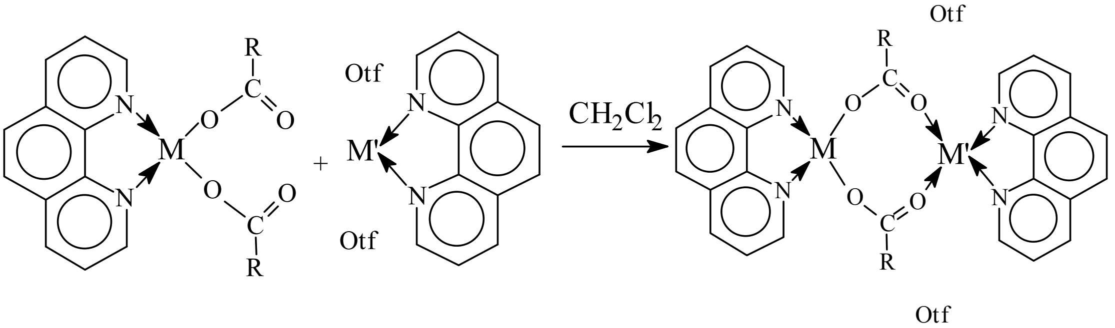
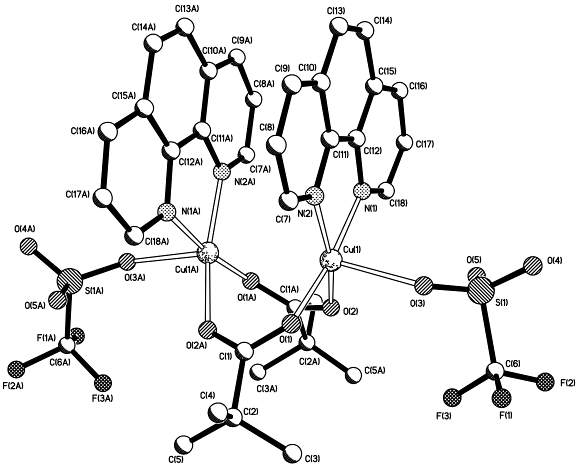
It was founded that triflates of transition metals (containing very weak anions) where two coordination sites are blocked by molecules of the phenanthroline, reacts in the mild conditions with the donor molecules, such as PhenM(OOCR)$_2$ (M = Cu, Zn, Co, Ni, R = Bu^t, Me).



Binuclear homo- and heterometallic complexes can be formed as result of this interaction

For example the reaction of phenanthroline-copper triflate with PhenCu(OOCR)$_2$ (R = Bu^t, Me)(CH_2Cl_2, r. t.) leads to the formation of binuclear Phen$_2$Cu$_2$(μ-OOCR)$_2$otf$_2$, with the geometry of the "Chinese semi-latern". In this complexes two bridging carboxylates ligands supplemented stacking interaction beetwing two coordinated Phen ligands with the delocalized electron density (C...C 3.57). After reaction of this complex with pyrazole or 3,5-dimethylpyrazole, pyrazoles molecules are coordinated in the axial position of the complex, displacing triftat-anions to the outer sphere, and bis-trifluoromethylpyrazole are deprotonated with the substitute one of the bridging pivalate anions.



Using as the starting complex in this reactions the palladium triflate with PhenM(OOCR)$_2$ (M = Cu, Zn, Co, Ni, R = But, Me) are formed heterometallic complexes with core Pd-Cu, Pd-Zn, Pd -Co, Pd-Ni. The structure of the obtained compounds are discussed by the X-ray data.

Acknowledgements- This work was supported by RFBR (projects 11-03-00824, 11-03-01157, 12-03-31339) and the Presidium of the Department of Chemistry and Materials Science, Russian Academy of Sciences, and the Council for Grants of the President of the Russian Federation (MK-4452.2013.03*)*

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Ni(II) COMPLEXES OF THE NEW PINCER-TYPE LIGANDS PIMCOP, PIM$^+$COP, AND NHCCOP.

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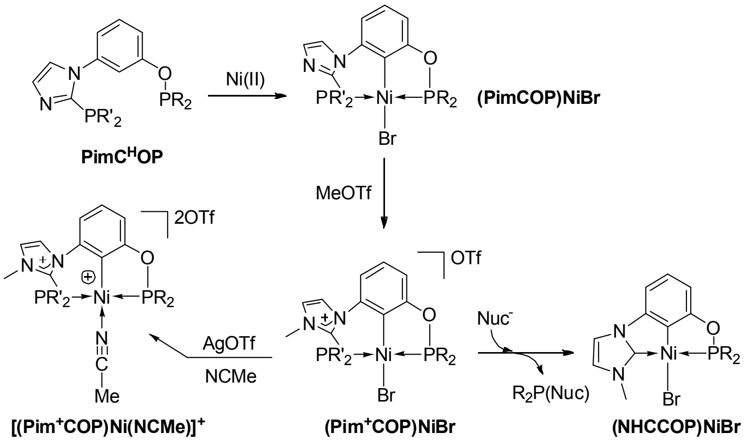
Various pincer complexes have found applications in catalysis thanks to their facile synthesis, enhanced thermal stabilities, and novel reactivities. In the past, we have reported on pincer-type complexes featuring phosphinite [1] and imidazolophosphine [2] donor moieties, and recently we have prepared complexes based on new ligands featuring both of these donor moieties. The modular synthesis of the unsymmetrical **PimCOP** ligands has allowed us to introduce electronic and steric diversity in these ligands, whereas their facile and direct C-H nickellation provides access to new Ni(II) complexes **(PimCOP)NiBr**. The latter undergo facile *N*-alkylation to give the imidazoliophosphine-phosphinito complexes **(Pim$^+$COP)NiBr**, which can further derivatized as follows: ionization at Ni gives the dicationic species **[(Pim$^+$COP)Ni(NCMe)]$^+$** whereas reaction with nucleophiles leads to the new NHC-phosphinito complexes **(NHCCOP)NiBr** [3]. Such post-synthesis derivatization protocoles of the imidazolophosphine moiety in PimCOP ligands thus provide rapid and efficient access to unsymmetrical, pincer-type systems featuring unusual and variable steric and electronic properties that should be of interest in catalytic applications [4]. We will present the structural, spectroscopic, and electrochemical properties of the title complexes and their catalytic application.



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[2] (a) N. Debono et al. *Eur. J. Inorg. Chem.* **2008**, 2991; (b) I. Abdellah et al. *Chem. Asian.* J. **2010**, *5*, 1225.
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Acknowledgements - Centre National de la Recherche Scientifique (CNRS), ANR program (ANR-08-JCJC-0137-01), NSERC of Canada, Centre in Green Chemistry and Catalysis (CGCC). Direction des Relations Internationales of Université de Montréal and Université Paul Sabatier.

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THE COMPLEXES OF Ti, Al, Zn BASED ON THE POLYDENTATE LIGANDS: SYNTHESIS, STRUCTURE, APPLICATION IN CATALYSIS

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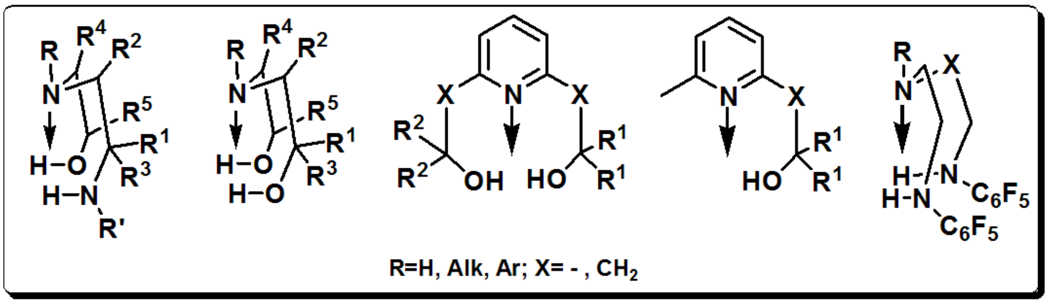
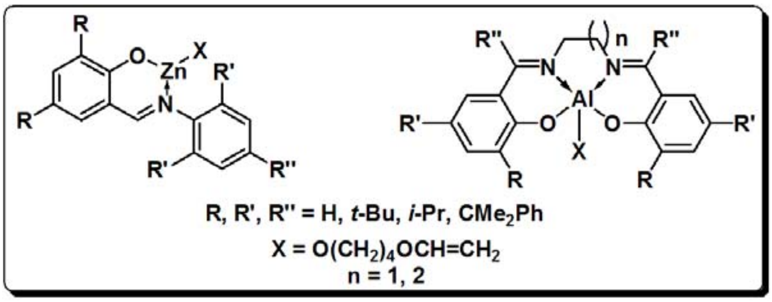
Materials based on aliphatic polyesters attract much attention due to their biodegradation and biocompatibility. The ring opening polymerization (ROP) using metal complexes as initiators is the most appropriate method for synthesis of such materials due to controlling type of process. The search of new catalysts of this polymerization is the actual task for modern organometallic chemistry.

In our work we synthesized and investigated:
-1) new complexes of Ti, Al, Zn based on dialkanolamines, pyridine containing alcohols and substituted diethylenetriamines. The complexes of presented type are active initiators of ROP of lactide and ε-caprolactone.



-2) mixed complexes of Al, Zn containing iminophenolate ligands and fragments of functionalized unsaturated alcohols. These compounds were used as catalysts in ring opening polymerization of cyclic lactones. The fragment of unsaturated alcohol is transferred to the end of polymer chain with high level of functionality. This synthetic strategy allows us to obtain **macromonomers** based on biodegradable materials with high degree of functionalization.



Acknowledgements - This work is supported by the RFBR (12-03-00206-a, 12-03-90020-Bel_a) and by President Grant for Young Russian Scientists (MD-3634.2012.3).

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THE REACTIONS OF 1,3-DIPOLAR CYCLOADDITION BETWEEN DIFFERENT NITRONES AND STYRENE AND ITS η^{6-}(ARENE)CHROMIUM TRICARBONYL COMPLEXES

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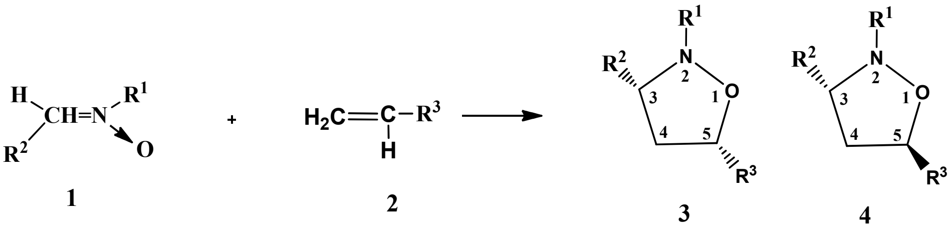
η^{6-}(Arene)chromium tricarbonyl complexes are very interesting reagents for selective organic synthesis. It is related with their typical accepting properties and a large size of chromium tricarbonyl group effectively shielding arene ring. An important field of application of η^6-(arene)chromium tricarbonyl complexes is the reaction of 1,3-dipolar cycloaddition, also known as a very available and effective method of construction of heterocyclic rings. The reaction proceeds between 1,3-dipoles and unsaturated systems containing multiple bonds. In order to obtain a number of new individual η^{6-}(arene)chromium tricarbonyl complexes of isoxazolidines and to investigate the influence of chromium tricarbonyl moiety on the reaction 1,3-dipolar cycloaddition, we carried out a series of experiments that occur in accordance with scheme:



1: R^1 = Me, R^2 = Ph (a)
R^1 = Ph, R^2 = Ph (b)
R^1 = Bu^t, R^2 = Ph (c)
R^1 = Me, R^2 = Ph[Cr(CO)$_3$] (d)
R^1 = Ph, R^2 = Ph[Cr(CO)$_3$] (e)
R^1 = Bu^t, R^2 = Ph[Cr(CO)$_3$] (f)
2: R^3 = Ph (a)
R^3 = Ph[Cr(CO)$_3$] (b)

The formed derivatives - free and coordinated isoxazolidines **3** and **4** were isolated and characterized by UV, IR and ^{1}H NMR – spectroscopy and X-ray diffraction. Purity of compounds was confirmed by HPLC. It is shown that all the products are 5-substituted isoxazolidines. It is found that the introduction of chromium tricarbonyl group into nitrone or alkene molecule significantly increases the stereoselectivity of the cycloaddition process, increasing the yield of cis-isomer products (table 1).

Table 1. The ratio of cis- and trans-isomers isoxazolidines in 1,3-dipolar cycloaddition

Nitrone (**1**)	Alkene (**2**)	The ratio of cis- and trans-products (**3**:**4**)	Nitrone (**1**)	Alkene (**2**)	The ratio of cis- and trans-products (**3**:**4**)
1a	2a	67:33	1d	2a	100:0
1b	2a	90:10	1e	2a	100:0
1c	2a	100:0	1f	2a	100:0
1a	2b	83:17	1d	2b	100:0
1b	2b	100:0	1e	2b	100:0
1c	2b	100:0	1f	2b	100:0

Acknowledgements -This work was supported Russian Ministry of Education and Science ("Federal target program of scientific and scientific-pedagogical personnel of innovation of Russia on 2009-2013") and Russian Foundation for Basic Researches (Proj. 11-03-00074a).

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Poster Presentations

SYNTHESIS OF *N*-METHYLPYRROLIDINO[70]FULLERENE DERIVATIVES BEARING ORGANIC AND ORGANOMETALLIC SUBSTITUENTS IN 2-POSITION OF A HETEROCYCLIC RING

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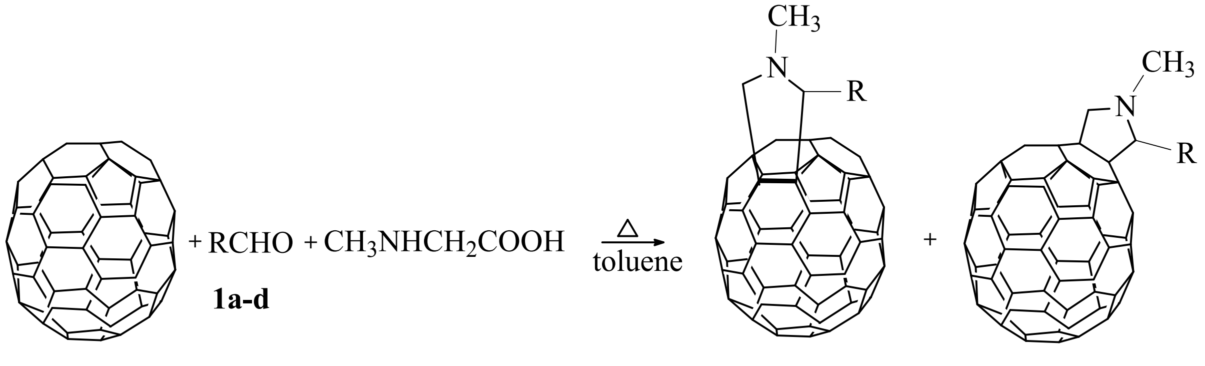
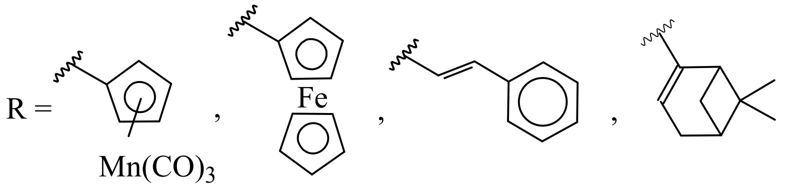
In the continuation of our study of the Prato reaction with C_{60} [1, 2], novel derivatives of *N*-methyl[70]fullerenepyrrolidine containing some organic and organometallic residues in position 2 of the pyrrolidine ring have been synthesized.



1a-d

2a-d **3a-d**



a **b** **c** **d**

Two isomeric monoadducts were separated by column chromatography in each reaction: cycloadduct at the 1,9 position and 7,8 position of C_{70}.

In the course of the Prato reaction between C_{70} and natural (-) myrtenal, a new chiral centre C-2 arises and, correspondingly, 4 diastereomers are formed. CD spectroscopic studies were carried out for the synthesized optically active compounds **2d**, **3d**.

[1] N. Abramova, S. Peregudova, A. Emel’yanova, A. Pleshkova, V. Sokolov, *Russ. Chem. Bull., Int. Ed.*, **2007**, *56*, 361-363.

[2] N. Abramova, K. Babievski, S. Peregudova, S. Manuylov, V. Sokolov, *"Advanced Carbon Nanostructures" (ACN'2011)*, St.Petersburg, Russia, July 4-8, **2011**, 238.

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GOLD(III) "TRICARBOXYLATE" COMPLEXES: SYNTHESIS, SPECTROSCOPY AND QUANTUM-CHEMICAL STUDY

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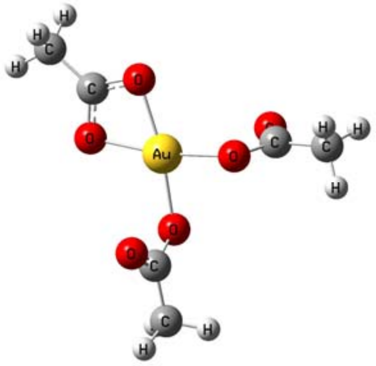
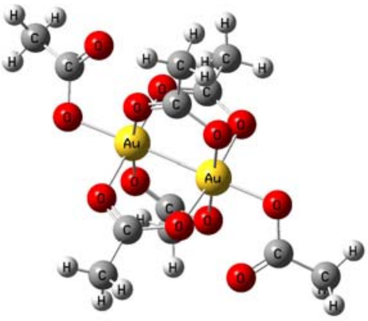
Binary gold(III) carboxylates are perspective gold-containing compounds, which can be used as precursors for both homogenous and heterogeneous catalysts. However, information about structures and properties of these compounds is still rather limited. It is known, that gold(III) carboxylates can be prepared by change of chloride ligands in $AuCl_3$ by different carboxylate anions [1]. At the same time only gold(III) acetate usage is mentioned in literature, but not any other carboxylates. Also authors noted some traces of decomposition even for just-supplied samples [2]. That makes a development of synthesis and study of properties of binary gold(III) carboxylates be an actual goal of modern chemistry of noble metals.

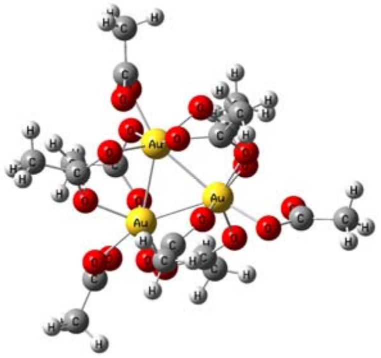
We have prepared a series of gold(III) carboxylates $Au(RCO_2)_3$, where R are different in electronic and steric properties (R = Me, CMe_3, CF_3). We used the following reaction:

$$HAuCl_4 + 4RCO_2Ag = Au(RCO_2)_3 + RCO_2H + 4AgCl$$

The reaction proceeds in glacial acetic acid (with addition of acetic anhydride) for R = Me or dry acetonitrile for R = CMe_3 and CF_3. It was shown that gold(III) pivalate (R = CMe_3) and trifluoroacetate (R = CF_3) can be obtained by change of acetate groups in $Au(CH_3CO_2)_3$ under 1.5-2-times excess of corresponding carboxylic acids. IR- and NMR-studies of gold(III) carboxylates indicated a presence of two types of carboxylates groups in solid state and in solutions. According to IR-spectroscopic data complexes contain terminal and bridging carboxylate groups in a ratio 1:2. That was confirmed by quantum chemical calculations for structures $Au(RCO_2)_3$, $Au_2(RCO_2)_6$ and $Au_3(RCO_2)_9$ (R = Me, CF_3) (DFT/lanl2dz). $Au_2(\mu\text{-}RCO_2)_6$ and $Au_3(\mu\text{-}RCO_2)_9$ structures have lower energy for $Au(RCO_2)_3$ unit compare to $Au(RCO_2)_3$ itself. Thus one can assume that binary gold(III) carboxylates have non-monomeric structures.







[1] T.E. Nappier, *Gold carboxylates and process for preparing the same*, Pat. 5210245 USA, C07F 1/12 556/114; 556/115; assignee Mooney Chemicals, Inc. – 852673; filed: 17.03.92; date of patent: 11.05.93.
[2] S.D. Bakrania, G.K. Rathore, M.S. Wooldridge, *J. Therm. Anal. Calorim.*, **2009**, *95*, 117–122.

Acknowledgements - We are grateful to the Council of the President of the Russian Federation for young scientists for financial support (project 977.2012.3).

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REACTIONS OF DIETHYLSTANNYLIUM CATIONS ET_2SNT^+ WITH OXYGEN-CONTAINING COMPOUNDS

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One of the mostly studied object during the beginning of the XXI century are tricoordinated cations ot the 14th group elements, that are R_3M^+ (M=Si, Ge, Sn, Pb). This interest is mainly determined by the comparison of their properties and their role as intermediates in chemical processes, as well as their role as catalysts of numerous reactions.

The problems of generation of R_3M^+ cations in the condensed phase resulted in the scarce number of works dealing with their chemical properties. We proposed the use of the nuclear-chemical method (NCM) which allows us to generate R_3M^+ cations and to study their reactions in different aggregate states. The R_2TSi^+ (R=T, Me, Et, Ph) ions and germylium R_2TGe^+ ions (R=Me, Et) were studied by this method.

In this presentation we report the extension of the NCM to the generation of diethylstannylium cations with oxygen-containing compounds.

It was found that the interaction of these catins with alcohols and ethers (BuOH, MeOt-Bu) leads to the formation of stannylation products. In the reaction with alcohol, in contrast to the similar reaction with silylium and germylium cations, stannanol is formed rather than an alkoxyderivative. The plausible reaction mechanisms are proposed based on experimental results and the results of quantum-chemical calculations (B3LYP) of the equilibrium geometries of main isomers in the $C_4H_{11}Sn^+$ system and activation barriers for their interconversion.

It was found that in the course of ion-molecule reactions cations undergo isomerization with further elimination of hydrocarbons. However, stannylium ions eliminate ethane in contrast to silylium and germylium cations which decompose with elimination of ethane. This fact may be rationalized takimg into account quantum-chemical data which reveal the tendency of stabilization of complexes with alkanes on going from silicon to tin.

Experiment and theory both indicate the growing predominance of the other decomposition channel, i.e. homolytic dissociation of the M-C bond on going from Si to Pb.

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THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS OF REDOX-ISOMERIC O-SEMIQUINONIC COBALT COMPLEXES

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Redox-isomerism phenomenon is of great interest during last three decades due to possible application in molecular devices. o-Semiquinonic complexes of cobalt exhibit a redox-isomerism, i.e. the ability to exist in two forms differing by valent and spin state of metal and ligands. It was shown that the conversion of redox isomers is accompanied by phase transition.

Phase transition of o-semiquinonic cobalt complexes with 2,2’-dipyridil (2,2’-bpy)Co(3,6-DBSQ)$_2$ (**1**) and 1,10-phenanthroline (1,10-phen)Co(3,6-DBSQ)$_2$ (**2**) were quantitatively characterized [1, 2]. Complexes **1** and **2** are isomorphous and form solid solutions one in another with any ratio. Each solid solution reveals phase transition which follows redox-isomeric transformation upon temperature change. Thermodynamic parameters of phase transitions depend on the composition of solid solution. The heat capacity of solid solution (1:1) was studied in the range 7–350 K in an adiabatic vacuum calorimeter and the other ones were investigated by differential scanning calorimetry.

Resulting diagrams “transition temperature – composition”, “enthalpy – composition” allow us to evaluate the reciprocal influence of isomorphic lattices belonging to different redox-isomeric complexes.

[1] B. Lebedev, N. Smirnova, G. Abakumov, V. et al., *J.Chem.Thermodynamics*, **2002**, *34*, 2093-2103.
[2] M. Bubnov, N. Skorodumova, A. Bogomyakov, et al., *Russ.Chem.Bull., Int.Ed.*, **2011**, *60*, 440-446.

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2,3-DIHYDROXY-4,6-DI-TERT-BUTYL-BENZALDEHYDE - BUILDING-BLOCK FOR SYNTHESIS OF STERICALLY HINDERED CATECHOLES/O-QUINONES

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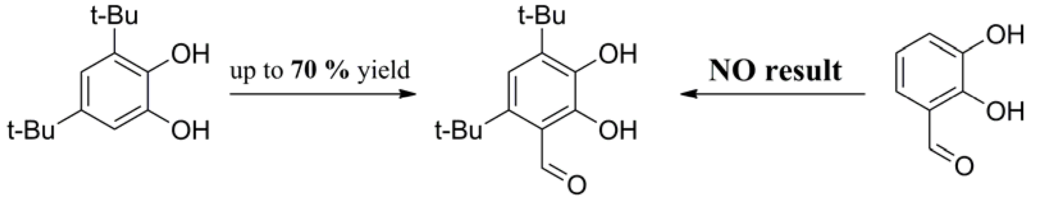
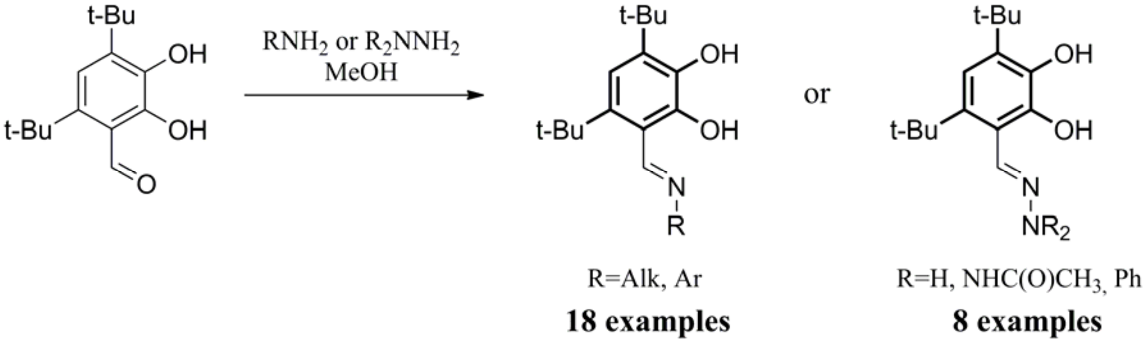
Last three decades transition metals complexes with redox-active and paramagnetic ligands have studied intensively. These ligands are sterically hindered o-quinones/catecholes, phenols, nitroxyl radicals and other. Progress in organic chemistry of phenols and nitroxyl radicals allow to use these fragment as building-blocks for prepare supramolecular paramagnetic systems. On other hand available building-block for synthesis of sterically-hindered o-quinones/catecholes (with two tert-butyl groups) have not been synthesized up to present.

We suggest using 3-hydroxy-4,6-di-tert-butylsalycilyc aldehyde (**t-Bu-Sal**) as buildind block for sterically-hindered o-quinones/catecholes. This compound has non-typical for sterically-hindered salicylic aldehyde disposition of tert-butyl-groups. It was synthesized from 3,5-di-tert-butylcatechol, and can be oxidized to the corresponding o-quinone.



t-Bu-Sal is well active in condensation and it was use for synthesis of Shiff-base and hyndrazones, which contain sterically-hindered catechol-fragment. These compounds can be used for further forming sterically-hindered o-quinones or catecholes ligand.



Acknowledgements: This work was carried out in the framework of the Federal Target Program "Scientific and Pedagogical Specialists of Innovative Russia for 2009–2013" (Contract GK_8460 from 31.08.2012 and "Target aspirant" agreement N14.132.21.1462 from 01.10.2012), and was financially supported by Russian President Grant supporting scientific schools (NSh-1113.2012.3).

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SYNTHESIS AND STRUCTURE OF THE FIRST PHOSPHORYLATED IRON(II) CLATHROCHELATES

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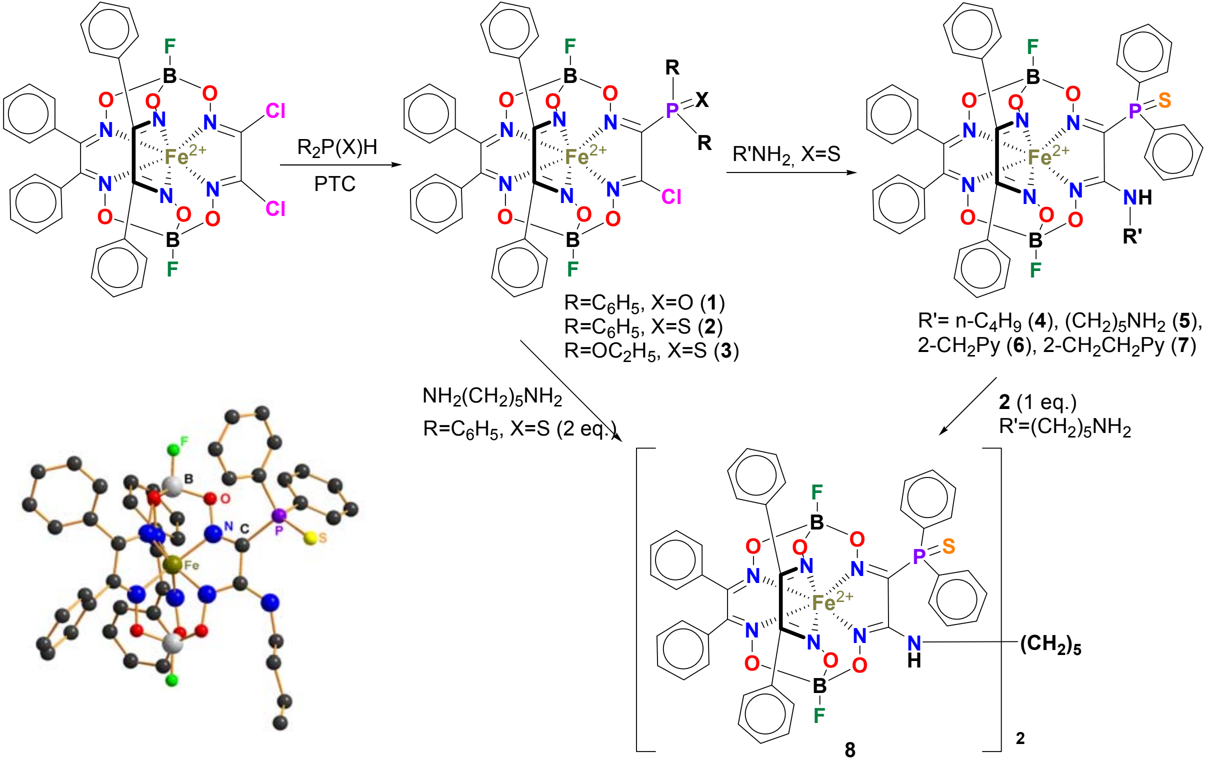
Up to date, some synthetic pathways to a number of tris-dioximate clatrochelates with encapsulated iron, ruthenium(II) and cobalt(I,II,III) ions, being of the theoretical and practical interests, have been elaborated [1]. However, none of these compounds contained phosphorus-bearing groups, which are the functionalities that could impart both the specific bioactivity and the coordination-chemical properties to the resulting complexes.

We have found that an iron(II) dihalogenoclathrochelate readily reacts with (thio)hydrophosphoryl compounds under phase transfer catalysis conditions affording monophosphorylated macrobicyclic complexes **1**–**3** (Scheme). The reaction rate depends on the acidity of the phosphorylated agent and is substantially higher in the case of the hydrothiophosphoryl compounds.



Scheme

The reactive chlorine atom of the monophosphorylated iron(II) clatrochelates undergoes nucleophilic substitution with primary and secondary amines as nucleophiles, yielding the corresponding mono- (**4**–**7**) and bis-clathrochelates (**8**), which were characterized using elemental analysis, IR, UV-vis, multinuclear NMR spectroscopy, MALDI-TOF spectrometry and by X-ray crystallography.

[1] Y.Z. Voloshin et al., *Clathrochelates: synthesis, structure and properties*, **2002** ; *Angew. Chem. Int. Ed.*, **2005**, 3400; *EJIC*, **2010**, 5401, **2012**, 4507 ; *Inorg. Chem*., **2012**, 51, 8362; *Dalton Trans*. **2012**, 746; 921; 6078, **2013**, 42, 4373; *Chem.Com*. **2011**, 47, 7737.

Acknowledgements. This work was supported by RFBR (grant 12-03-31581).

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SYNTHESIS OF HETEROLIGAND LANTHANIDE COMPLEXES BASED ON 3 - (2-BENZOTHIAZOLE-2-YL)-2-NAPHTHOL FOR ORGANIC LIGHT-EMITTING DIODES.

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Recently the main attention has attracted on the application of metal complexes as electroluminescent materials for organic light emitting diodes (OLED). A growing interest has been attracted to the Nd, Er, and Yb derivatives as the efficient materials emitting in near-infrared regions. The heteroligand ytterbium complexes $Yb_2(NpSON)_4q_2$ (**1**) and $Yb_2q_4(NpSON)_2$ (**2**) were prepared by the metathetical reactions of $Yb[N(SiMe_3)_2]_3$ with 3-(2-benzothiazol-2-yl)-2-naphthole (HNpSON) and 8-hydroxyquinoline (Hq) in DME (dimethoxyethane) solution. The products were isolated as yellow crystalline powders soluble in DME, THF and MeCN. According to MALDI-TOF mass spectrometry of the reaction afford, besides the desired complexes **1** and **2,** two homoleptic byproducts $Yb_2(NpSON)_6$ and Yb_2q_6, which can be separated by crystallisation.

The simple three layer devices ITO/TPD/**2**/BATH/Yb, consisting of ITO on a glass substrate as the anode, N,N$^{/}$ -bis(3-methylphenyl)-N,N$^{/}$ -diphenylbenzidine (TPD) as the hole-transporting layer, the lanthanide heterocyclic complex as a neat emission layer, 4,7-diphenyl-1,10-phenanthroline (BATH) as an electron-transport layer and Yb as the cathode, were fabricated.

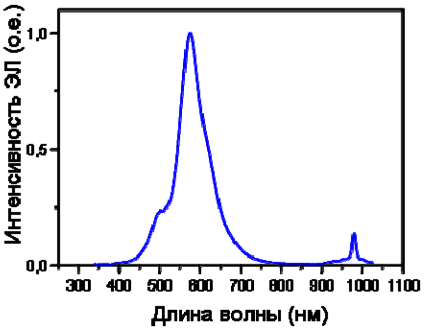

Figure 1. EL spectra of single layer device ITO/TPD/**2**/ BATH /Yb.

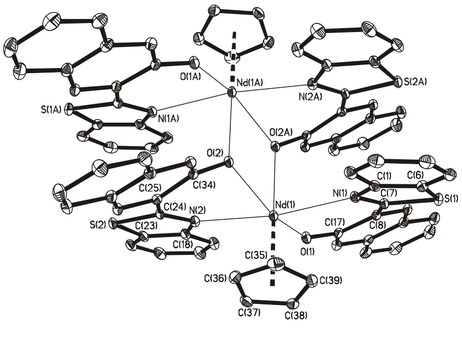

Figure 2. Molecular structures of **3**.

The EL spectra of **2** exhibited a broad band with maximum at 580 nm originated from NpSON ligand (Fig. 1) and the band at 978 nm is attributed to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb^{3+} ion. Difficulties associated with the isolation of the pure desired products, have led to the need to find other methods of synthesis of these compounds. It has been found that the reaction of Cp_3Nd with HNpSON in a ratio 1: 2 leads to the formation of complex $Cp_2Nd_2(NpSON)_4$ (**3**) (Fig. 2). The Yb analogue $Cp_2Yb_2(NpSON)_4$ (**4**) has been prepared similarly. Its reaction with two equivalents of Hq afforded pure complex $Yb_2(NpSON)_4q_2$ in 66 % yield, which exhibited high metal-centered emission.

Acknowledgements - This work was supported by the Russian Foundation of Basic Research (Grants, No. 13-03-00097, 13-03-97046)

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COPPER(I) PYRAZOLONATE COMPLEXES AND COPPER-CONTAINING NORBORNENE BASED COPOLYMERS. SYNTHESIS, CHARACTERIZATION, LUMINESCENT PROPERTIES

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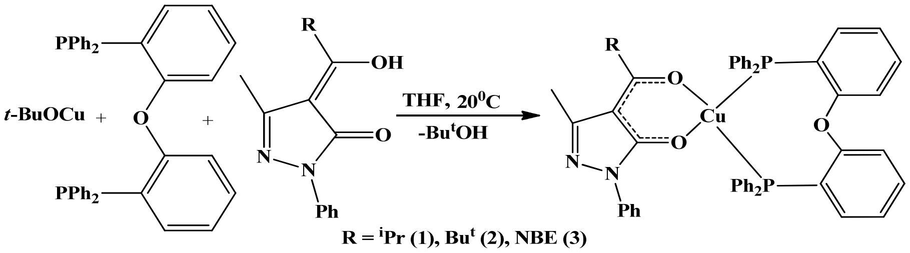
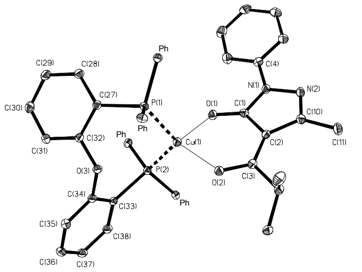
Pyrazolonate copper(I) complexes were synthesized and fully characterized.

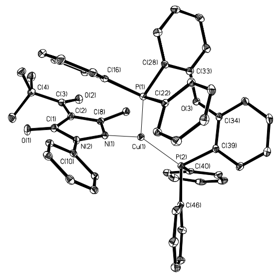


R = ^{i}Pr (1), Bu^t (2), NBE (3)

The structures of compounds **1** and **2** were determined by X-ray analysis.

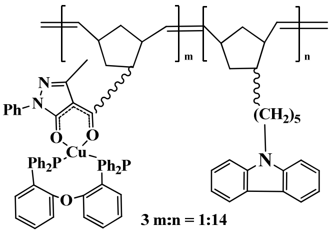


1

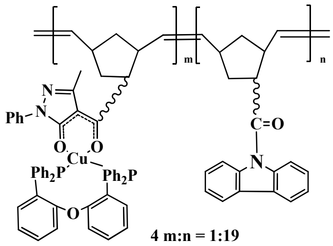


2

Complex **3** was copolymerized via ring-opening metathesis polymerization with carbazole substituted norbornene monomers.



3 m:n = 1:14



4 m:n = 1:19

Compounds **1-3** were used as emitting materials in organic light-emitting diodes (OLEDs) of the structure ITO/TPD/**1-3**/BATH/Alq$_3$/Yb. The OLED devices generated electroluminescence of yellow-orange color with maximum brightness of 280 cd/m^2. Photoluminescence spectra of polymeric complexes **4** and **5** consist of broad bands attributed to carbazole units (in the region of 370-450 nm), and copper-containing fragments (in the region of 480-560 nm).

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P, S-LIGANDS BASED ON THE THIOPHOPHITES AND THIOPHOPHETANES FOR THE COMPLEXATION WITH I AND VIII GROUP METALS

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To continue our study of bidentate ligands containing P and S donor atoms in complexation with transition metals we synthesized some Cu(I), Ag(I), Au(I), Co(II), Fe(II) complexes based on the P(III)-S- and P(IV)-S-ligands as well: thiophosphites, trialkyltetrathiophosphates (R = i-Pr, Bu), ammonium salts of octathiotetraphosphetane, respectively. The newly synthesized compounds were characterized by elemental analysis, X-ray single crystal diffraction, spectral (IR/Raman, fluorescence, SEM) studies.

The P(III),S-ligands, trialkyltrithiophosphites and their derivatives, react with Cu(I) halides to yield 1:1 [metal-ligand] complexes of various structure and coordination modes: the cyclic chain polymeric structure with bidentate type of copper coordination via P and S atoms, which was found to be the most common one for trithiophosphite complexes. The tetrameric cubane structure with monodentate type of metal coordination via P atom for the steric charged P(III),S-ligands and ligands containing P-S-, P-C - bonds.

The P(IV)-S-ligands, in particular $S{=}P(SR)_3$ (R = i-Pr, Bu) have formed 2:1 [metal-ligand] Cu(I) complexes with bidentate coordination of metal via S - atoms both of thiol and thion groups as it was shown by means of the X-ray data.

Piperidinium and triethylammonium salts of octathiotetraphosphetane $\{[P(S)]_4(S^{-}HN^{+}R)_4\}$; $R{=}(-CH_2-)_5$; $(C_2H_5)_3]$, due to the presence of donor sulfur atoms and cyclic structure comprising the $[P_4S_8]^{4-}$anion, act also as P(IV),S-ligands and coordinate the metal ion though all sulfur atoms. The experimental and calculated IR/Raman spectral analysis in the combination with quantum-chemical calculations at DFT level reveals common spectral characteristics corresponding both to Cu(I), Ag(I), Au(I), Fe(II), Co(II) complexes and to $P_4S_8^{4-}$ anion of “free” ligand, the latter is affected by complexation with metal halides being somewhat distored in complexes. This fact demonstrates that the $P_4S_8^{4-}$ moiety is preserved in the structure of complexes regardless of the metal used as well as the conditions of binding of transition metal – ligand, and each sulfur atom is coordinated by metal.

Some of the tetraphosphetane derivatives have been identified as promising anti-fungal (*Candida albicans*) agents whose activity is comparable to that of Amphotericin B, the metal derivatives possessing the fungicidal activity exceeding twice that of original ammonium salts of octathiotetraphosphetane.

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Synthesis and structure of the novel silicon and germanium C,O-, O,O- and O,S-chelates based on dimethylamides of 2-hydroxy- and 2-thioacids

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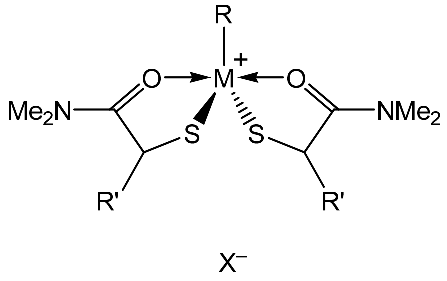
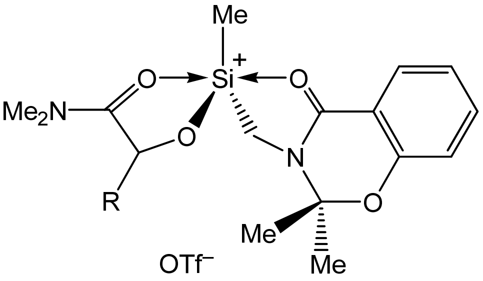
Chelates of hypercoordinated silicon and germanium are well known due to their high reactivity, biological activity, structural diversity and stereodynamic behaviour in solutions. In the present work, we report the synthesis and structures of new cationic Si and Ge complexes containing the fragments of 2-hydroxy- and 2-thioacids.

Bischelates **1a**,**b** and **2–3** were synthesised by the reactions of $MeSiCl_3$, *t*-$BuGeCl_3$ and $MeGeBr_3$, respectively, with two equivalents of corresponding *S*-trimethylsilyl-*N*,*N*-dimethyl-2-thioamides. The *O*-analogues of these complexes, $\{MeGe[OCHR'C(O)NMe_2]_2\}^+Br^-\cdot H_2O$ (**4**, R' = Me, Ph), were prepared in a similar manner. All cationic bischelates were hygroscopic, so in some cases they were isolated as hydrates. In contrast, the corresponding triflates were not sensitive to moisture and could be crystallised in anhydrous form. In particular, a very stable complex $\{t\text{-}BuGe[OCH_2C(O)NMe_2]_2\}^+OTf^-$ (**5**) was prepared by the reaction of *t*-$BuSiCl_3$, $Me_3SiOCH_2C(O)NMe_2$ and Me_3SiOTf.



1, M = Si, X = Cl, R = Me (**a**), *t*-Bu (**b**), R' = Me
2, M = Ge, X = Cl•H₂O, R = *t*-Bu, R' = H
3, M = Ge, X = Br•H₂O, R = Me, R' = H



6, R = H, Me, Ph

Cationic complexes **6** containing both *C*,*O*- and *O*,*O*-chelate ligands were synthesised from equimolar mixtures of $MeSiCl_3$, silylated ligands and Me_3SiOTf. These mixed bischelates were particularly stable and could be isolated with good to excellent yields.

According to X-ray data, the Si and Ge atoms in compounds **1**–**6** are pentacoordinate and have coordination environments intermediate between trigonal bipyramid and square pyramid, with two coordinating oxygen atoms in axial positions.

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MONONUCLEAR GALLIUM COMPLEXES WITH ACENAPHTHENE-1,2-DIIMINE LIGANDS: SYNTHES, REACTIONS WITH ALKYNES

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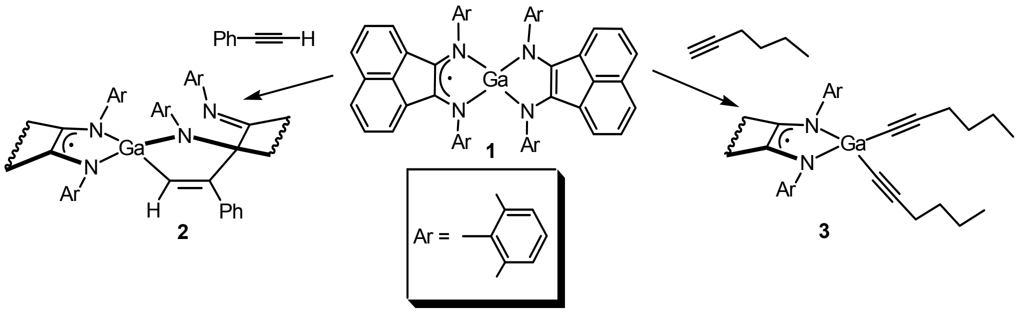
1,2-Bis(arilimino)acenaphthene ligands have attracted rising attention in recent years [1]. Recently we have found the reversible addition of alkynes to a (dpp-bian)Ga-Ga(dpp-bian) (dpp-bian - 1,2-bis[(2,6-diisopropylphenyl)-imino]acenaphthene) to give addition products [(dpp-bian)(RC=CR′)Ga-Ga[(R′C=CR(dpp-bian)]. The alkyne adds across the Ga-N-C section, which results in new carbon-carbon and carbon-gallium bonds. The bisgallium complex was found to be a highly effective catalyst for the hydroamination of phenylacetylene with anilines. [2]

Here we report the synthesis of monogallium complexes with bis(arylimino)acenaphthene ligands. Reduction of 1,2-bis[(2,6-dimethylphenyl)-imino]acenaphthene (dmp-bian) with gallium metal in toluene leads to bis-ligand gallium compound (dmp-bian)$_2$Ga (**1**) which containing one radical-anionic ligand and one dianionic ligand. The reaction compound **1** with phenylacetylene affords addition product (dmp-bian)Ga(HC=CPh)(dmp-bian) (**2**). The phenylacetylene adds across the Ga-N-C section of dianionic ligand which results in new carbon-carbon and carbon-gallium bonds. The reaction **1** with hexyne-1 in the presence of diphenylacetylene leads to formation of complex (dmp-bian)Ga(C≡C-Bu)$_2$ (**3**) containing radical-anionic dmp-bian ligand.



The exchange reaction of [(dpp-bian)Ga(I)]$_2$ with (Me$_2$NCH$_2$CH$_2$)C$_5$H$_4$K of the reagent ratio 1:2 leads to complex (dpp-bian)Ga(η^1C$_5$H$_4$(CH$_2$CH$_2$NMe$_2$) (**4**) in which Cp-ring is connected with gallium by η^1-type, and atom of nitrogen coordinates of the metal atom. The compound **4** behave with phenylacetylene with formation of a complex (dpp-bian)Ga(C≡CPh)$_2$ (**5**).

Paramagnetic complexes **1**, **2**, **3** and **5** have been characterized by EPR- and IR-spectroscopy. Dianion compound **4** have been characterized by ^{1}H NMR-spectroscopy. Molecular structures of **1-5** have been determined by single crystal X-ray analysis.

[1] N. Hill, I. Vargas-Baca and A. Cowley, *Dalton Trans.*, **2009**, *2*, 240-253.
[2] I. Fedushkin, A. Nikipelov, A. Morozov, A. Skatova, A. Cherkasov and G Abakumov, *Chem. Eur. J.*, **2012**, *18*, 255-266.

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CYCLOMETALATED PLATINUM(II) COMPLEXES WITH PYRAZOLONATE ANCILLARY LIGAND. SYNTHESIS, CHARACTERIZATION AND LUMINESCENT PROPERTIES

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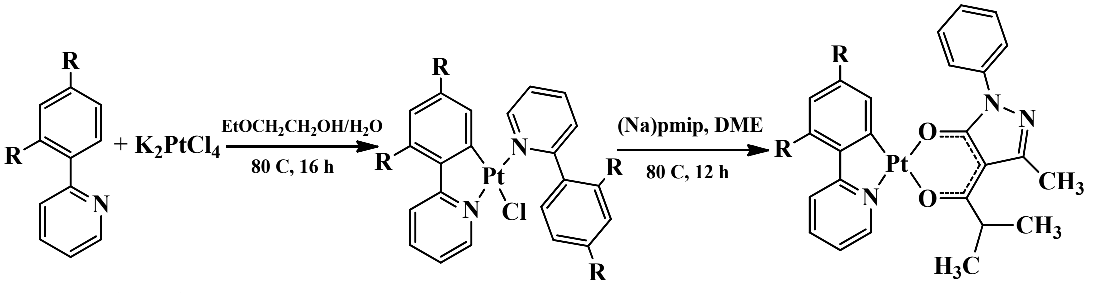
New cyclometalated platinum(II) complexes with pyrazolonate ancillary ligand were synthesized and structurally characterized.



R = H (**1**); F (**2**)

Both compounds revealed square-planar geometry. The crystal cell of **1** was found to contain the monomer molecules of platinum compound whereas dimer molecules of **2** with short Pt/Pt contacts of 3.2217(3) A were observed in the crystal cell of **2**.

Photophysical and electrochemical properties of **1** and **2** were investigated in detail. The highly resolved photoluminesence spectra of the platinum complexes in solution contain emission bands in the region of 470-550 nm attributed to monomer compounds **1** and **2**. The triplet-state energies of **1** and **2** obtained from DFT calculations agree very well with the experimental data. In the crystalline state complex **2** revealed excimer emission as a structureless broad band at ca. 584 nm related to dimmer molecules of platinum compound presented in the crystals.

Compounds **1** and **2** were used as emissive materials in OLED devices with the structure of ITO/TPD/**1** or **2**/BATH/Yb. Electroluminescence (EL) of orange color was observed and assigned to eximer emission of platinum complexes. The maximum of brightness of 5300 cd/m^2 and current efficiency of 16.47 cd/A were reached. When complexes **1** and **2** were doped into poly-9-vinylcarbozole (1-10 %) color of EL were found to depend on the dopant concentration and changed from green to yellow to white.

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REDOX PROPERTIES AND ANTIRADICAL ACTIVITY OF NOVEL ORGANOTIN COMPOUNDS WITH HINDERED PHENOL PENDANTS

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Organotin complexes with thiol ligands demonstrate the selective cytotoxic activity towards cancer cells [1,2]. The toxicity of organotin compounds is related with the binding of Sn atom with proteins SH-groups as well as with the induced oxidative stress. The hindered 2,6-di-alkylphenols are wide used antioxidants in industry and medicine as a models of vitamin E.

A series of novel organotin complexes with 2,6-di-tert-butylphenol pendants of general formula $R_nSn(SR')_{4-n}$: n=2, R′ = 3,5-di-*tert*-butyl-4-hydroxyphenyl, R = Me (**1**); Et (**2**); Bu (**3**); Ph (**4**); R′ (**5**); n=3, R = Me (**6**); Ph (**7**) were synthesized and characterized by NMR, IR and elemental analysis. The oxidation of **1-7** that leads to the relatively stable phenoxyl radicals formation was studied by ESR and CVA let us to expect the antioxidative activity of complexes.

The radical scavenging activity of complexes was monitored by model reaction with stable 2,2-diphenyl-1-picrylhydrazyl radical (DPPH). The antiradical activity of complexes was demonstrated to exceed that of and thiophenol ligand (RSH). Complex **5** (Fig. 1) with four phenol groups was found the most effective radical scavenger (EC_{50} = 8 μM).

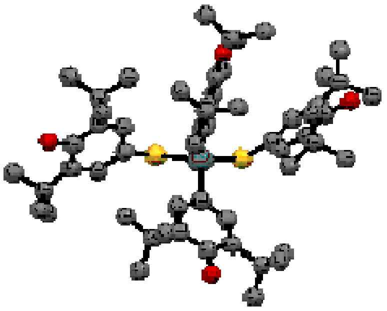

Fig.1. The molecular structure of $R'_2Sn(SR'_2)$ (**5**).

The antioxidant properties of complexes were studied in Z-9-octadecenoic (oleic) acid peroxidation. All compounds at 1 мM concentration were found to decrease the oleic acid hydroperoxides content up to 15 - 20 % (37 °C) and 70 - 80 % (65 °C). Complex **5** was the most active antioxidant. The corresponding diorganotin dichlorides and triorganoton chlorides were inhibitors of peroxidation [2]. Thus, the presence of hindered phenol groups changes the prooxidant activity of organotin scaffold that is eccential for search of new anticancer agents.

[1] D.B. Shpakovsky, E.R. Milaeva, et. al., *Dalton Trans*., **2012**, *41*, 14568-14582.
[2] E.R. Milaeva, V.Yu. Tyurin, D.B. Shpakovsky, O.A. Gerasimova, Zhang Jinwei, Yu.A. Gracheva, *Heteroatom Chem.,* **2006**, *17*, 475-480.

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COMPONENTS OF ADVANCED CERAMIC COMPOSITES BASED ON NANOHAFNIUMCARBOSILANES

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Ceramic metallopoly(oligo)carbosilanes – nanohafniumcarbosilanes are the base for a promising component of composite materials. Nanohafniumcarbosilanes were synthesized by thermal co-condensation of oligocarbosilane (the product of thermal polydimethylsilane rearrangement) and alkyl amide compounds of hafnium. These compounds do not contain harmful for carbide ceramics oxygen and chlorine impurities, are readily soluble in aliphatic and aromatic solvents, under normal conditions have sufficient thermal stability and, at the same time begin to lose their organic framing at a temperature above 140 °C. Energy of D(M □- N) bond dissociation is higher than that of D(N -□ Alk) bond, therefore at the thermal alkyl amide decomposition at first N □- Alk bond will be broken, and part of nitrogen may remain in the synthesized polymer. The nitrogen remaining in the polymer plays a positive role, then transforming in nitride ceramic phase, which further contributes to the stabilization of SiC-ceramics. Advantages of ceramic nanohafniumcarbosilanes are: no uncontrolled impurities, high compatibility of the components in the composite, the possibility of micro- and macro-modeling of ceramics at the stage of ceramic poly(oligo)carbosilane synthesis, and the fabrication of complex geometry nanoceramics without excessively high temperatures and pressure. The presence of refractory metal (Hf) homogeneously distributed in the polymer carbosilane matrix should provide monophasic structure, help to stabilize homogeneous ultrafine ceramics at high temperatures.

Nanohafniumcarbosilanes introduction in graphite and silicon carbide ceramics will significantly improve the structure and strength of the products fabricated from these materials (heat-resistant liners, bearings, drilling equipment, special cutting tools, etc.).

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SYNTHESIS, STRUCTURES AND MAGNETIC PROPERTIES OF METAL-CHELATES OF N,O,O(N,O,S) TRIDENTATE SCHIFF BASE PYRAZOLE DERIVED LIGANDS

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The syntheses of a series of novel N,O,O and N,O,S donor tridentate Schiff base ligands *via* the condensation of 5-hydroxy(mercapto)-3-methyl-1-phenyl-1H-pyrazole-4-carbaldehyde with *o*-hydroxymethylaniline and their Co(II), Ni(II), Cu(II), Fe(III) and Mn(II) complexes are reported. The compounds are characterized by the elemental C, H, N, S analysis, IR spectroscopy; ^{1}H NMR data for ligands, low-temperature magnetic measurements, X-ray absorption spectroscopy. The crystal structures for Ni(II) and Cu(II) coordination compounds with the composition NiL^1_2 and $Cu_2L^1_2$ are established by X-ray crystallography (Fig. 1):

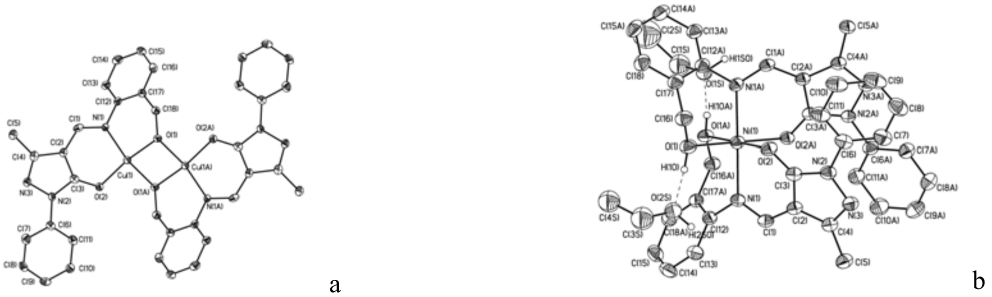
a
b

Fig.1. The general view of binuclear Cu complex (a) and mononuclear Ni complex (b).

Depending on the metal center two types of metal-chelates based on N,O,O and (N,O,S) tridentate pyrazole derived Schiff bases were obtained. Mn(II), Co(II) and Ni(II) complexes are characterized by the octahedral environment with an additional coordination of non-deprotonated hydroxy group of *o*-hydroxymethylaniline moiety, whereas the Cu(II) and Fe(III) ions form μ_2-oxo bridged binuclear compounds. The copper(II) complex is diamagnetic at room temperature that is consistent with a very strong ($2J \sim 1000$ cm^{-1}) antiferromagnetic exchange between the two copper centers through the oxygen bridges. The antiferromagnetic exchange interactions between the Fe(III) ions were also observed within a binuclear structure with $J = -18.1$ cm^{-1}.

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AMIDOPHENOLATE AND O-IMINOSEMIQUINOLATE TIN(IV) COMPLEXES

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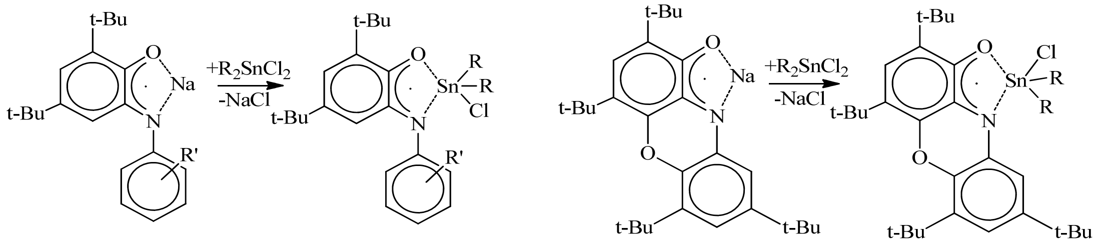
In present work we report the synthesis of new various amidophenolate (AP) and o-iminosemiquinolate (imSQ) tin complexes.

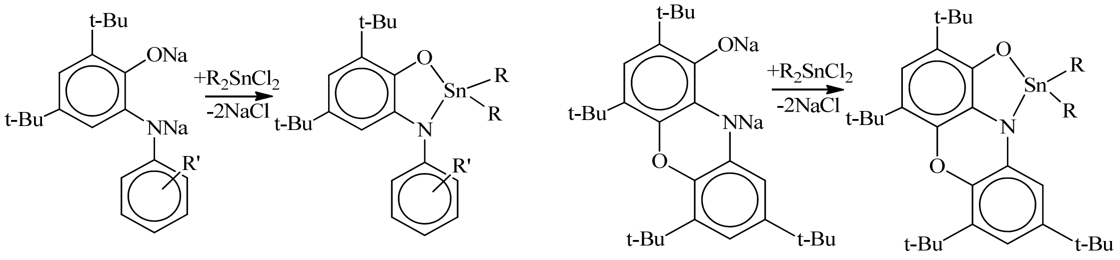
The interaction of sodium o-iminosemiquinolate with organotin chlorides in THF produces paramagnetic compounds with general formula - imSQSnR$_2$Cl (Scheme 1).



R = Me, Et, Bu^t, Ph

Scheme 1.

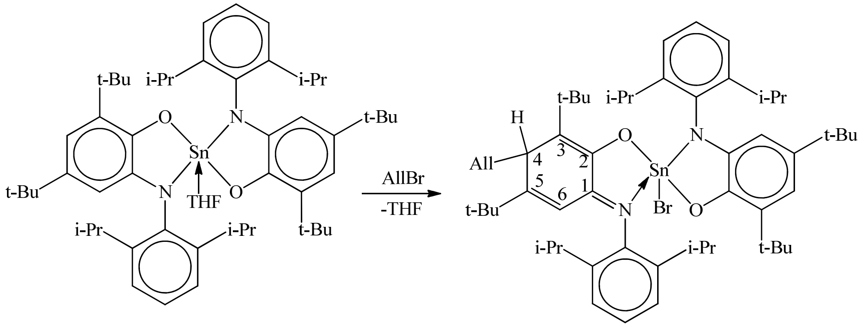
The diamagnetic tin compounds APSnR$_2$ were obtained as a result of the reaction between sodium amidophenolate and organotin chlorides in THF (Scheme 2).



R = Me, Et, Bu^t, Ph

Scheme 2.

Amidophenolate complexes of tin were found to demonstrate redox-activity in reactions with different reagents such as alkyl halides (Scheme 3) or halogens.



Scheme 3.

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AMIDINATE COMPLEXES OF YB$^{II/III}$: FEATURES OF CONFORMATIONAL STRUCTURES

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We have carried out X-ray analysis of the molecular and crystal structures of a series of ytterbium amidinate complex which are by derivatives of $[\{^tBuC\text{-}(NC_6H_3\text{-}2,6\text{-}^iPr_2)_2\}Yb^{II}(\mu\text{-}H)]_2$ (**1**) compound: amidinate complexes of Yb^{II} - $[\{^tBuC\text{-}(NC_6H_3\text{-}2,6\text{-}^iPr_2)_2\}Yb(\mu\text{-}Cl)]_2$ (**2**), $[\{^tBuC(NC_6H_3\text{-}2,6\text{-}^iPr_2)_2\}Yb(\mu\text{-}H)(\mu\text{-}PPh_2)Yb\{^tBuC(NC_6H_3\text{-}2,6\text{-}^iPr_2)_2\}]$ (**3**), $[\{^tBuC\text{-}(NC_6H_3\text{-}2,6\text{-}^iPr_2)_2\}Yb(\mu\text{-}SCH_2Ph)]_2$ (**4**), Yb^{III} - $[\{^tBuC(NC_6H_3\text{-}2,6\text{-}^iPr_2)_2\}Yb(\mu\text{-}SCH_2Ph)_2]_2$ (**5**) and mixed-valence ion-pair Yb^{II}/Yb^{III} complex $[\{^tBuC(NC_6H_3\text{-}2,6\text{-}^iPr_2)_2\}Yb(DME_2)]^+[\{2,6\text{-}^iPr_2C_6H_3NC(H){=}C(H)NC_6H_3\text{-}2,6\text{-}^iPr_2\}_2Yb]^-$ (**6**). Complex **1** features a rather unusual κ-N,η^6-arene type of coordination of amidinate ligand with a surprisingly robust Yb^{II}..η^6-arene interaction. The X-ray study established that such coordination type is retained in **2**-**4** complexes. At the same time, one-electron oxidation of the ytterbium center to the trivalent state in **5** and **6** leads to switching of the coordination mode of amidinate ligand from κ-amido,η^6-arene to "classical" κ-N,κ-N-chelating.

*Table 1. G and amidinate ligand $G(L)_{2.28}$ values in complexes **3**-**6**.*

	3	**4**	**5**	**6**
Amidinate ligand coordination type	*κ-N,η^6-Ar*		*κ-N,κ-N*	
G, %	90.0(2)	91.7(2)	91.9(2)	86.9(2)
$G(L)_{2.28}$, %	48.5(2)	49.4(2)	40.0(2)	37.6(2)

G – percentage of the Yb coordination sphere shielded by all ligands, $G(L)_{2.28}$ – solid angle of amidinate ligand "normalized" to the M-L distance of 2.28 Å.

On purpose to analyze relationship between coordination type of amidinate ligand and radii values[1] of Yb$^{II/III}$ cations (R(Yb^{II}) = 1.02 Å, R(Yb^{III}) = 0.868 Å) we have carried out calculation of percentage of the shielded metal coordination sphere in **3-6** complexes by using the method of ligand's solid angles[2]. *G* values in **3-6** complexes lies in the rather wide range 86.9(2)-91.9(2)%. The solid angle $G(L)_{2.28}$ of the amidinate ligand in **3**, **4** is equal to 49% and significantly exceeds of similar characteristic in **5**, **6** (39%). Realization of κ-N,κ-N-coordination mode of amidinate ligand in **3**, **4** will lead to unsaturated Yb coordination sphere (G ~ 80%) and kinetic instabillity of complexes. On the contrary, G ~ 100% in **5**, **6** will be the result of amidinate ligand coordination by κ-N,η^6-arene mode. Such value of G-parameter is too high that lead to instability of these complexes as in **3** and **4**. κ-N,κ-N-coordination type in **5**, **6** allows to decrease amidinate ligand steric volume and to minimize non-bonded interactions in Yb^{III} coordination sphere. Thus, changing of Yb radii and therefore decreasing of the Yb coordination sphere dimension may be the cause of the amidinate ligand coordination type modification. Results of this study were published[3] in "Organometallics".

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THE SYNTHESIS AND THE MEMBRANE-TRANSPORT PROPERTIES OF CHIRAL AMINOPHOSPHONATES AND AMINOPHOSPHINE OXIDES DERIVED FROM NATURAL AMINO ACIDS

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The development of new methods and reagents for the synthesis of organophosphorus analogues of natural compounds represents an important task for synthetic organoelement chemistry. These compounds are interesting as biologically active compounds, as well as lipophilic phosphorylated amines and azopodands that can be used as an effective carriers of the rare metals ions We have synthesized a series of lipophilic α-aminophosphine oxides from the (*S*)-enantiomers of amino acids using the Kabachnik-Fields reaction in a ternary system: the dioctylphosphineoxide, paraform and the aminoacid hydrochloride. By this procedure we have obtained the enantiomerically pure bis- and monomethylphosphinylated derivatives of alanine, valine, leucine, serine, threonine, glutamic and aspartic acids respectively in good yield (above 87%). Also, we have synthesized (S_P,*R*)-diastereomers of phosphinylated amino acids by introducing to the reaction system of the (R_P)-phenyldecylphosphine oxide. The reaction leads to the inversion of configuration at the phosphorus atom and to the formation of (S_P,R)-diastereomers of phosphorylated amino acids.

For the obtained compounds membrane transport properties in relation to glycine, alanine, valine, leucine, serine and aspartic acids were studied. The rate of transfer is strongly influenced by the steric volume of the substituent on the α-carbon atom of the substrate as well as the carrier. The steric hindrance reduces the stability of the membrane-transport complex, therefore valine worse transferred through the membrane by all the studied compounds than glycine, alanine and leucine.

We have developed the method for the preparation of phospha-β-homoproline and phosphonic analog of glutamic acid. The synthesis of phospha–β–homoproline was developed staring from natural L-proline, which was converted to the N-Boc-prolinal, then to the hydroxyphosphonate as a (*S,S*)+(*S,R*) diastereomeric mixture of 2:1 ratio. Deoxygenation of hydroxyphosphonate by means of Barton-McCombie method leads to the formation of the protected phospha–β–homoproline. The depropection and acid hydrolysis of the latter provide the phospha–β–homoproline, which was isolated as an optically pure solid.

The synthesis of phosphonic analog of glutamic acid was developed starting from the t-butyl N-t-butoxycarbonylaspartate. The carboxy-group of this compound was reduced with sodium borohydride in methanol giving the t-butyl-(*S*)-N-(t-butoxycarbonyl)homoserine. The latter was converted into the bromide by the Appel reaction Then the bromide was introduced into the Arbuzov reaction with $(EtO)_2POSiMe_3$ to yield phosphonate, deprotection of which with diluted hydrochloric acid resulted in the phosphorus analog of glutamic acid.

This work was supported by RFBR (13-0390448-a) and SFBR of Ukraine (Ф53.3/016) grant programs.

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NEW POLYNUCLEAR Cu(I) CHELATES OF THE THIOUREA-BASED LIGANDS

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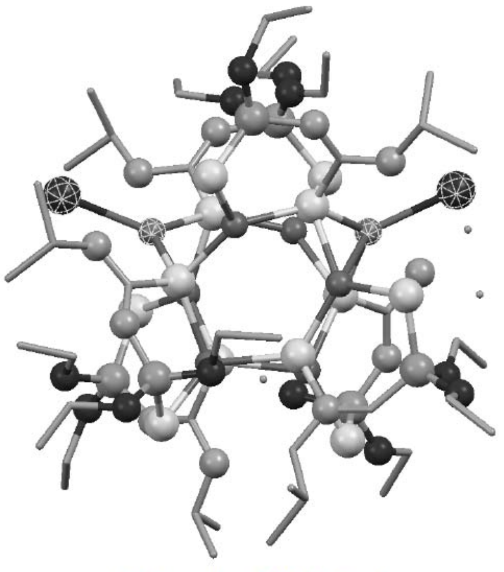
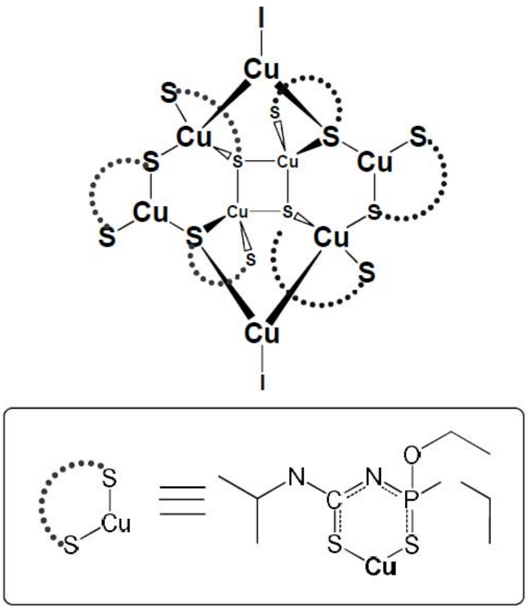
Polynuclear complexes of d^{10}-metal cations are of interest due to their photophysical behavior and catalytic properties. They were successfully used as precursors to the nanolayers and nanoparticles of the metals and metal chalcogenides. We synthesized and studied the new family of Cu(I) complexes based on the ligands of general formula RC(S)NHP(S)(R`)$_2$ (HL), were R = PhNH, morpholyn-N-yl, i-PrNH, t-BuNH; R` = OBu-i, OEt. New polynuclear Cu(I) chelates of formulas $[Cu_nL_n]$ and $[Cu_6(L)_6{\cdot}2CuI)]$ were obtained. Their structure were characterized by ESI mass-spectrometry and IR, NMR ^{1}H and ^{31}P spectroscopy. A new polynuclear Cu^I mixed-ligand complex $[Cu_6(L)_6{\cdot}2CuI)]$ (L = [^{i}PrNHC(S)NP(S)(OEt)$_2$-*S,S`*]$^-$) has been structurally and spectroscopically characterized. It has a cage-like structure formed by two $[Cu_3L_3]$ cycles interconnected by four S-Cu-S bridges.



$[Cu_6L_6]$*2CuI



Comparison of the obtained and literature data gave the new information about influence of the structures of R and R` (substituents in HL) on the structure of the obtained polynuclear chelates. We suggest that relatively small steric volume of the PhNH and i-PrNH substituents and their ability to H-bonding can promote formation of the large polycyclic $[Cu_nL_n]$ aggregates with $n > 4$. On the contrary, steric hindrance caused by the bulky substituents, e.g. morpholyn-N-yl, makes the further association impossible. Thus, the aggregation process stops at the simple trimetric ($n = 3$) or tetrameric ($n = 4$) molecules formation.

This work was supported by RFBR (12-03-00474-a) grant program.

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OPTICALLY CONTROLLED SYNTHESIS OF THE METAL-CONTAINING POLYMERS BASED ON O-QUINONEMETHACRYLATES

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An optically controlled synthesis of the metal-containing polymers based on *o*-quinonemethacrylates was elaborated. For this purpose, studies on the synthesis of monomeric quinonemethacrylates, their polymerization and copolymerization with mono- and dimethacrylic monomers, photochemical transformation of o-quinones fragments in monomers and polymers, revelation of optimal condition for photo-formation of metal-containing polymers with a specified distribution of metal concentrations were performed. *o*-Quinonemethacrylates were synthesized in two ways: methacrylation of 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone by methacryloyl chloride with alkali and alkoxylation of 3,6-di-*tert*-butyl-*o*-benzoquinone by monomethacrylic glycol ethers. New monomers polymerization allowed synthesis of polymers with *o*-quinone group in each link of polymer chain. It was found that the most active monomer in the bulk polymerization is *o*-quinone based on ethylene glycol monomethacrylate (QMEG). Polymers containing potassium, copper, thallium, manganese and antimony complexes were synthesized from poly-*o*-quinonemethacrylate by reaction with metal (K, Cu, Tl), photolysis ($Mn_2(CO)_{10}$), metathesis with Cu(I) complex and oxidative addition ($SbPh_3$). Addition of metal-framefork to *o*-quinone-containing polymers allows synthesis of metal-containing polymers with specified molecular weight characteristics of quinone-containing polymers. Also synthesis of antimony-containing polymer was realized *in-situ* by polymerization of *o*-quinonemethacrylate solution in the presence of $SbPh_3$ (oligomeric products, ~10 link). Investigation of kinetics of buthylacrylates (BA) and buthylmethacrylates (BMA) polymerization in the presence of QMEG (initiator was AIBN, 70°C) demonstrated, that QMEG forms copolymers with BA and BMA and shows properties of weak inhibitor and chain transmitter. Performed spectrophotometric studies showed *o*-quinone fragment of QMEG and poly-QMEG to be reduced efficiently to catechol by visible light in both solution and polymeric film. Either QMEG or amines (N,N-dimethylaniline, N,N-dimethylcyclohexylamine) can serve as a donor of hydrogen. Two methods of selective metal addition to quinone-polymeric layers were studied. The first way was creating of complexes on exposed surfaces of polymer. In this area quinone was reduced to catechols adsorbing the metal ions from water solution accompanied with the metal complexes formation in the films. The dependence of the metal complexes concentration in the layer on exposure is S-shaped. This way was released using Mo, V and Fe salts. The second way was creating of complexes at non-exposed area by the reaction of oxidative addition of metal-fragments and *o*-quinone. This method was demonstrated using $SbPh_3$. Treatment of polymer films in THF solution with $SbPh_3$ leads to oxidative addition of $SbPh_3$ to polymer at non-exposed area. These antimony containing polymers are capable to reversibly join molecular oxygen many times.

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PROBLEMS OF C–H BONDS ACTIVATION IN 1,10-PHENANTHROLINES IN *NON-DEHYDROGENATIVE* C*H*–C*H* COUPLING BY IONS OF d-ELEMENTS IN THE SYNTHESIS OF BIOACTIVE σ^H-1,10-PHENANTHROCYANINE COMPLEXES

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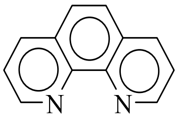
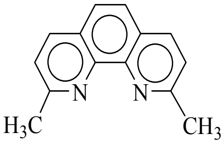
Species of **C–H bonds activation** in *electron-deficient* 1,10-phenanthrolines in direct non-dehydrogenative isohypse **C*H*–C*H* coupling** (S_N^H or ***SET***) by ions of d-elements in the synthesis of the **new class *apocyanine* chromophores-fluorophores** – ***electron-rich* σ^H-1,10-phenanthrocyanines** of d-elements as *novel anion receptors*, DNA *complexones*, potential *photosensitizers* or *photocatalysts* of **singlet oxygen O_2 (S_1)** or **superoxide-anions $O_2^{-\bullet}$** and **hydroxide-radicals $^\bullet$OH** generation in DNA visible light photodamage, ***potent biocides*** (potential inductors of oxidative stress), *potential antitumor agents* and inductors of apoptosis have been considered.

Results of the investigation of **C–H bonds activation** in 1,10-phenanthrolines:





in direct non-dehydrogenative isohypse ***metal-assisted*** (**d**^{3} –Cr(III), **d**^{5} –Mn(II), **d**^{6} –Rh(III), **d**^{7} –Co(II), **d**^{8} –Ni(II), Pd(II), Pt(II), **d**^{10} –Zn(II), Cd(II)) C*H*–C*H* coupling reactions inclusive of ***nucleophilic substitution of hydrogen*** S_N^H (addition (Add), anion control) or ***single electron transfer*** (***SET,*** from a reducing agent to a 1,10-phenanthroline complex) stages in the synthesis of the **new class chromophores-fluorophores** – glassy (solid phase) or hemi-colloidal (in solutions) bioactive ***electron-rich*** **homobinuclear bridget σ^H-1,10-phenanthrocyanines:**

$$[L_mM^{n+}(\mu\text{-N,N–N',N'-}\textit{phencyanines})M^{n+}L_m]^{z+}$$

(**μ-N,N–N’,N’-*phencyanines*** = **μ-*phencyanine*, z+ = 2n+ or (μ-*phencyanine*)$^-$, z+ = (2n-1)+**) containing ***π****-conjugated (quasiheteroaromatic) tautomeric* ***dihydro-bi-***1,10-phenanthroline ligand systems (**μ-N,N–N’,N’-*phencyanines***) [1, 2] are presented. Intensive optical excitation of 1,10-phenanthrocyanine complexes in visible region (450 – 580 nm) relates with *μ-1,10-phenanthrocyanine ligand-centered* π→π*-electron transitions:

$$[L_mM^{n+}(\mu\text{-}\textit{phencyanines})M^{n+}L_m]^{2n+} + h\nu \rightarrow [L_mM^{n+}(\mu\text{-}\textit{phencyanines})^*M^{n+}L_m]^{2n+}.$$

Electron-rich complexes in solutions to associative binding with anions, including DNA are inclined. New compounds have antibacterial, antiviral and antitumor properties stronger (on order and more) than their 1,10-phenanthroline complex precursors.

[1] V. Demidov, S. Simanova, A. Savinova et al., *Ross. Khim. Zhurn.* (*Russian J. Chem.)*, **2009**, *53*, 128-134.
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POLYMERIZATION OF STYRENE AND METHYL METHACRYLATE IN THE PRESENCE OF MONOCATHECHOLATE COMPLEXES OF TIN(IV)

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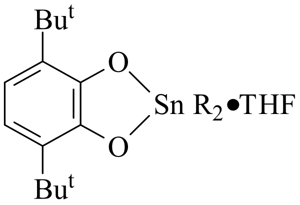
Bis-catecholate complexes of germanium(IV) and tin(IV) reversibly reacts with macroradicals and therefore can be used as a chain growth regulator in polymerization of different vinyl monomers [1].

The aim of our work was to investigate the influence of mono-catecholate complexes of tin(IV) on polymerization of styrene (**St**) and methyl methacrylate (**MMA**) initiated by azobis(isobutyronitrile) (**AIBN**) at 70°C. Complexes ***1-3*** were studied in this processes.



*there R = Me (**1**), Et (**2**) or Ph (**3**)*

It was shown that introduction of each of the complexes ***1-3*** leads to a decrease of the St polymerization rate. The maximum yield of polySt at a ratio of complex / AIBN = 1 / 1 is ~ 50-60%. The presence of these metallocomplexes providing a linear growth of MW polySt with conversion.

In case of MMA the role of these catecholates of tin(IV) depends on their composition. Complex ***1*** has no effect on either rate of MMA polymerization or molecular weight characteristics polyMMA at 70°C regardless of the concentration. The presence of ***3*** at a ratio of ***3*** / AIBN = 2 / 1 reduces the rate of polymerization of MMA and providing a proportional growth of MW polyMMA.

The MMA polymerization rate with **2** extremely dependent on its concentration. Increasing the ***2*** / AIBN ratio leads to a change in the form of curves of molecular weight distribution (**MWD**). In case of ***2*** / AIBN = 2 there is a bimodal MWD and the share of high-molecular modes increases with conversion.

Formation of the *o*-semiquinone complexes of tin(IV) in monomers for each of ***1-3*** was proved by the ESR method. At the initial stage of St polymerization with ***1-3*** and synthesis of polyMMA in the presence of ***3*** fixed five-coordinate *o*-semiquinones. The paramagnetic derivatives of ***1-2*** in MMA is six-coordinate and containing in its structure the molecule of monomer.

Thus, the ability of complexes tin(IV) to act as a chain growth regulator defined of its composition and structure of the respective paramagnetic derivatives.

[1]. Vaganova, L.B., Maleeva, A.V., Piskunov, A.V., and Grishin, D.F., *Izv. Akad. Nauk, Ser. Khim.*, 2011, №8, P.1594–1601.

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POLYNUCLEAR CYMANTRENECARBOXYLATES CONTAINING Ln^{III} AND Mn^{II}

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Carboxylate derivatives of stable organometallic molecules are perspective building blocks for construction of polynuclear *3d-4f*-heterometallic complexes which are able to combine specific properties of an organometallic moiety and a rare earth ion. Until recently mostly the derivatives of ferrocene (see references in [1-3]) were known. Lately we have obtained and studied *3d-4f*-carboxylates containing the cyclopentadienyltricarbonylmanganese (cymantrene) moiety, the ions of cerium group lanthanides and THF [1], pyridine [2] or DMSO [3] as neutral ligands.

On a basis of yttrium group Ln^{3+} ions and cymantrenecarboxylic acid $CymCO_2H$ (Cym = $(\eta^5\text{-}C_5H_4)Mn(CO)_3)$) new *3d-4f*-heterometallic clusters $[Ln^{III}{}_2Mn^{II}{}_2(\mu_3\text{-}OH)_2(\mu_2\text{-}O_2CCym)_8(THF)_2]$ (Ln = Dy (**1**), Ho (**2**), Er (**3**), Yb (**4**)), having analogous «defect dicubane» structure of the metal core (Fig. 1), trinuclear centrosymmetric $[Er^{III}{}_2Mn^{II}(\mu_2\text{-}O_2CCym)_6(\eta^2\text{-}O_2CCym)_2((MeO)_3PO)_4]\cdot 2MePh$ (**5**) and cationic tetranuclear $[Tb^{III}{}_4(\mu_3\text{-}OH)_4(O_2CCym)_6(H_2O)_3(THF)_4][Mn^{II}Cl_4]\cdot 4CH_2Cl_2\cdot 6THF$ (**6**) were obtained and characterized by X-ray analysis. Mn^{2+} ions appear in the structures due to photolytic destruction of the cymantrenecarboxylate moiety in the solution. Magnetic properties of the complexes are indicative of ferromagnetic exchange interactions between the paramagnetic ions in cases of **1** and **5** (Fig. 2); in case of **6** antiferromagnetic interactions prevail. Thermal decay of **1** - **4** was studied by means of DSC and TGA techniques, the products of thermolysis in air according to X-ray powder diffraction data contain $LnMn_2O_5$ phases, some of which exhibit the properties of multiferroics.

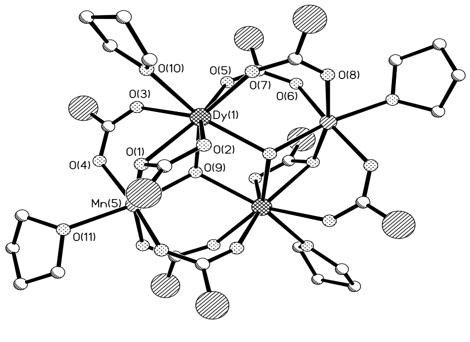

Fig. 1. Molecular structure of **1** - **4**.

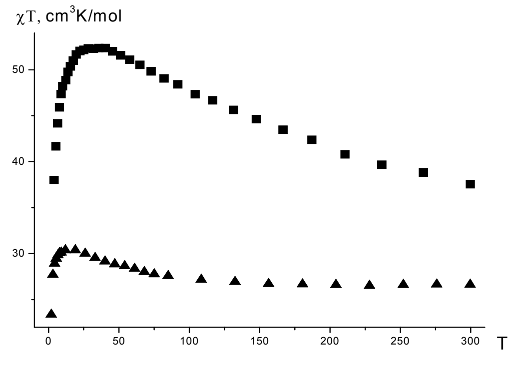

Fig. 2. Magnetism of **1** (■) and **5** (▲).

[1] P.S. Koroteev, M.A. Kiskin, Zh.V. Dobrokhotova *et al*, *Polyhedron,* **2011**, 30, 2523–2529.
[2] P.S. Koroteev, Zh.V. Dobrokhotova, M.A. Kiskin, A.S.Lermontov *et al*, *Polyhedron*, **2012**, 43, 36–46.
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STRUCTURE, MAGNETIC BEHAVIOR AND THERMOLYSIS OF NEW RARE EARTH FERROCENECARBOXYLATES

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Discovered in the middle of the last century, ferrocene, in addition to many other interesting properties, is a potential building block for construction of heterometallic complexes. Organometallic compounds containing Fe as a part of the ferrocene fragment and another metal in the ionic form, represent a peculiar type of heterometallic complexes as they are able to combine the specific properties of ferrocene and the properties of the second metal [1,2].

New rare earth ferrocenecarboxylate complexes, $[Ln_2(\mu\text{-}O,\eta^2\text{-}O_2CFc)_2(\mu_2\text{-}O,O'\text{-}O_2CFc)_2(\eta^2\text{-}NO_3)_2(DMSO)_4]$ (Ln = Gd (**1**), Tb (**2**), Y (**3**)) and $[Gd_2(\mu\text{-}O,\eta^2\text{-}O_2CFc)_2(\eta^2\text{-}O_2CFc)_4(DMSO)_2(H_2O)_2]\cdot 2DMSO\cdot 2CH_2Cl_2$ (**4**), were prepared and characterized by X-ray analysis. In contrast to all the previously known rare earth ferrocenecarboxylates (e.g., [3]), in structures of **1**-**3** the Ln^{3+} ions are connected by four bridging carboxylates (two of them are chelate-bridging; Fig. 1), but complex **4** has "traditional" structure with two chelate-bridging carboxylates. Coordination number of Ln^{3+} in **1** - **4** is 9. Thermolysis of **1** – **3** was studied by means of DSC and TGA techniques. The final products of thermolysis both under air and in inert atmosphere contain the garnets $Ln_3Fe_5O_{12}$ which are valuable magnetic materials, the perovskites $LnFeO_3$, and Fe_2O_3 in different ratios. Magnetic properties of **2** are indicative of distinct ferromagnetic interactions between the Tb^{3+} ions (Fig. 2). Weak aniferromagnetic ($J_{Gd\text{-}Gd'}$ = -0.03979±0.00253 cm^{-1}) and ferromagnetic ($J_{Gd\text{-}Gd'}$ = 0.02179±0.00285 cm^{-1}) interactions were found in complexes **1** and **4** respectively.

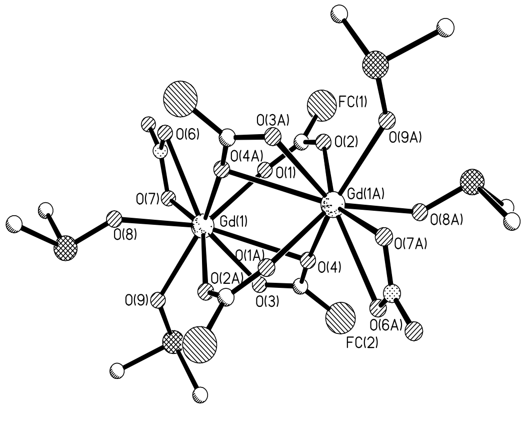

Fig. 1. The molecular structure of **1** - **3**.

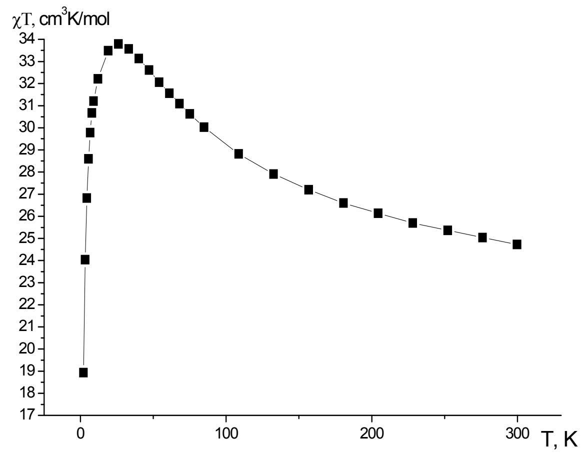

Fig. 2. Magnetism of **2**.

[1] W.R. Cullen, J.D. Woollins, *Coord. Chem. Rev.*, **1981**, *39*, 1-30.
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This study was financially supported by the RFBR (project nos. 11-03-00644, 11-03-00556, 12-03-31395), the Council on Grants of the President of the Russian Federation (grants, NSh-1670.2012.3, SP-6585.2013.5), the Ministry for Education and Science of the Russian Federation (SC-8437)

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BOND LENGTHS IN ORGANOMETALLIC COMPLEXES AND POLARIZABILITY EFFECT

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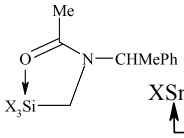
The literature data on X substituents influence on the bond lengths d have been analyzed for 11 narrow series of complexes $XCNAg^+$ (Ag–N, DFT [1]), $X_2Ge{\cdot}CH_4$ (Ge–C, DFT [2]), $X_2Ge{\cdot}H_2C{=}CH_2$ (Ge–C, DFT [3]), $X_2Cl_2Sn{\cdot}phen$ (phen=1,10-phenanthroline, Sn–N, X-ray [4]), (Si←O, X-ray [5]), (Ge←N, DFT [6]),

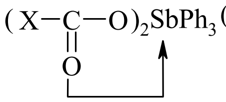


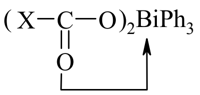

$XSn(OCH_2CH_2)_3N$ (Sn←N, DFT [6]),


$XGe(OCH_2CH_2)_3N$


$X_2Sn(SCH_2CH_2)_2O$ (Sn←O, X-ray [7]),


$XPb(OCH_2CH_2)_3N$ (Pb←N, DFT [6]),


$(X{-}C(=O){-}O)_2SbPh_3$ (Sb←O, X-ray [8]), and


$(X{-}C(=O){-}O)_2BiPh_3$ (Bi←O, X-ray [9]).

The distinctive feature of these narrow series is such that for each of them the indicator centre (bond Ag–N, Ge–C, Sn–N, etc.) remains fixed whereas the substituents X vary. Therefore these series are well suited for the study of substituents effects on d, using the correlation analysis. With this method, we have obtained a number of equations which relate the d values with the inductive σ_I, resonance σ_R (σ_R^+, σ_R^-), polarizability σ_α, and steric E_s' parameters of X substituents. For all narrow series the best fitting correlation equations are of the form

$$d = d_0 + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-) + c\sigma_\alpha + kE_s'$$

These equations are distinguished from the other possible ones by their highest adjusted correlation coefficients and the smallest standard errors of approximation. Besides, all coefficients (a, b, c, k) of these equations are statistically significant. This is strong proof that the bond lengths d depend on the joint influence of the inductive, resonance, polarizability, and steric effects of substituents. The reason for the occurrence of the polarizability effect (an ion-dipole interaction between the charge q and the dipole moment induced by q in the substituent X) is the appearance of an excess charge q on the atoms of the test bond as a result of the charge transfer from the donor centre of the complex to the acceptor one.

Thus it is impossible to obtain a clear knowledge of substituent influence on the bond lengths in organometallic complexes without considering the polarizability effect.

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SYNTHESIS AND COORDINATION PROPERTIES OF NOVEL LIGAND CONTAINING PHENOL AND DIAZABUTADIEN FRAGMENTS

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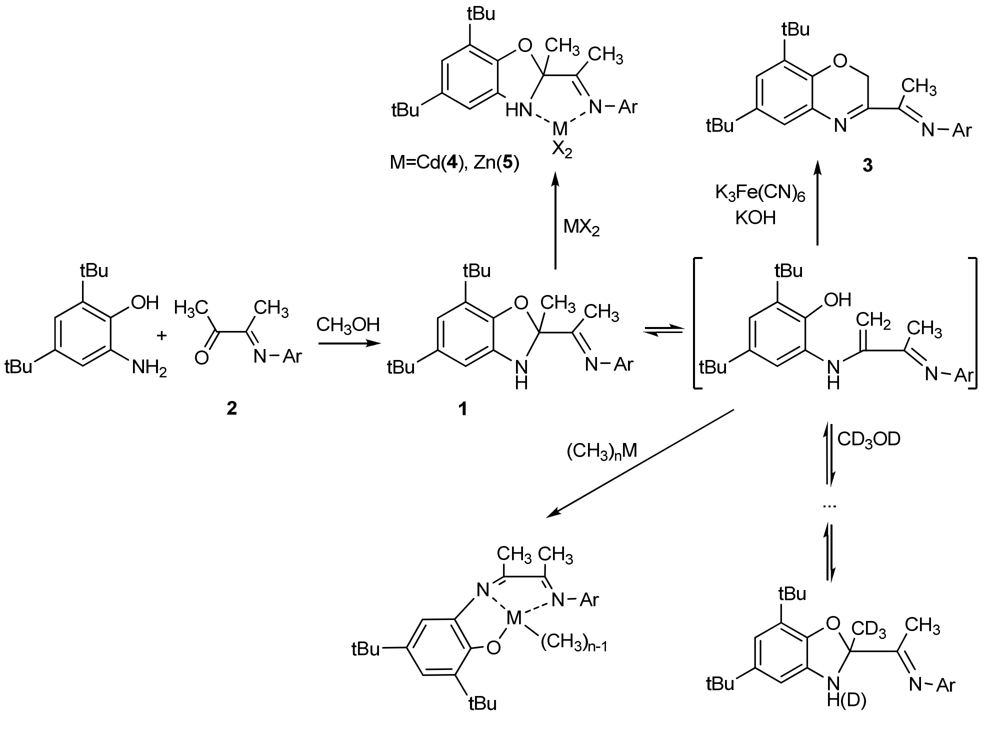
N-(1-(5,7-di-tert-butyl-2-methyl-2,3-dihydrobenzo[d]oxazol-2-yl)ethylidene)-2,6-diisopropylaniline **1** was obtained by condensation of 2-amino-4,6-di-tert-butylphenol with α-iminoketone **2**. It has been found that compound **1** undergoes ring open process to form enamine species of ligand. It has been shown that the selective deuteration of methyl group at the imine carbon atom takes place in methanol solution. The oxidation of compound **1** with alkaline solution of potassium ferricyanide leads to substituted benzoxazine **3**. Coordination properties of ligand **1** were investigated. The reaction of **1** and zinc or cadmium iodide results in neutral complexes (**4**, **5**). The addition of methyl derivatives of group 12 and 13 metals (Me_2Cd and Me_3M, M=Al, Ga, Tl respectively) in diethyl either solution to an equimolar solution of **1** results in formation of the crystalline thallium, aluminium, gallium and cadmium phenolate compounds **6**-**9**.



M=Cd(**6**), Al(**7**), Ga(**8**), Tl(**9**)
Ar = 2,6-di-iso-propylphenyl

Compound **1**, **3**-**9** were characterized by NMR spectroscopy. The structure of compound **1**, **4**, **6**, **8**, **9** were confirmed by the data of X-ray analysis.

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AMIDOPHENOLATE GALLIUM(III) COMPLEXES IN REDOX TRANSFORMATIONS

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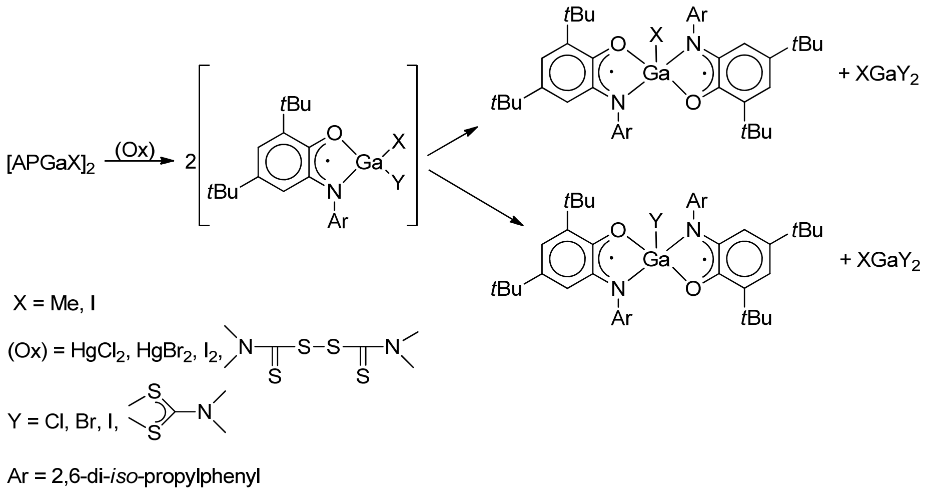
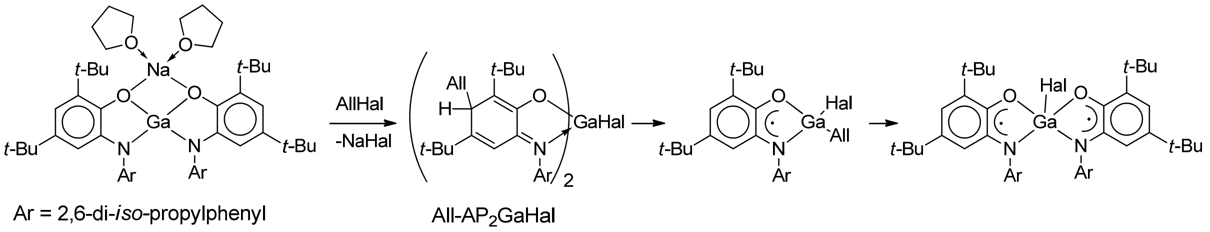
Amidophenolate gallium(III) complexes reactivity towards various oxidizers was investigated. It was observed that the main products of oxidation reactions of $[APGaX]_2$ are five-coordinated bis-iminobenzosemiquinolate gallium(III) complexes with the general formula $imSQ_2GaX$ (X = Me, Cl, Br, I). These compounds form as a result of disproportionation of intermediate monoradical four-coordinated complexes.



The interaction between $[AP_2Ga]Na{\cdot}2THF$ and allyl halides leads to the allyl fragment addition to the both of amidophenolate ligand rings. The migration of allyl substitute was found to proceed under heating conditions in the All-AP_2GaHal complexes. The EPR-spectra of these reaction mixtures belong to the monoradical gallium(III) complexes imSQGa(Hal)All. As mentioned above such type compounds appear to undergo symmetrization to produce biradical complexes $imSQ_2GaX$ (X = Cl, Br, I).



Acknowledgements - We are grateful to the FSP ''Scientific and Scientific-Pedagogical Cadres of Innovation Russia'' for 2009–2013 years (GK 8465), Russian Foundation for Basic Research (grant 13-03-97048-r_povolzh'e_a), Russian President Grants (NSh-1113.2012.3) for financial support of this work.

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CRYSTALS OF CU(II) COMPLEX WITH NITRONYL- AND IMINONITROXIDE EXHIBITING MECHANICAL ACTIVITY

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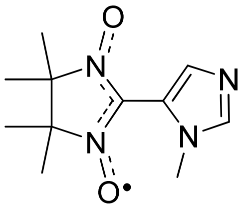
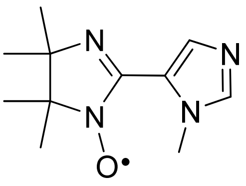
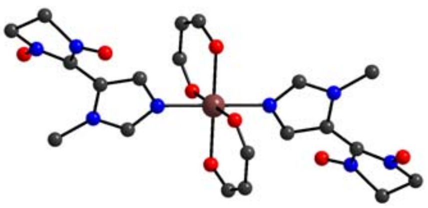
Previously, it was shown that deoxygenation of L in crystals of heterospin complexes [Cu(hfac)$_2$L$_2$], where hfac is hexafluoroacetylacetonate anion, L is 2-(*N*-methyl-1*H*-imidazol-5-yl)-4,4,5,5-tetramethyl-2-imidazoline-3-oxide-1-oxyle, accompanied by a specific mechanical behavior of crystals – jumps and various movements [1]. In course of our study of multispin compounds exhibiting a chemomechanical activity, we synthesized and investigated a series of new heterospin solids [Cu(hfac)$_2$L$_x$L$^1_{2-x}$], [Cu(hfac)$_2$L^1], [Cu$_2$(Piv)$_4$L$^1_2$]·0.5C$_6$H$_{14}$, [Cu$_2$(hfac)$_2$(Piv)$_2$L$^1_2$], where L^1 is 2-(*N*-methyl-1*H*-imidazol-5-yl)-4,4,5,5-tetramethyl-2-imidazoline-1-oxyle, Piv is 2,2-dimethylpropionate anion. It was shown that only solid solutions [Cu(hfac)$_2$L$_x$L$^1_{2-x}$] crystals (where L predominates, $1.728 \le x < 2$) had packing similar to [Cu(hfac)$_2$L$_2$] and able to chemomechanical activity. On the contrary, [Cu(hfac)$_2$L$_x$L$^1_{2-x}$] crystals (where L^1 predominates, $0 < x \le 0.708$) possessed structural characteristics similar to [Cu(hfac)$_2$L$^1_2$] and did not show any thermo- or photoactivated chemomechanical activity, because of [Cu(hfac)$_2$L$_2$] and [Cu(hfac)$_2$L$^1_2$] belong to different groups of symmetry, they could not form a continuous series of solid solutions and flowing solid phase process [Cu(hfac)$_2$L$_2$]$_{(s)}$ → [Cu(hfac)$_2$L$^1_2$]$_{(s)}$ + O$_{2(g)}$ should cause the tension in the "original" structure and its subsequent destruction.



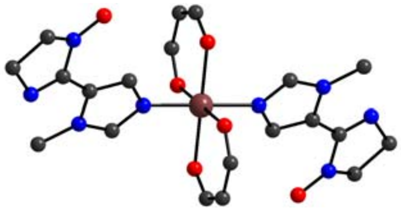
L



L^1



[Cu(hfac)$_2$L$_2$]



[Cu(hfac)$_2$L$^1_2$]

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SYNTHESIS AND CHARACTERIZATION OF NEW BINUCLEAR (Sm_2 AND Sm, Tb) LANTHANIDE PIVALATES

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The high-temperature solid-state desolvation under an inert atmosphere was studied for two new homobinuclear polymorphic complexes of the same composition $(bath)_2Sm_2(piv)_6\cdot 2EtOH$ (Piv = $(CH_3)_3CCO_2^-$, bath = 4,7-diphenyl-1,10-phenanthroline), which differ in the structural functions of the bridging carboxylate anions. This resulted in the synthesis of new non-solvated pivalate $(bath)_2Sm_2(piv)_6$. New heterobinuclear complexes $(bath)_2SmTb(piv)_6\cdot 2EtOH$ and $(phen)_2SmTb(piv)_6$ (phen = 1,10-phenanthroline) were synthesized by solution chemistry methods. The solid-state thermal decomposition of homobinuclear Sm pivalates with chelating N-donors, such as 2,2'-bipyridyl, phen [1], and bath, and heterobinuclear (Sm, Tb) pivalates with phen and bath ligands, was studied, the composition of the complexes in the gas phase was determined, and the magnetic and photoluminescent properties were analyzed. All complexes were characterized by X-ray diffraction.

Luminescent metal-organic lanthanide compounds have attracted considerable interest as highly promising substances in the preparation of hybrid functional materials such as «molecule in the polymer matrix», including the method of supercritical fluid (SCF) impregnation. The physicochemical properties of binuclear (Sm_2 and Sm, Tb) lanthanide pivalates obtained and known $(Hpiv)_6Tb_2(piv)_6$, $(bpy)_2Tb_2(piv)_6$, $(phen)_2Tb_2(piv)_6$, and $(bath)_2Tb_2(piv)_6\cdot 2EtOH$ [2], after treatment in conditions SCF technology were studied. The experiments were carried out with the use of a $SC-CO_2$ (SC-carbon dioxide) as the SCF.

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CIS-CONFIGURED MONONUCLEAR PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF CHALCOGENO *O*-CARBORANES

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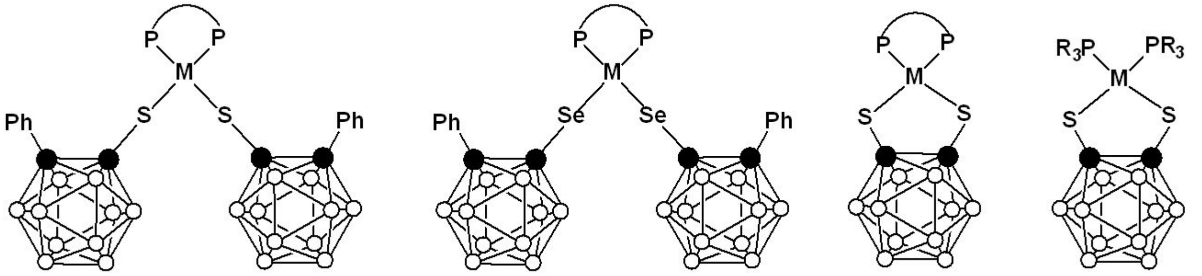
The reactions of $[MCl_2(P^\frown P)]$ and $[MCl_2(PR_3)_2)]$ with 1-mercapto-2-phenyl-*o*-carborane, NaSeCarbPh and 1,2-dimercapto-*o*-carborane yield mononuclear complexes of composition, $[M(SCarbPh)_2(P^\frown P)]$, $[M(SeCarbPh)_2(P^\frown P)]$ (M = Pd or Pt; $P^\frown P$ = dppm (bis-(diphenylphosphino)methane), dppe (1,2-bis(diphenylphosphino)ethane) or dppp (1,3-bis(diphenylphosphino)propane)) and $[M(SCarbS)(PR_3)_2]$ (Carb = $C_2B_{10}H_{10}$, $2PR_3$ = dppm, dppe, $2PEt_3$, $2PMe_2Ph$, $2PMePh_2$ or $2PPh_3$) [1].



M	$P^\frown P$
Pd	dppm
Pd	dppe
Pt	dppm

M	$P^\frown P$
Pd	dppe
Pt	dppm
Pt	dppe
Pt	dppp

M	$P^\frown P$
Pd	dppm
Pd	dppe
Pt	dppm
Pt	dppe

M	PR_3
Pd	PEt_3
Pd	$PMePh_2$
Pd	PPh_3
Pt	PEt_3
Pt	PMe_2Ph
Pt	$PMePh_2$

● = C ○ = BH

These complexes have been characterized by elemental analysis and NMR (^1H, ^{31}P, ^{77}Se and ^{195}Pt) spectroscopy. The $^1J_{(Pt-P)}$ values and ^{195}Pt NMR chemical shifts are influenced by the nature of phosphine as well as thiolate ligand.

Molecular structures of $[Pt(SCarbPh)_2(dppm)]$, $[Pt(SeCarbPh)_2(dppm)]$, $[Pt(SCarbS)(PMe_2Ph)_2]$ and $[Pt(SCarbS)(PMePh_2)_2]$ have been established by single crystal X-ray structural analyses. The platinum atom in all these complexes acquire a distorted square planar configuration defined by two *cis* bound phosphine ligands and two chalogenolates donor atoms. The carborane rings are mutually *anti* in $[Pt(SCarbPh)_2(dppm)]$ and $[Pt(SeCarbPh)_2(dppm)]$.

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HEMIN PEROXIDASE ACTIVITY IN MICROHETEROGENEOUS MEDIA

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Hemin (Fe(III) protoporphyrin IX chloride) is often used in biomimetic catalysis as a model of some oxidoreductases and oxygen transport proteins containing heme as a prosthetic group. Catalytic activity of such model compounds is known to be influenced by the aggregation state of the porphyrin macrocycle, which strongly depends on the solvent nature, medium acidity and the presence of potential extraligands (especially π-donors) in the reaction system.

In this paper we report on hemin peroxidase activity in o-phenylenediamine (o-PDA) oxidation using hydrogen peroxide as an oxidant in surfactant and polyelectrolyte media. Peroxidase activity was determined by monitoring the increasing absorbance at 430 nm characteristic of the o-PDA oxidation product (2,3-diaminophenazine) in the course of the reaction.

Hemin monomeric species predominant in anionic (sodium dodecyl sulfate, SDS) or neutral (Triton X-100) surfactants were found to possess a significant peroxidase activity due to both steric and electrostatic factors favouring the H_2O_2 molecule binding to the ferric central atom, leading to the formation of ferryl-type intermediates (Fe^{4+}=O) - major oxidising agents. In alkaline medium with the predominant dimeric form of the catalyst such high-valence particles are responsible for rapid hemin oxidative destruction, and hence, the absence of peroxidase activity.

In contrast, aggregated hemin species in acidic medium and hemin-surfactant or hemin-polyelectrolyte ionic associates in cationic surfactant (CTAB, hexadecyltrimethylammonium bromide) micellar solutions or cationic polyelectrolytes (polydiallyldimethylammonium chloride, PDDA) exhibited extremely low peroxidase activity and oxidation rate, indicating the importance of extracoordination in the catalytic mechanism. Inorganic polyanions (SHMP sodium hexametaphosphate) were shown to significantly increase hemin peroxidase activity.

The above findings correlate with the earlier obtained data on the rate of hemin oxidative destruction by hydrogen peroxide in various media, suggesting the novel mechanisms of catalytic activity regulation and switching between peroxidase and catalase activity for hemin-based enzyme models.

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INVESTIGATION OF ORGANOMETALLIC COMPOUNDS BY JOINT USE OF MALDI-TOF MS AND CYCLIC VOLTAMMETRY

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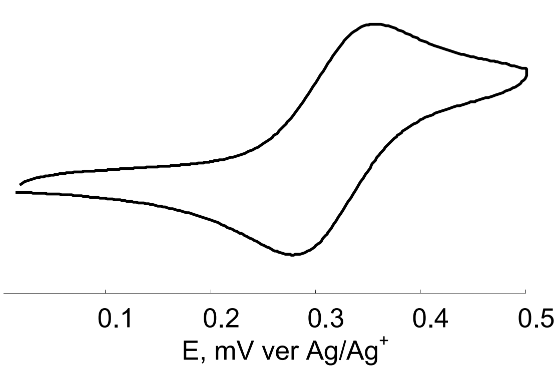
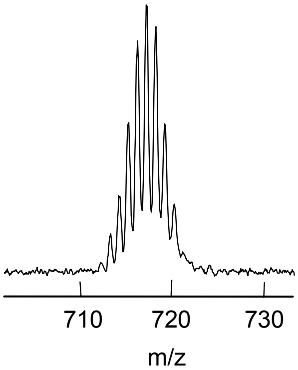
MALDI TOF MS is a powerful tool for analysis of labile and volatile compounds, such as organometallic species. A mechanism of molecular ion formation may be represented by a loss of an electron from HOMO orbital or transfer of electron from laser generated plum to LUMO. The molecular ions formed are either detected by mass analyser of undergo decomposition in case of their low stability. Their fragments are detected in the latter case. Cyclic voltammetry (CV) is a useful tool for exploration of electron transfer processes proceeding in liquid media. The stability of ions formed from organometallic compounds via oxidation or reduction is reflected in the reversibility of electrochemical processes. In this work the correlations between redox properties of organometallic compounds in CV studies and their MALDI MS spectra are done.

Ferrocene and its derivatives such as (di)bromoferrocene and different mono- and bis(phosphino)ferrocenes undergo reversible one-electron oxidation in electrochemical cell in 1.2-dichloroethane. Such complexes give strong cation signal in positive mode mass-spectra.

Paramagnetic ferracarboranes with diphosphine ligands undergo irreversible oxidation and irreversible reduction. No molecular ion is observed in their mass spectra. Fragmentation products are clearly seen indicating possible mechanism of decomposition.

17-electron ruthenium carborane complexes easily accept electron giving stable 18-electron species. It is reflected in reversible reduction to Ru(II) species in electrochemical cell and strong signals from molecular anions in mass spectra.





So, it was found that compounds disposed to reversible oxidation give strong spectra in positive mode, while reversibly reducing compounds give spectra in negative mode.

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HIDROGEN BONDING AND OTHER SECONDARY INTERACTIONS IN IONIC LIQUIDS

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Hydrogen bonds (H-bonds) have been suggested to be one of the molecular features which determine the properties of ionic liquids (ILs). Present study of the main features of H-bonds and other secondary interactions functioning in ILs is based on joint analysis of single-crystal X-ray data, quantum-chemical computations of isolated ion pairs and clusters of the ion pairs, and infrared spectra of several imidazolium- and phosphonium-based Ls.

The general conclusion from this study and literature data is that H-bonds in isolated ion pairs are stronger than in the clusters and in bulk IL. In other words, H-bonding between counterions in IL is anticooperative. At the same time, cooperative strengthening of H-bonds formed between some self-associated cations is possible in bulk IL. These cooperativity/anticooperativity effects are especially pronounced in case of H-bonds formed with participation of strongly coordinating halide anions. The effects are not so dramatic for H-bonds formed by weakly coordinating perfluoroanions. In particular, OH...F bonds in IL are of approximately equal strength to analogous bonds formed in solutions of the same perfluoroanions in neutral molecular solvents of low polarity.

Nevertheless, multiple secondary interactions functioning in bulk ILs, even being much weaker than interionic interactions within isolated ion pair, essentially influence the structure and vibrational spectra of ILs. Thus, such models as the isolated ion pairs or clusters of ion pairs cannot reproduce/predict the abovementioned characteristics of bulk ILs in detail.

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DENDRITIC IRON(III) COMPLEXES: SYNTHESIS AND PHASE BEHAVIOR

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One of the most important problem of modern chemistry is a creation of materials with controlled structure and target properties. Thereby coordination compounds containing Fe ions with azomethine ligands are of particular interest. One of their most important features is the ability of small modifications in the structure to significantly alter the key properties of the corresponding complexes.

In this work a 29 iron(III)-containing mono- and biligand complexes based on azomethine were synthesized and characterized, which differ in structure of ligand and kind of counter-ion. A number of physicochemical methods were used to determine of the spatial environment of iron. Thus the formation of Schiff base (a strong absorption band at 1639 cm^{-1}, which is characteristic of the (HC=N) bond) and the presence of the coordinated Fe^{3+} in the structure of the complexes (characteristic bands of the Fe(III) ion: Fe-N bond stretching vibrations, Fe-O bond stretching vibrations, M-anion bond vibrations in the far-infrared spectrum [1]) were established by FT-IR spectroscopy. The matrix assisted laser desorption/ionization (MALDI-ToF-MS) data indicate the existence of a series of stable ions characterizing the azomethine and iron(III) ions in its immediate environment. In addition IR spectra combined with data of mass-spectrometry and elemental analysis allow us judge about the symmetry of coordination of iron(III) ion with ligand and presence of one or another counter-ion and water molecules in complexes [2].

It was found that the structure of ligand effects on parameter of phase transition. Compounds based on azomethine formed by 2-aminopyridine exhibit mesomorphic properties in the absence of spin-crossover. Linear alkyl (dodecyl) on a periphery of ligand promotes ordering of complex structure. It is confirmed by reversible «crystal-crystal» phase transition in the cycle of heating and cooling and by high temperature of decomposition. In addition nature of counter-ion determines presence and behavior of phase transitions of branched chelate complexes of iron(III). Mesomorphic properties are characteristic for complexes with counter-ions, which can form associate by hydrogen bond: PF_6^-, BF_4^-, ClO_4^-.

Spin state of iron ion was investigated to a number of complexes. For the first time branched biligand iron(III) complex based on azomethine 3,5-di(4-cyclohexanebenzoyloxi)benzoyl-4-salicyliden-N'-ethyl-N-ethylenediamine with counter-ion Cl- was synthesized. This complex demonstrates spin transition (S=1/2 ↔ S=5/2) which induced and controlled by temperature [3].

[1] I.M. Cheremisina, *Russ. J. Str. Chem.*, **1978**, *19*, 336.
[2] M.S. Gruzdev, U.V. Chervonova, A.M. Kolker and N.E. Domracheva, *Russ. J. Str. Chem.*, **2011**, *52 (1)*, 83-90.
[3] M.S. Gruzdev, N.E. Domracheva, U.V. Chervonova, A.M. Kolker and A.S. Golubeva, *J. Coord. Chem.*, **2012**, *65 (10)*, 1812-1820.

Acknowledgements – The work was carried out with the financial support of the grants of Russian Fundation for Basic Research № 12-03-31006-mol_a, № 11-03-01028 and Program of Presidium RAS № 24.

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COMPLEXATION OF TRINUCLEAR COPPER(I) AND SILVER(I) 3,5-BIS(TRIFLUOROMETHYL)PYRAZOLATES WITH HALIDE LIGANDS

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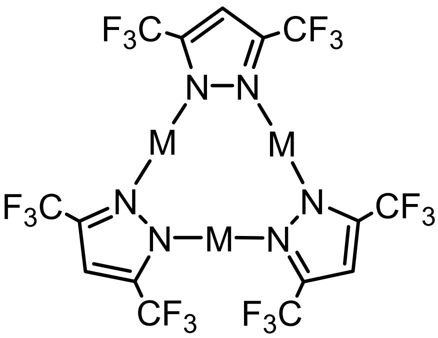
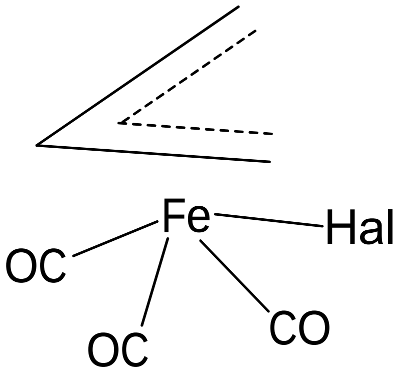
Macrocyclic pyrazolates of 11 group metals represent an important class of coordination compounds that can be used in areas such as supramolecular assemblies, host-guest chemistry and eximeric complexes with specific photophysical properties [1].



M = Ag, Cu



Hal = Cl, Br

Earlier we presented our studies of complex formation of macrocyclyc pyrazolates with boron hydrides [2] and the high affinity to hydride atom was shown. Halide and hydride ligands have somewhat similar chemical properties. Therefore we use organometallic compounds with halide ligands as guests for macrocycles.

The complexation was investigated by means of IR spectroscopy (230-290K) in low-polar solvents (CH_2Cl_2, hexane). Reversible complex formation of these macrocycles with halide containing bases was demonstrated on the example of iron π-allyl complexes (($R-C_3H_4)Fe(CO)_3X$; R = H, Me, Ph, X = Cl, Br) for the first time. The sites of coordination, composition and thermodynamic parameters ($\Delta H°$, $\Delta S°$) were determined for all studied complexes in the solution. The two types of complexes (1:1 and 1:2 compositions, i.e. two molecule of base per one molecule of macrocycle) were determined in case of silver macrocycle at low temperature. The significant influence of the metal nature on complexation process was shown. The values of complex formation constants of π-allyl compounds with silver macrocycle greater by order of magnitude comparing to the copper analogue.

[1] Omary, M. A.; Rawashdeh-Omary, M. A.; Gonser, M. W. A.; Elbjeirami, O.; Grimes, T.; Cundari, T. R.; *Inorg. Chem.* **2005**, *44*, 8200-8210.
[2] V. N. Tsupreva, O. A. Filippov, A. A. Titov, A. I. Krylova, I. B. Sivaev, V. I. Bregadze, L. M. Epstein, E. S. Shubina, *J. Organomet. Chem.*, **2009,** 694, 1704–1707.

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NOVEL B-SUBSTITUTED CARBORANYLPROPYL-(ORGANO)CHLOROSILANES. SYNTHESIS AND PROPERTIES

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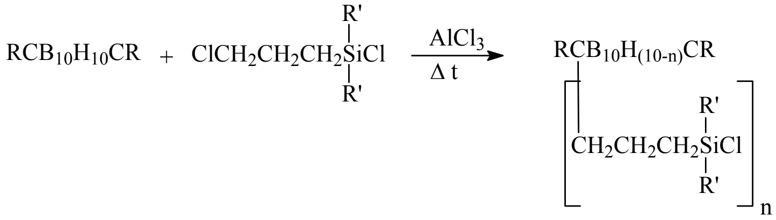
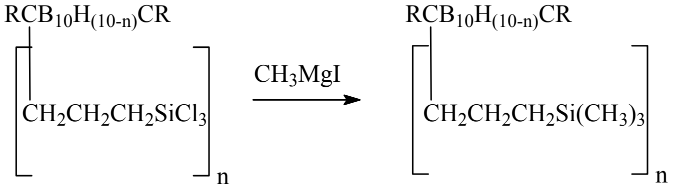
The reaction of silicon alkylation of *o*-, *m*-, *p*-carboranes by chloropropyl-tri-, chloropropyl(methyl)di- and chloropropyl(dimethyl)clorosilane in the presence of catalysts of Friedel-Crafts reaction is studied. It is stated that specified organochlorosilanes silicopropilate are bounded the carborane cage by B-H bond.



где, R= H, Ph; R'= Cl, Me; n= 1, 2.

The catalysts of this reaction can be arranged in a line according to their activity:$AlCl_3$ > $AlBr_3$>BF_3·Et_2O>$SnCl_4$>$FeCl_3$. Chloric iron was inactive.

Apart from the ratio of the initial reagents, the mixture of mono- and disiliconepropyl derivatives of carborane nuclear is formed, easily separable by distillation, especially after methylation:



где, n=1, 2.

The structure of trimethylsilylpropyl radical and his connection with boron atom but not with carbon atom of the carborane was proved by IR-, PMR- and mass-spectra.

In addition, some of the compounds obtained were introduced into the reaction with reactants, reacting with the active hydrogen atom (C-H) of the carborane cage. For this purpose we used the reaction with Grignards reagents, carried out in the Tserevitinov device, which allowed to determine quantitatively the existence of C-H bonds in compounds obtained by the volume of the released hydrocarbon

The products of siliconpropilation and their methyl analogs are colourless liquids, distilling under vacuum. Chlorosylil derivatives are easily to hydrolized on air, alkoxysilylate by alcoholes, acylate by acetic acid, aminate by amines and ammonia, at the same time their tremethyl analogs are stable and can be stored on air for a long time without changing.

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ORGANOANTIMONY AND ORGANOBISMUTH COMPOUNDS AS MONOMERS IN THE SYNTHESIS OF METAL CONTAINING POLYMERS

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Triphenylantimony and triphenylbismuth derivatives can be used for the preparation of scintillation detectors in high energy physics. These compounds could increase the radiation stability of the scintillators. They also have some advantages over organometallic compounds of the lead and tin, which have previously been used for these purposes. They are less poisonous, more soluble in the monomers, more cheap. Furthermore C=C double bonds in the molecules, could provide the possibility to be copolymerized with the monomers and stabilize the polymers.

The aim of the work was to obtain some triphenylantimony and triphenylbismuth derivatives with the carbonic acids, copolymerization of them with MMA and styrene to give metal containing polymers. Crotonic and cinnamic acids were used.

The synthesis was carried out with the oxidation addition reaction of triphenylantimony or triphenylbismuth, acid and hydrogen peroxide or *tert*-butylhydroperoxide according to the reaction:

$Ph_3M + 2RCH{=}CHCOOH + H_2O_2 \rightarrow Ph_3M[O_2CR]_2 + 2H_2O$

M=Sb, Bi; R= $CH_3CH{=}CH$-, $C_6H_5CH{=}CH$-

The obtained organometallic compounds were investigated by X-ray diffraction with the use of single-crystal diffractometer Oxford diffraction Geminis, ^{1}H-NMR spectroscopy with Agilent DD2 400 and IR spectroscopy with Shimadzu IRPrestige-21. These compounds have trigonal bipyramidal structure with three phenyl groups in the base of the pyramid and two carboxylate groups in apical positions.

Polymers containing different quantity of organometallic compounds were prepared and investigated with different methods.

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RADICAL POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE SOME OF *O*-IMINOQUINONES

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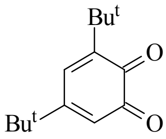
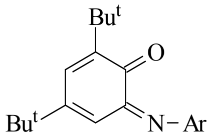
The sterically hindered *o*-quinones and *o*-iminoquinones are widely used as ligands in coordination and organometallic chemistry. The use of different quinones in macromolecular chemistry was studied in detail while the *o*-minoquinones are still unexplored.

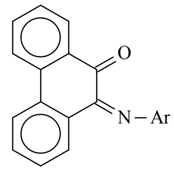
Comparison of the influence of compositions and structure some of *o*-quinones and *o*-iminoquinones on the radical polymerization of methyl methacrylate (**MMA**) initiated by azobis(isobutyronitrile) (**AIBN**) at 70-90°C was investigated. The following compounds were studied in this processes:



Q



imQ



imPhenQ

there Ar – 2,6-diisopropylphenil

It was found that the role of these compounds in radical polymerization of MMA strictly depends on their structure. The benzoquinone ***Q*** under the reaction conditions acts as an inhibitor. Maximum conversion in ratio Q / AIBN = 1 / 1 at 70°C does not exceed 30%.

The use of ***imPhenQ*** in equimolar ratio to the initiator has no effect either on the rate of the polymerization of MMA or the molecular weight characteristics polyMMA at 70-90°C.

The introduction of ***imQ*** reduces the rate of polymerization of MMA in proportion to its concentration. Number average molecular weight of polyMMA increases linearly with conversion. The index of polydispersity of polymers is ~ 1.5-1.8 up to high degrees of monomer conversion.

The postpolymerization of MMA and synthesis of block-copolymers of MMA with styrene were performed on the basis of the macroinitiators obtained with participation of the studied imQ. These processes indicate possibility of reinitiating of polymerization and the directed functionalization of polymers. The obtained data evidence of simultaneous realization both the reversible acceptance of radical by imQ.

These imQ stated above are capable of acting as regulators of chain growth for the polymerization of MMA.

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COORDINATION ABILITIES OF N,N-DISUBSTITUTED PHENANTHRENE-9,10-DIIMINES

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and V. Cherkasov[a]

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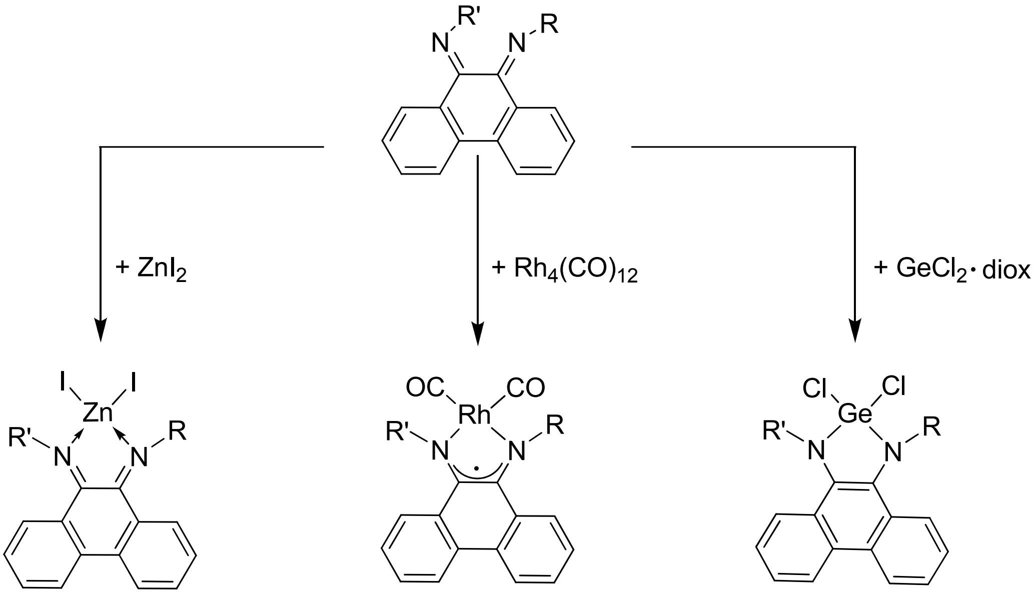
The series of novel N,N-disubstituted phenanthrene-9,10-diimines (PHDIIM) was synthesized by the condensation of 9,10-phenanthrenequinone with primary amines[1]. In the present research coordination properties of PHDIIM were studied. Compounds PHDIIM can act as neutral, radical-anionic and dianionic ligands in complexes depending upon the nature of the metal atom. The neutral complexes were synthesized in their reaction with the II group metal salts. The interaction of PHDIIM with excess of metallic potassium has not led to o-semiquinonediimine complexes, that is in good agreement with the CVA data. The electrochemical reduction of PHDIIM is a two-electron process for nearly all compounds. In the reaction with rhodium carbonyl, radical-anionic complexes with chelate bonded metal atom were registrated by EPR spectroscopy in solution. The oxidative addition of PHDIIM to germanium dichloride leads to complexes of dianionic PHDIIM ligands.



[1] V.K. Cherkasov, N.O. Druzhkov, T.N. Kocherova, A.S. Shavyrin, G.K. Fukin. *Tetrahedron,* **2012**, *68*, 1422-1426.

Acknowledgements - This work was supported by Russian Foundation for Basic Research (13-03-97103_r_povolzh’e_a, 12–03–31348_mol_a), Program for support of Leading Scientific Schools (NSh-1113.2012.3) and Ministry of Education and Science of the Russian Federation (FTP “Scientific and Scientific-Pedagogical Personnel of Innovative Russia in 2009–2013” (Contract № 8465)).

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DIFFERENT MECHANISMS OF RADICAL POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF COBALT COMPLEX WITH STERICALLY HINDERED O-IMINOBENZOQUINONE LIGANDS

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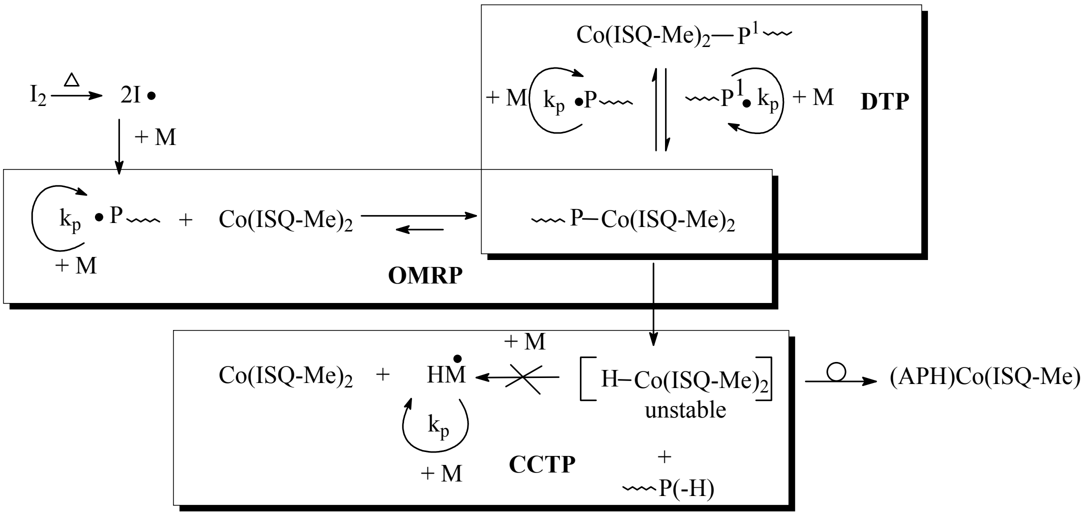
During the past fifteen years many techniques of controlled radical polymerizations (**CRP**) were developed for a wide range of monomers to attain well-defined polymers with controlled molecular weights, end functionalities, and narrow molecular weight distributions. The cobalt complexes find extensive application in the synthesis of macromolecules over the past decades. These complexes can mediate controlled polymerisation of various monomers via different mechanisms. Investigation of the mechanism of such processes is a major research focus of polymer science.

In our work the different mechanisms of radical polymerization of methyl methacrylate (**MMA**) initiated by azobis(isobutyronitrile) (**AIBN**) in the presence of bis-[4,6-di-tert-butyl-N-(2,6-dimethylphenyl)-o-iminobenzosemiquinonato]cobalt(II) (**Co(ISQ-Me)$_2$**) were investigated (scheme). Processes were described by first-order of semilogarithmic plots of ln([M]$_0$/[M]) versus time, linear growth of MW with conversion of monomer and synthesis of block copolymers. Additives of amines did not affect on the polymerization.



The analysis of polymers by MALDI-TOF, IR, UV and NMR spectroscopy showed that the probability of β-hydrogen transfer (direction of CCTP) between the cobalt complex with sterically hindered iminobenzoquinone ligands and initiating or growing radicals minimized. The kinetic data of the MMA polymerization in the presence of various AIBN concentrations and a fixed concentration of Co(ISQ-Me)$_2$ showed that the major mechanism of polymerization is DTP mechanism.

Acknowledgements - This work was supported by Russian Foundation of Basic Research (pr. №11-03-00074).

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STIMULATED RADIATION BY ORGANIC SEMICONDUCTORS

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Investigation of stimulated radiation by organic semiconductors in thin films under photoexcitation is urgent from the viewpoint of creating organic semiconductor injection lasers that have not yet been created. It’s known that, organic semiconductors, which are used for OLED fabrication, are the most suitable types of materials for organic semiconductor lasers [1,2].

In the present work low- and high-molecular organic semiconductors DA-BuTAZ [3], metallo-organic complex with Zn(DFP-SAMQ)$_2$ [4], biphenyls [5] and copolyfluorenes are investigated [6].

It was established, that upon excitation by radiation of the third harmonics of Nd^{3+}:YAG lasing all compounds (except Zn complex) generate stimulated radiation in solutions and films. Spectra of spontaneous emission under photo- and electroexcitation are similar. Stimulated radiation for all researching compounds, except Zn complex, is established. It was shown that DA-BuTAZ generated stimulated radiation in TGF solutions ($\lambda_{gen} = 450$ nm) and films ($\lambda_{gen} = 412$ nm). The Zn(DFP-SAMQ)$_2$ complex did not generate radiation even in solutions when the pump power density changed from 2.4 to 31.4 MW/cm^2 and the radiation pulse duration exceeded twice the pump pulse duration. Theoretical and experimental investigation of the nature of the radiative state for Zn complex are continuing.

Well radiating biphenyls in the simplest compositions under photoexcitation have both low-threshold generation and electroluminescence that are of undoubted interest for investigation of deactivation of the excitation energy of various types in such structures and creation of organic injection lasers.

Generation was observed in the region of polyfluorene emission $\lambda_{gen} = 440$ nm with efficiency = 12% (W = 10 MW/cm^2) for copolymer 1 and efficiency = 5% (W = 7 MW/cm^2) for copolymer 2. In films, copolymers generate in the region of polyfluorene emission, $\lambda_{gen} = 448$ nm.

Results demonstrate possibility of creation photoexcitated organic semiconductor lasers and it could be the first stage to the creation organic semiconductor injection lasers.

[1] I.D.W. Samuel, G.A. Turnbull, *Chemical Reviews*, **2007**, *107*, 1272-1295.
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[4] Т.Н. Копылова, А.В. Кухто и др., *Российские нанотехнологии,* **2010**, *5 (7-8)*, 117-120.
[5] Г.Н. Носова, Д.А. Лыпенко и др., *Высокомолекулярные соединения,* **2013**, в печати.

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DYNAMIC PROCESSES IN CYCLOMETALLATED O-SEMIQUINONIC PALLADIUM COMPLEXES: EPR STUDY

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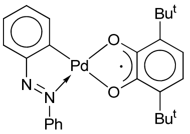
In present work we report on coordination of different phosphines to *o*-semiquinonic azophenyl palladium complexes and studying of different kinds of *o*-semiquinonic palladium complexes with pincer ligands.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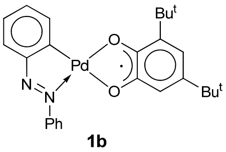
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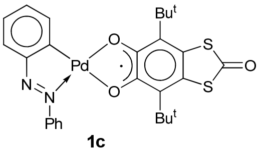
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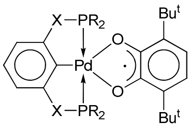
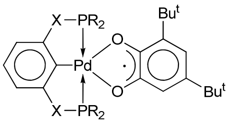
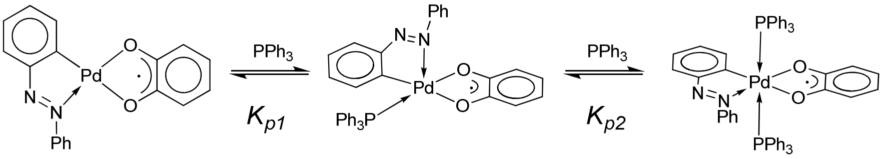
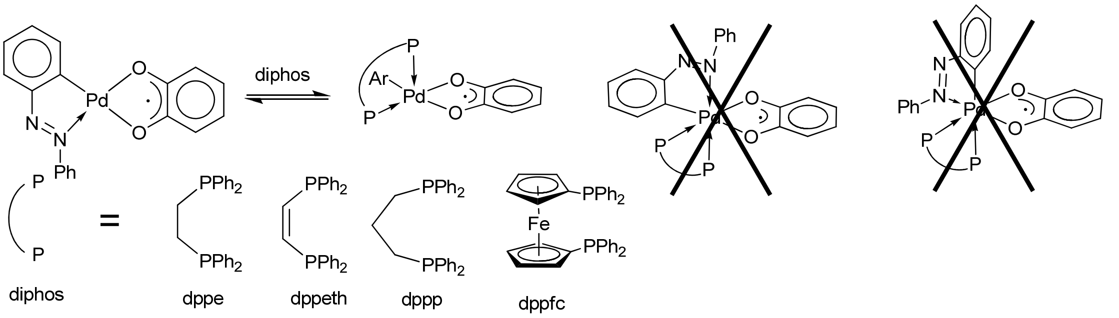

2a R = Cyp, X = CH$_2$
3a R = NEt$_2$, X = O


2b R = Cyp, X = CH$_2$
3b R = NEt$_2$, X = O

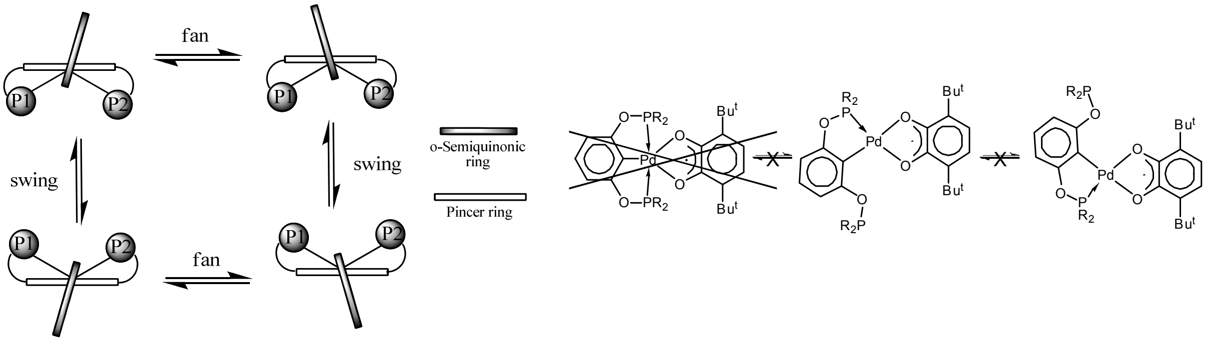
Reaction of azophenyl complexes **1a-c** with PPh$_3$ leads to reversible coordination of one or two phosphine molecules.



Reaction with bidentate phosphines leads to formation of five-coordinated products.



Bis-cyclometallated phosphine pincer complexes **2a-b** demonstrates “fan” and “swing” oscillations whereas their phosphite analogs **3a-b** exist as four-coordinated complexes without any coordination sphere dynamics.



Acknowledgements – the work was supported by RFBR (grants 12-03-31087 and 13-03-01000) and Russian President (grant NSh-1113.2012.3).

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O-QUINONES FUNCTIONALIZED WITH DIPHENYLMETHYL SUBSTITUENTS. LIGANDS CAPABLE TO CARRY MORE THEN ONE UNPAIRED ELECTRON.

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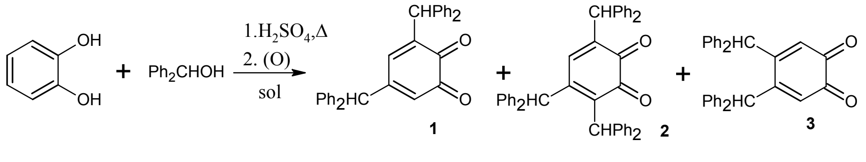
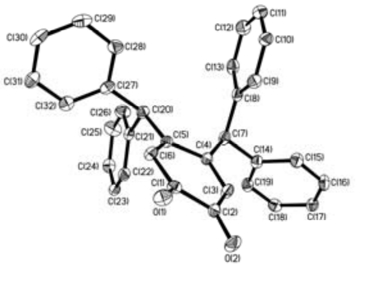
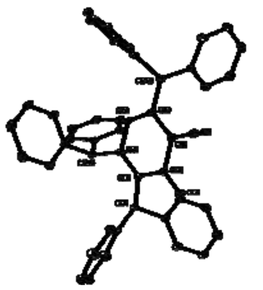
Catechol has been alkylated with diphenylmethanol. The reaction proceeds at mild conditions and results in three main products. 3,5-, 4,5- and 3,4,5-substituted adducts have been isolated from the reaction mixture.







Formation of essential amount of products **2** and **3** where bulky substituents are situated in the adjacent positions was surprising.

Due to existence of methine proton in substituent these compounds potentially can be oxidized to give trityl-like stable radical. So, these quinones are regarded as potential multi-spin ligands.

Chemical properties and coordination abilities of new quinones will be discussed.

Acknowledgements - We are grateful to the Russian Foundation for Basic Research (grants N 13-03-01000, 13-03- 97103 r_povolzh’e_a), President of Russian Federation (grants NSh-1113.2012.3) for financial support of this work. This work was made according to FSP “Scientific and scientificpedagogical cadres of innovation Russia” for 2009e2013 years (Contract 8465 from 31.08.2012).

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NMR INVESTIGATION OF LIGANDS EXCHANGE IN THE CALCIUM-β-DIKETONATE COMPLEX

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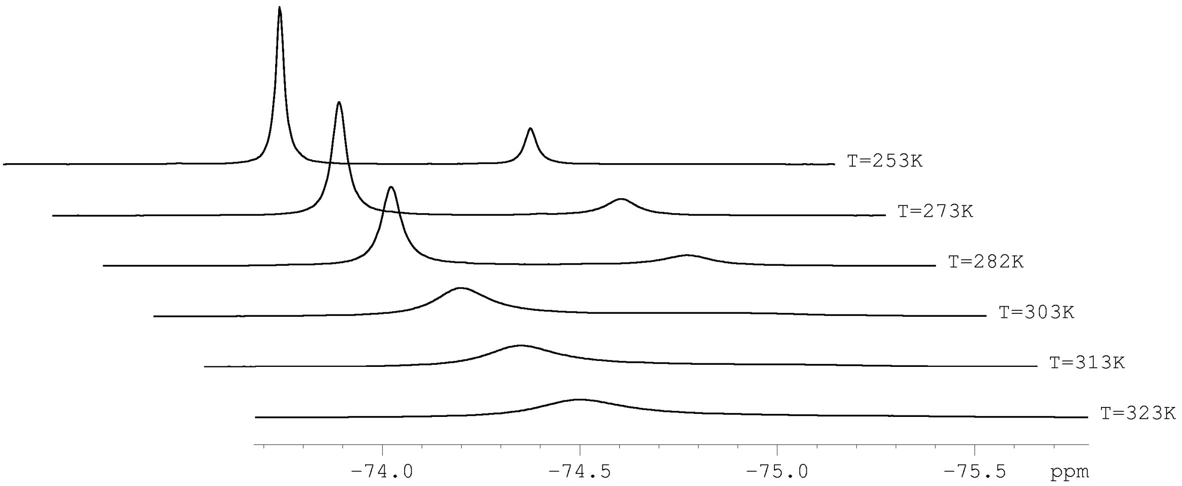
The motivation for investigation of properties of mixed ligands calcium-β-diketonate complexes with neutral poly-oxygen donor ligands is based on their use as high volatile compounds for preparation of calcium stable isotopes and a precursors for MOCVD. The complex $[Ca_2(adtfa)_4](18\text{-crown-}6)](H_2O)_2(C_2H_5OH)$ (adtfa = 1,1,1-trifluoro-4-(1-adamantyl)butanedionate-2,4), is the ion-paired solvated adduct, containing the cation $[Ca(adtfa)(18\text{-crown-}6)(H_2O)]^+$, the anion $[Ca(adtfa)_3(H_2O)]^-$ and solvated C_2H_5OH molecule, as showed by X-ray and NMR [1].

There are two forms of adtfa ligands with 3 : 1 stoichiometric ratio in the complex solution according to ^1H and ^{19}F NMR spectra at low temperature. The first one corresponds to the anion and the second – to the cation. Exchange of adtfa-ligands between the cation and the anion forms has been found by NMR. Rate constants of exchange at different temperatures have been determined by means of program Topspin 2.1 (DNMR). Rate of the reaction depends on ethanol concentration. Mechanism of the exchange reaction has been suggested and thermodynamic parameters have been determined.

$$[Ca(adtfa)(18\text{-crown-}6)(H_2O)]^+\,[Ca(adtfa)_3(H_2O)]^- + C_2H_5OH \leftrightarrows$$
$$\leftrightarrows [Ca(adtfa)_2(18\text{-crown-}6)] + [Ca(adtfa)_2(H_2O)_2(C_2H_5OH)]$$



Temperature dependence of the complex NMR ^{19}F spectra in $C_6D_5CD_3$

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BOND DISSOCIATION ENERGIES IN ORGANOMETALLIC COMPOUNDS: POLARIZABILITY EFFECT

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Many studies of intramolecular interactions are used the correlation analysis of the so-called narrow series X_nR_C where R_C is an indicator centre and X_n are substituents (Alk, Ph, F, …). For each of these series the centre R_C remains fixed whereas the substituents X_n vary. The literature data on X substituents influence on the bond dissociation energies (BDE) have been analyzed for 10 narrow series of compounds XHgCl ([1], R_C=Hg–Cl), XHgBr([1], R_C=Hg–Br), X_2BCl ([1], R_C=B–Cl), $XC(O)SiH_3$ ([2], R_C=Si–C), $XC(O)GeH_3$ ([2], R_C=Ge–C), $XC(O)SnH_3$ ([2], R_C=Sn–C), $XC(O)PbH_3$ ([2], R_C=Pb–C), $X_3P{=}S$ ([1], R_C=P=S), $XBMn(\eta^5\text{-}C_5H_5)(CO)_2$ ([3], R_C=Mn–B), and $XC(O){-}Ir(CO)Cl_2(PMe_2Ph)_2$ ([4], R_C=Ir–C).
Up to now, the mechanism for the influence of X on BDE is not understood. It is unlikely that the BDE values of Hg–Cl, Hg–Br, B–Cl, Si–C, Ge–C, Sn–C, Pb–C, P=S, Mn–B, and Ir–C depend only on the inductive and resonance effects of substituents.
Our approach is based on comparison of the two-parameter

$$BDE = BDE_0 + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-) \qquad (1)$$

and four-parameter

$$BDE = BDE_0 + a\sigma_I + b\sigma_R(\sigma_R^+, \sigma_R^-) + c\sigma_\alpha + dE_s' \qquad (2)$$

equation, where σ_I is the universal inductive constant of substituents X; σ_R, σ_R^+, and σ_R^- are the parameters characterizing the resonance effect of X in the presence of a small, large positive and large negative excess charge q, respectively, on the centre R_C; σ_α and E_s' are the polarizability and steric constants of substituents X. In all series in going from Eq. (1) to Eq. (2) the adjusted correlation coefficients increase, whereas standard errors of approximation decrease. This clearly demonstrated that BDE values depend on the inductive, resonance, polarizability, and steric effects of substituents.
The homolytic dissociation of a bond (e.g. XHgCl→XHg + Cl) produces change in electronic structure of R_C and thus gives rise to the excess charge q on R_C. The polarizability effect consists in an electrostatic attraction between the q and the dipole moment induced by this charge in X substituents.

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SYNTHESIS, STRUCTURES AND LUMINESCENT PROPERTIES OF LANTHANIDE HEXAFLUOROISOPROPOXIDES

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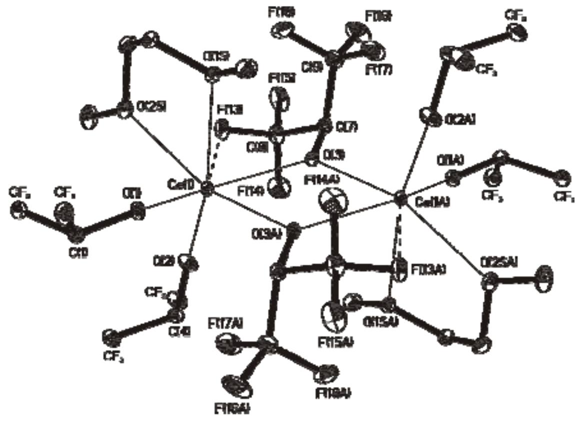
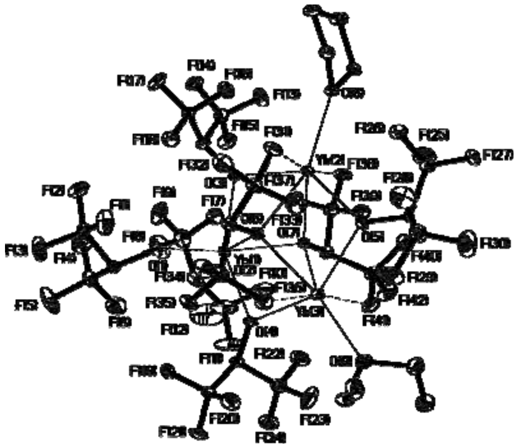
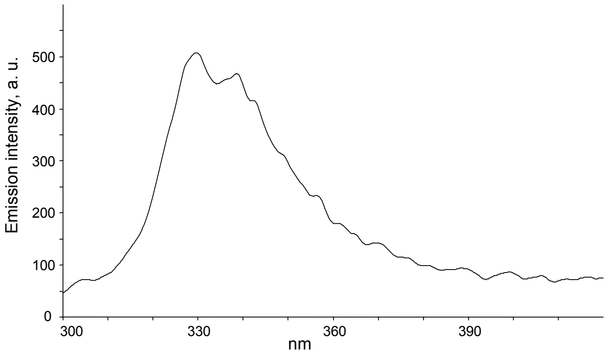
The isopropoxides $Ce(OPr^F)_3$ and $Gd(OPr^F)_3$ ($Pr^F = CH(CF_3)_2$) were synthesized by the reactions of corresponding silylamide complexes $Ln[(Me_3Si)_2N]_3$ with Pr^FOH in DME medium. The products were isolated as colorless crystals. X-ray analysis revealed that cerium complex $Ce_2(OPr^F)_6(DME)_2$ is a centrosymmetric dimer where two isopropoxide ligands are bridging and four ligands are terminal.





The reaction of $EuI_2(THF)_2$ with two equivalents of $KOPr^F$ affords the europium(II) isopropoxide $Eu(OPr^F)_2(THF)_2$. Efforts to synthesize the analogous ytterbium(II) complex were unsuccessful. X-ray analysis showed that the Yb isopropoxide is a mixed-valence trinuclear cluster $Yb_3(OPr^F)_7(THF)(Et_2O)$ which contains one trivalent and two divalent ytterbium ions.

Among the obtained isopropoxides only europium complex has shown photoluminescence. Its emission spectrum contains a broad band in UV region picked at 330 nm which can be assigned to the rarely observed $4f^65d^1 \rightarrow 4f^7$ transition of Eu(II).



Acknowledgements - The work was supported by the Russian Foundation of Basic Research (Grants 13-03-00097 and 12-03-31273 mol_a).

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THE THERMODYNAMIC CHARACTERISTICS OF PYRAZOLONATE RARE-EARTH COMPLEXES

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Rare-earth pyrazolonates have the electroluminescent properties and have attracted growing attention as emissive materials for organic light-emmiting diodes (OLEDs). However, quantitative data on the volatility of these compounds are absent in the literature.

The aim of this study was investigation of the thermochemical properties and vapor phase composition of pyrazolonate rare-earth complexes $Ln(PMIP)_3$ (Ln = Y(**I**), Nd (**II**), Tb (**III**), Ho (**IV**), Er (**V**) Tm (**VI**), Lu (**VII**); PMIP-1−phenyl−3−methyl−4−isobutyryl −5−pyrazolonate).

The complexes **I-VII** were synthesized according to the procedure described in [1]. These complexes are white amorphous powder. Rare-earth pyrazolonates were characterized by elemental analysis, IR spectroscopy and ^{1}H NMR spectroscopy. The received compounds were purified by sublimation in vacuum for further experiments. The final compounds are crystalline substances and are dimeric $[Ln(PMIP)_3]_2$ (according to X-ray diffraction study).

The thermal properties of new pyrazolonate rare-earth complexes were studied by differential scanning calorimetry (DSC), by the Knudsen's effusion method (**I**, **IV-VII**) and by the Knudsen's effusion method with mass spectrometrical determination of the composition of the gas phase on a standard MI-1201 mass spectrometr modified for thermodynamic studies and an APDM-1 monopolar mass analyzer adjusted to work with molecular beams over the mass range extended to 2500 amu (**II** and **III**).

Melting and thermodynamic parameters of the melt were obtained using a differential scanning calorimeter DSC204F1 Phoenix (DSC) (Netzsch Gerätebau, Germany). The endothermic transition was detected for all complexes. This transition was associated with melting. Thermodynamic parameters of melting are calculated.

The temperature dependence of the vapor pressure of these complexes was measured by the Knudsen's effusion method. Vaporization temperature interval was chosen according to the DSC data (216-300 °C). Thermodynamic parameters of sublimation are calculated: for complex **I** $\Delta_sH=130.3\pm1.9$ kJ/mol, for complex **II** $\Delta_sH=205.9\pm2.7$ kJ/mol, for comlexes **III** $\Delta_sH=208.0\pm4.0$ kJ/mol, for complex **IV** $\Delta_sH=90.8\pm1.2$ kJ/mol, for complex **V** $\Delta_sH=83.9\pm1.4$ kJ/mol, for comlex **VI** $\Delta_sH=81.5\pm1.3$ kJ/mol and for complex **VII** $\Delta_sH=83.42\pm1.1$ kJ/mol.

It was found established that the dimeric complexes **II** and **III** are monomeric in the gas phase. This observation suggests that the complexes **I**, **IV-VII** behave similarly. In addition, according to mass spectrometry, the calculation of the vapor pressure was performed for the sublimation process into the monomeric vapor.

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NONBENZENOID AROMATIC SYSTEMS WITH PARTICIPATION OF A METAL ATOM. VIBRATIONAL SPECTRA AND QUANTUM CHEMISTRY STUDY

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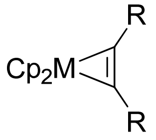
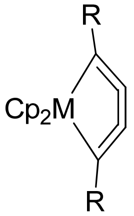
Nonbenzenoid aromatic systems were a subject of Mark Vol'pin's particular interest. Specifically, he paid much attention to creation chemistry of metallacyclopropenes, and the first example of such kind, namely, a complex $Cp_2Ti(PhC_2Ph)$ not containing additional ligands was synthesized by him and co-workers in 1982, the three-membered metallacycle of this complex was considered as aromatic, its π-electron delocalizes system involving two π-electrons of carbon atoms and the vacant orbital of the Cp_2Ti species [1].

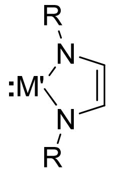
In this study, vibrational spectra of three types (I-III) of aromatic compounds, in which a metal atom participates in cyclic π-electron delocalization, will be presented and discussed. These are two-electron metallacyclopropenes (I) as well as six-electron metallacyclocumelenes (II) [2] and Arduengo type N-heterocyclic unsaturated compounds (III): silylene [3] and germylene [4].



I



II



III

M=Ti, Zr, Hf
M'=Si, Ge

Aromaticity of compounds of these types will be estimated using different modern criteria, both experimental and theoretical (calculations of NICS and ISE).

References:

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SYNTHESIS AND STRUCTURAL STUDY OF COMPLEX COMPOUND OF COPPER WITH CYSTEAMINE

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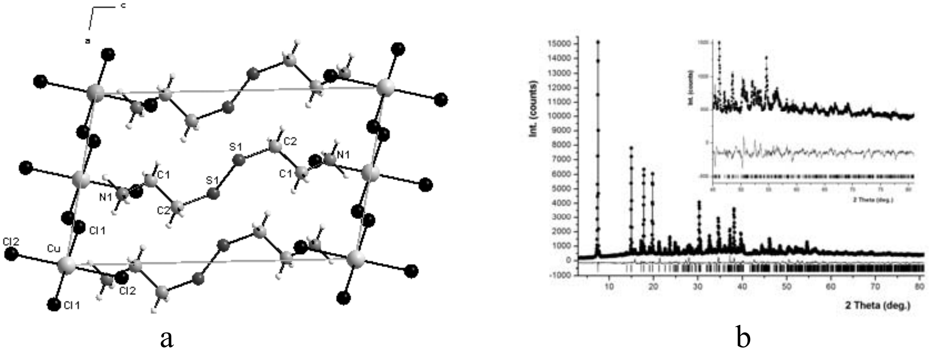
Reversible oxidation-reduction transformations between thiols (–SH) and disulphides (–SS–), play the important role in formation of ternary protein and enzyme structures. The reactions can be catalyzed by transition metal ions (Pd^{2+}, Cu^{2+}, Fe^{3+}) [1,2]. In this respect the reactions of aminoacids with mentioned cations giving corresponding salts or complex compounds present certain interest for the protein biochemistry.

In the present work the reaction between dihydrochloride cystamindium $CystaH_2Cl_2$ and $CuCl_2$ following according to the equation:

$$CystaH_2Cl_2 + CuCl_2 \rightarrow CystaH_2[CuCl_4]\downarrow, \qquad (1)$$

was studied and the product was structurally characterized using X-ray powder diffraction techniques and IR spectrum. $CystaH_2[CuCl_4]$ was obtained from the acidic solution of the reactants with the molar ratio Cysta : M^{2+} = 1 : 2. The 10 mol/l HCl was used as the solution to prevent a precipitation of $CystaH_2Cl_2$. The latter condition ensures the formation of the thermodynamically low stability anion $[CuCl_4]^{2-}$ in the solution.

According to thermal analysis, the decomposition of $CystaH_2[CuCl_4]$ begins at 200°C, giving CuO at 600°C (weight loss 74.1%). To determine the structure of the complex IR spectrum of $CystaH_2[CuCl_4]$ was compared to $CystaH_2Cl_2$. The minor displacement of the bands at 2900–3200 cm^{-1} [$\nu(NH_2)$] and at 1560 –1600 cm^{-1} [δ(C–N)] were indicated and explained as the lack of coordination of Cu^{2+} by nitrogen. This is confirmed by the presence of the bands at 1447–1462 $cм^{-1}$ and at 1578 – 1593 $cм^{-1}$, referred to the symmetric bending vibrations of $–NH_3^+$ groups. The presence of $CystaH_2^{2+}$ cation into $CystaH_2[CuCl_4]$ was confirmed by X-ray crystal structure investigation, Figure 1:



a b

Figure 1 – Crystal structure and Rietveld plot of $CystaH_2[CuCl_4]$
a – the structure of $CystaH_2[CuCl_4]$ unit cell (a=7.18(3) Å; b=7.50(3) Å; c=12.01(1) Å; β=101.2(0)°; V=635.1(4) $Å^3$; P 2_1/a); b – diffraction pattern of $CystaH_2[CuCl_4]$

The crystal structure of $CystaH_2[CuCl_4]$ has a layered type (Fig. 1 a). The layers are built from cations $CystaH_2^{2+}$ have a positive charge and alternate with layers consist of $[CuCl_4]^{2-}$. – NH_3^+ groups directed towards the corresponding halogen atoms from square planar $[CuCl_4]^{2-}$, whereby hydrogen bonds occur between them.

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[2] A.V. Eryomin, V.G. Antonov, N.S. Panina et al. // Rus. Chem. J. 2009. V. 53. № 1. P. 135.

OBTAINING NANOPARTICLES TYPE OF CORE - SHELL, IN WHICH THE CORE -POLYMER AND THE SHELL - SILICON DIOXIDE.

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Recently considerable interest is paid to the synthesis of porous nanoparticles based on silica. The intermediate phase for the synthesis of such particles is the production of core-shell type particles with followig removing of the core. The core is removed either thermally or by washing with solvent. The aim of our work is to develop methods for the preparation of nanoparticles in which a polymer is the core and silicon dioxide is the shell. Firstly, we prepared silica particles of 60-80 nm size by using the method of emulsifierfree emulsion polymerization of methyl metacrilate (MMA) and copolymerization of MMA with methacrylic acid (MAA), and vinylpyrrolidone and methacryloxyproryltrimethoxysilane (MPTMS). The particle size was determined by atomic force microscopy (ACM) on a microscope Solver P-47. The final particle size is given in the table. The resulting emulsion was carried out in an alkaline medium for hydrolysis of tetraethoxysilane (TEOS) for shell coating on the silica particles of polymethyl methacrylate and methyl methacrylate copolymers. The solution was dried to give films. Then again, the particle size was determined by the ACM. The average particle size increased, confirming availability of the silica coating on polymer nanoparticles. The data presented in the table.

Table.

size particles (nm)							
PMMA	**PMMA+TEOS**	**MMA:MPTMS**	**MMA:MPTMS + TEOS**	**MMA:MAA**	**MMA:MAA + TEOS**	**MMA:N-VP**	**MMA:N-VP+ TEOS**
90	127	92	110	102	129	118	127
102	119	87	113	122	130	111	134
106	131	87	108	127	120	115	110
94	119	89	105	102	120	117	130
116	131	92	111	122	128	124	132
102	**125**	**89**	**109**	**115**	**125**	**117**	**127**

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SYNTHESIS OF (CO)POLYMERS STYRENE IN THE PRESENCE OF SYSTEM ALKYLBORANE – QUINONE

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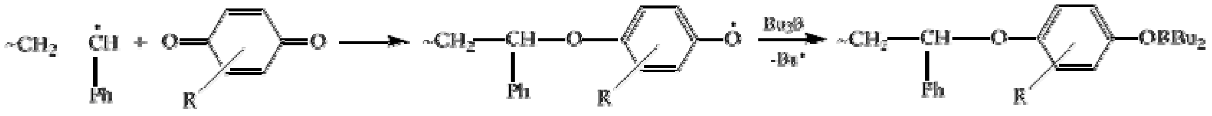
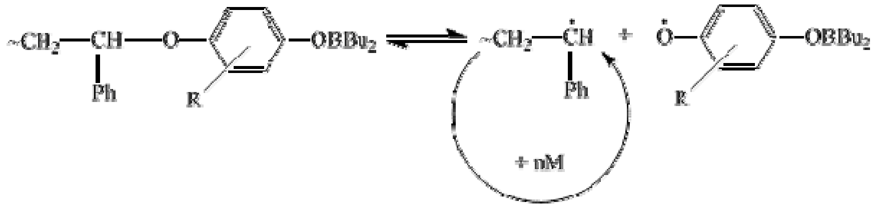
The polymerization of styrene at 80ºC initiated with AIBN has been studied in the presence of tri-*n*-buthylboron and a number of *p*-quinones: 2,3-dimethyl-benzoquinone, 1,4-naphthoquinone, 2,5-ditertbuthyl-benzoquinone, duroquinone. The polymerization proceeds in a controlled manner according to the mechanism of Stable Free Radical Polymerization (SFRP):



(I)

Formed adduct (I) is able to reinitiate (co)polymerization:



The most active macroinitiator has been obtained in the presence 2,3-dimethyl-benzoquinone and 1,4-naphthoquinone. The prepared macroinitiators were studied in the block-copolymerization with methyl methacrylate and *N*-vinylpyrrolidone. This process passes with high rate, average number molecular mass (M_n) of block-copolymers (1.09 – 2.03)$\times10^6$, $M_w/M_n = 1.29 – 1.49$. The content of styrene in the products ranges between 9 – 11% at deep conversion.

The binary copolymerization of styrene with vinyl acetate proceeds in a controlled manner in the presence of tri-*n*-buthylboron and 2,3-dimethyl-benzoquinone too. A gradient copolymer with low compositional heterogeneity was synthesized by this type of copolymerization.

BIS(IMINO)ACENAPHTHENE (DPP-BIAN)-SUPPORTED N-HETEROCYCLIC SILILENE

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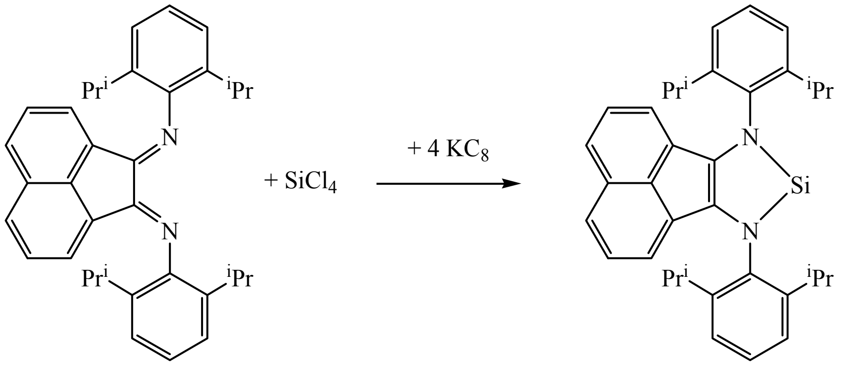
N-heterocyclic silelenes are not particularly amenable to ligand tuning by changing the steric and electronic characteristics of the substituents. Ligands of the bis(imino)acenaphthene (BIAN) class seemed like promising candidates for fusion to N-heterocyclic silelenes (NHSs), not only because of their structural rigidity, but also on account of their redox behavior. The annulation proposed herein would result in an Arduengo-type NHS.[1]

The bis(imino)acenaphthene-supported N-heterocyclic sililene (dpp-BIAN)Si has been prepared by reaction of dpp-BIAN with SiCl4 and potassium graphite.



Interaction of metal complexes with reduced dpp-BIAN^{-4} forms like (dpp-BIAN)Na$_4$ with SiCl$_4$ and SiBr$_4$ gives a lot of by-products. However reactions of (dpp-BIAN)Na$_2$ and (dpp-BIAN)Mg with SiCl$_4$ produce (dpp-BIAN)SiCl$_2$ with high yields.

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CONDUCTIVITY OF CRYSTALS AND VACUUM DEPOSITED FILMS OF COBALT O-SEMIQUINONATO COMPLEXES

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Molecular crystals of organic substances and organometallic complexes attract a great attention due to their unique properties such as conductivity and responsibility to light and heating. Some of these properties open possibilities for design of different sensors and active elements for molecular electronics.

In this work the temperature dependence of conductivity of crystals and thing films of cobalt o-semiquinonato complexes ((2,2’-bpy)Co(3,6-DBSQ)$_2$ (**I**) and (1,10-phen)Co(3,6-DBSQ)$_2$ (**II**)) have been investigated.

Crystals of a size until 2 mm length were grown from ether solutions. Electric contacts were created by thermal vacuum deposition of gold or by gluing of copper wares by a silver conductive paste. Thin films with thickness of 100-300 nm were produced by thermal vacuum deposition. They have polycrystalline or amorphous structures depending on the process conditions. For example, polycrystalline film can be made from amorphous one by annealing. Bottom electric contacts in sandwich structures were ITO on glass surface. Top electric contacts were produced by thermal vacuum deposition of gold.

It was shown that 1) thermal response in conductivity of all samples is reversible; 2) conductivity of crystals exhibits an anisotropy; 3) amorphous, polycrystalline and crystal samples have different dependences of conductivity on temperature. Maximal change of conductivity of crystals (until 10 % per K) was observed in temperature ranges 270-310 K for complex **I** and 140-230 K for complex **II**. These temperature regions match with temperature intervals of phase transitions which were observed earlier [1, 2]. Values of conductivity at temperatures exceeding the transition intervals approximate to “zero” (noise level). Total value of changes exceed 100 times.

It makes these complexes very promising to be applied for designing of uncooled bolometers.

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THE BIS-O-SEMIQUINOLATE COMPLEXES OF II GROUP METALS: THE CORRELATION BETWEEN STRUCTURE AND MAGNETIC PROPERTIES

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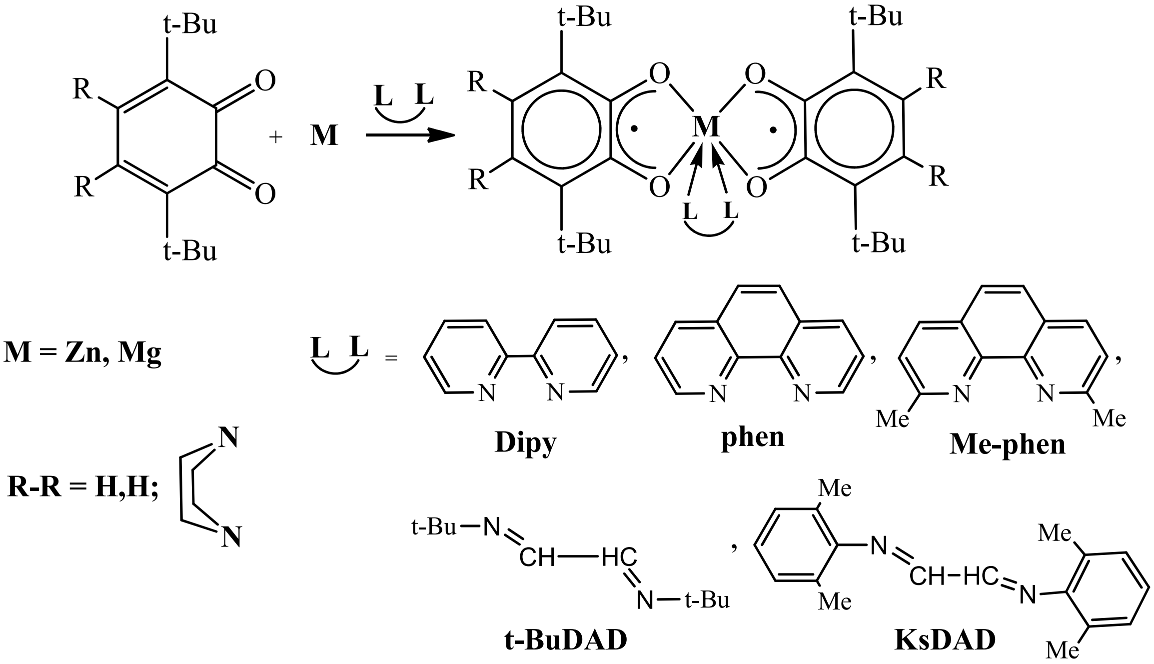
The present work is directed on the obtaining new metal complexes of redox-active ligands with the controlled geometry and magnetic properties. The application of non-transition metals will allow to establish the general regularities of the magnetic interaction between the radical ligands excluding the influence of the paramagnetic metal. The obtained data array will help us to reveal the patterns of control on the intramolecular electronic and magnetic interactions metal-ligand and ligand-ligand in order to identify approaches to building of molecular magnetic and molecular devices based on the organometallic and coordination compounds with redox-active ligands.

The series of zinc (or magnesium) bis-o-semiquinolate based on 3,6-di-tert-butyl-o-benzoqunone or 5,8-di-tert-butyl-2,3-dihydro-1,4-ethanoquinoxaline-6,7-dion with different N,N-ligands was synthesized:



All complexes were characterized using IR-, EPR-spectroscopy and elemental analysis. For some complexes measurements of magnetic susceptibility and X-ray structures were carried out. Two zinc complexes with phen and Me-phen ligands are monomers. The central metal atom in these complexes has an octahedral environment. In contrast to the latter, zinc complexes with diazabutadiene ligand are dimers. In this case μ-η^2-bound diazabutadiene has trans-configuration and environment of zinc is a distorted tetrahedral pyramid.

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REACTION OF DIPYRRIN BF$_2$(I) COMPLEX FORMATION: EXPERIMENTAL STUDY AND THEORETICAL CALCULATIONS

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Bodipy-based dyes (Boron Dipyrrin complexes) and their various derivatives are being considered as promising components of functional materials for a variety of practical applications due to their unique spectral and photophysical properties, namely a high extinction coefficient, high fluorescence and the sensitivity of the spectral and photophysical properties to small changes in pH as well as to the polarity of the medium and low concentrations of metal ions. Despite the considerable interest in the Bodipy chemistry, the complexation mechanism of these compounds is not fully understood. Earlier in our research group the formation of a stable intermediate (donor-acceptor complex or DAC) in the synthesis of Bodipy starting from alkylated dipyrrin was indicated for the first time by the analysis of the reaction mixture followed by chromatographic separation [1]. This study is aimed to a more detailed study of the formation of donor-acceptor complex and its transition to Bodipy.

Spectral analysis (IR, H^1 NMR and Electron Absorption spectroscopy) and computer modeling was used to study the reaction, to determine the energy and geometric characteristics of the starting compound, intermediate and products of the reaction, as well as for calculation of reaction PES profile.

It was shown that the formation of the DAC with BF_3, further stabilized by hydrogen bonds N-H···F-B, is the first stage of Bodipy formation. The stability constants (in benzene and dimethylformamide), structural and energy parameters (gas phase) of DAC were defined. Analysis of a two-step reaction route of Bodipy synthesis indicates a high activation barrier for the transition of intermediate to Bodipy. To create more favorable conditions elimination of HF in the last step of the reaction was recommended to use electron-donating reagents. The main factor determining the difference in the enthalpy of formation of the donor-acceptor complexes of dipyrrins with halides of B (III), Al (III), Ga (III), In (III), As (III) and Sb (III), is the mutual cancellation of the energies of formation donor-acceptor bonds N → Element(III) and $N\text{-}H\cdots Hal^-$. A significant contribution to the stabilization of complexes with *p*-elements fluorides is making by the hydrogen bonds $N\text{-}H\cdots F^-$. It was shown that the second stage – the closure of the coordination cycle is kinetically controlled. The kinetic parameters and activation energy for the reaction processes were determined, reaction intensification routes have been proposed.

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SOLVENT EFFECTS ON DIPYRRIN COMPLEXES SPECTRAL AND PHOTOPHYSICAL PROPERTIES

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Chemistry of dipyrrins and their complexes got under extensive development nowadays. Possibilities of using the dipyrrin compounds are determined by dipyrrin intense chromophoric and fluorescent properties. This fact could be explained by the presence in their structure the labile π-electron system which is sensitive to changes in the external environment and the complexes structure. These compounds could be used to create analytical sensors for determination of ions, molecules, characteristics of the environment and as markers for biologically active molecules. Variation of the types of intermolecular interactions in dipyrrin complexes solutions is one of the main ways of controlling the spectral and photophysical properties of the considered chromophores and thus their valuable characteristics. Taking that into account the study of dipyrrin complexes solvatochromic characteristics (i.e. environmental effects on the spectral and photophysical properties) is the topic of great interest.

The influence of solvents of different groups (electron and proton donor, polar and non-polar, viscous and fluid) on the characteristics of the absorption and fluorescence of dipyrrin complexes with *p*-and *d*-elements were examined as a part of the work. In the study of the viscosity influence binary solvent mixtures of ethanol and ethylene glycol, as well as the variation of the solution temperature was used to change the dynamic viscosity of the system. The solvent effects were examined using one-parameter and poly-parameter correlations of various solvent characteristics.

It is shown that the complexes exhibit negative solvatochromic effect, i.e. hypsochromic magnitude of displacements in the absorption and fluorescence spectra increases with increasing solvent polarity. It was found that specific solvent-solute interactions make considerable contribution to the spectral properties of the compounds. The dipyrrin complexes containing phenyl moiety in the molecular structure of the ligand exhibit the molecular rotor properties. The fluorescence intensity is increases with increasing the dynamic viscosity of the solvent for such compounds. The changes in viscosity by varying the composition of the solvent lead to extreme dependence in the fluorescence spectra due to specific solvation. At the same time, changes the dynamic viscosity due to changes in temperature leads to a linear change in the emission spectra and complexes quantum yield. The authors separated the contributions of temperature and viscosity on the spectral characteristics of the complexes. The obtained results provide additional insight into the influence of solvation factors on the spectral and photophysical properties of the dipyrrin complexes and form the single strategy of selection and application of the compounds of this class.

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MIXED LIGAND COMPLEXES OF REE CARBOXYLATES AND BETA-DIKETONATES WITH N,O- AND N,N-DONOR LIGANDS: FEATURES OF SYNTHESIS, STRUCTURES AND THERMAL STABILITY

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The mixed ligand complexes (MLCs) of rare earth elements (REE) carboxylates and beta-diketonates with organic neutral ligands are well studied and widely used classes of coordination compounds with different functional properties. So, in Chemical Solution Deposition (CSD) method, active developing recently for deposition REE-containing thin films, the combination of REE carboxylates and/or beta-diketonates with such amines (Q) as monoethanolamine ($NH_2CH_2CH_2OH$, MEA) or diethylenetriamine ($NH(CH_2CH_2NH_2)_2$, DETA) are recognized as effective precursors. These amines exhibit dual nature. On the one hand, they are weak bases and promote to hydrolysis of REE coordination compounds. On the other hand, both MEA and DETA are N,O- and N,N-donor ligands which can take part in formation of mixed ligand complexes with unique structure and properties. The chemical behaviour of these amines in respect to REE carboxylates and beta-diketonates depends on thermodynamic stability of REE compounds, synthesis procedure.

The interaction features of REE carboxylates, $Ln(Carb)_3$, and beta-diketonates, $Ln(\beta\text{-dik})_3$, (Ln = La, Eu, Ce, Lu, Y) with MEA and DETA were studied by examples of four carboxylic acids: acetic (HAcet), propionic (HProp), pivalic (HPiv), trifluoroacetic (HTfa) and two beta-diketones - acetylacetone (Hacac) and dipivaloylmethane (2,2,6,6-tetramethyl heptanedione, Hthd). Here we present interesting examples of new REE MLCs, which formed as polynyclear hydroxocompounds or as mononuclear compounds with ancillary amine ligands.

For syntheses of MLCs we suggested new synthetic approach - interaction of hydrated REE nitrates with ion pairs of general formula $[QH_x^{x+}][Carb^-]_x$ (Q = MEA, DETA) or Schiff bases (from Hacac or Hthd and Q). The formation of these ion pairs and Schiff bases was confirmed in non-aqueous solutions by potentiometry, electrospray ionization mass spectrometry (ESI MS), ^1H NMR analyses and in solid state by X-ray crystal analysis.

The hydrolysis process is suppressed completely only in syntheses with $[QH_x^{x+}][Piv^-]_x$ ion pairs and Schiff bases. The MLCs of general formula $[Ln(L)_{3-x}(NO_3)_x(Q)_y)]$ (HL = HPiv, Hacac, Hthd) were obtained and crystal structures of $[Ce(Piv)_5(MEAH^+)][MEAH^+]$ (**I**) $[Ln(Piv)_2(DETA)_2](NO_3)$ Ln = Lu(**II**), Y(**III**)) and $[Ce_6(O)_8(Piv)_8(DETA)_4]$ (**IV**) were determined. Complexes **I-III** are the rare examples of mononuclear REE carboxylates with bulk ancillary ligands. In complexes **I-IV** carboxylate ligands did not show bridging function. Complex **I** is the first example of compound where MEA acts as O-coordinated and NH_3^+-protonated ligand simultaneously.

The results obtained are of interest to REE coordination chemistry as well as to chemistry of CSD precursors, as properties of these precursors strongly depend on MLCs composition.

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FIRST USE OF THE PHOSPHORYLATED CAGE METAL COMPLEXES AS CHELATING LIGANDS: PALLADACYCLES FORMED BY IRON(II) CLATHROCHELATES WITH P,N-DONOR RIBBED SUBSTITUENTS AND THEIR CATALYTIC ACTIVITY IN SUZUKI CROSS-COUPLING REACTIONS

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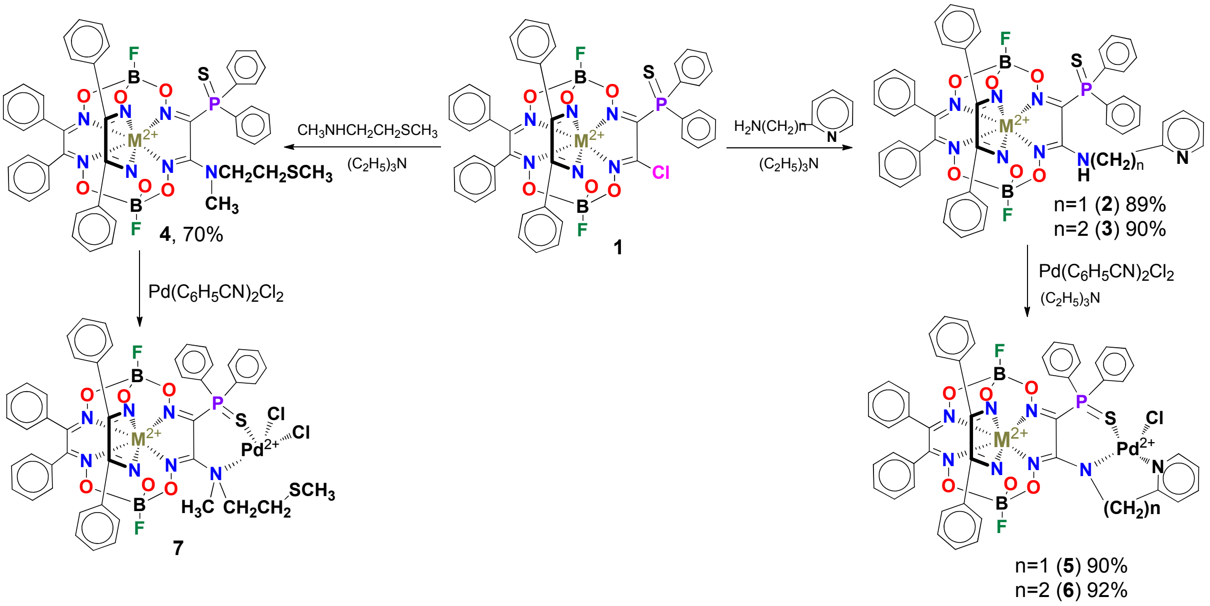
Recently reported phosphorylated iron(II) clathrochelates [1] with donor groups are promising ligands for the design of polytopic and multifunctional molecular and supramolecular systems, in particular, redox-switchable homogeneous catalysts. New phosphorylates iron(II) clathrochelates with P,N-donor functionalizing ribbed substituents were obtained by nucleophilic substitution of the macrobicyclic precursor **1** with primary (**2** and **3**) and secondary (**4**) amines as nucleophiles (Scheme).



Scheme

Their reactions with $Pd(C_6H_5CN)_2Cl_2$ afforded the corresponding clathrochelate-containing palladacycles: one formed by ternary donor amino group (**7**) is unstable and was spectrally detected only in a solution, but those with deprotonated secondary amino groups were isolated and characterized using elemental analysis, MALDI-TOF mass spectrometry, IR, UV-vis, ^{57}Fe Mössbauer, ^{1}H, ^{11}B, ^{19}F, ^{13}C{^{1}H} and ^{31}P NMR spectroscopies, and by X-ray crystallography. These clathrochelate-containing palladacycles showed high catalytic activity in model Suzuki cross-coupling reactions.

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PROCESS FOR PREPARING NONSOLVATED ALUMINUM HYDRIDE IN DIBUTYL ETHER

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The existing technology of obtaining nonsolvated aluminum hydride is based on Schlesinger, which consists of interaction lithium aluminum hydride and aluminum chloride in the mixture of diethyl ether and toluene. One of the main weaknesses of this technology is using diethyl ether, as this solvent is a precursor and a low-boiling one. In technological terms, one of the weaknesses is to use of large amounts of solvents mixture, which complicates their regeneration. In this regard, there is need to replace the system of solvents on the individual solvent. As solvent was selected dibutyl ether because this solvent is high boiling, not a precursor. In addition the use of this individual solvent increases the effective concentration of aluminum hydride.

In connection with high demands to the quality of raw materials used in the synthesis of hydride compounds, was developed a method of deep cleaning of dibutyl ether from impurities such as peroxides, t-BuOH, BuOH and water [1]. It was studied the influence of impurities formed during decomposition of dibutyl ether, on the processes of synthesis and crystallization of aluminum hydride. Were investigated the following parameters of the processes of synthesis and crystallization of aluminum hydride: change the effective concentration of aluminum hydride, excess of lithium aluminum hydride, temperature regimes of synthesis and crystallization of aluminum hydride, type of seed(). Based on these studies were selected conditions of synthesis and crystallization of aluminum hydride in dibutyl ether. In result on the research was obtained β - and a-modification of aluminum hydride in dibutyl ether medium.

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MOLECULAR CONDUCTORS: CHAINS OF THE COMPOUNDS CONTAINING ELEMENT-ELEMENT (Ge, Si, Sn) BONDS

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At present time, the so-called "molecular wires" are of special scientific interest and is of practical importance in molecular electronics and nanotechnology. Usually the main objects of study in this area are organic compounds containing a system of conjugated carbon-carbon bonds. However, recently molecules containing non-carbon chain atoms, such as Ge, Si, Sn (**E**), attract significant attention. Electrons of the single E-E bond are delocalized over the entire chain of atoms of elements (**σ-conjugation**). Thus, the existence of σ-delocalization in oligogermanes and related compounds leads to the appearance of properties which are characteristic for unsaturated hydrocarbons (conductivity, thermochromism, non-linear optical properties *etc.*). The changes in the structure of compounds effect on these properties. The most important are: 1) the number of atoms of the elements in the chain [1]; 2) introducing additional donation to one of the atoms (Ge, Si or Sn) in chain [2]; 3) the electronic properties of substituents (electron withdrawing or electron donating groups) at atoms of Ge (Si, Sn) in the chain [3].

The report presents the results on the synthesis of oligogermanes and related compounds containing germanium-silicon and germanium-tin bonds.

$(C_6F_5)_3Ge\text{-}GeAr_3$
$Alk_3Ge\text{-}GeAr_3$
$(C_6F_5)_3Ge\text{-}GeAr_2\text{-}GeAlk_3$

A

Ar = Ph, *p*-Tol
Alk = Me, Et

$Ar_3Ge\text{-}GeR_2\text{-}GeAr_3$

B

R = Me, Ph, *p*-Tol
Ar = C_6F_5, *p*-$F_3CC_6H_4$, *p*-FC_6H_4

$Ar_3Ge\text{-}SiMe_2\text{-}SiMe_3$
$Ar_3Ge\text{-}Ge(SiMe_3)_3$
$Ar_3Sn\text{-}Ge(SiMe_3)_3$

C

Ar = Ph, *p*-Tol

The structures of all compounds were investigated by multinuclear NMR spectroscopy, UV spectroscopy, and in some cases by X-ray analysis.

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DIVERSITY OF GOLD (I) COMPLEXES OF 1,5-DIAZA-3,7-DIPHOSPHACYCLOOCTANES.

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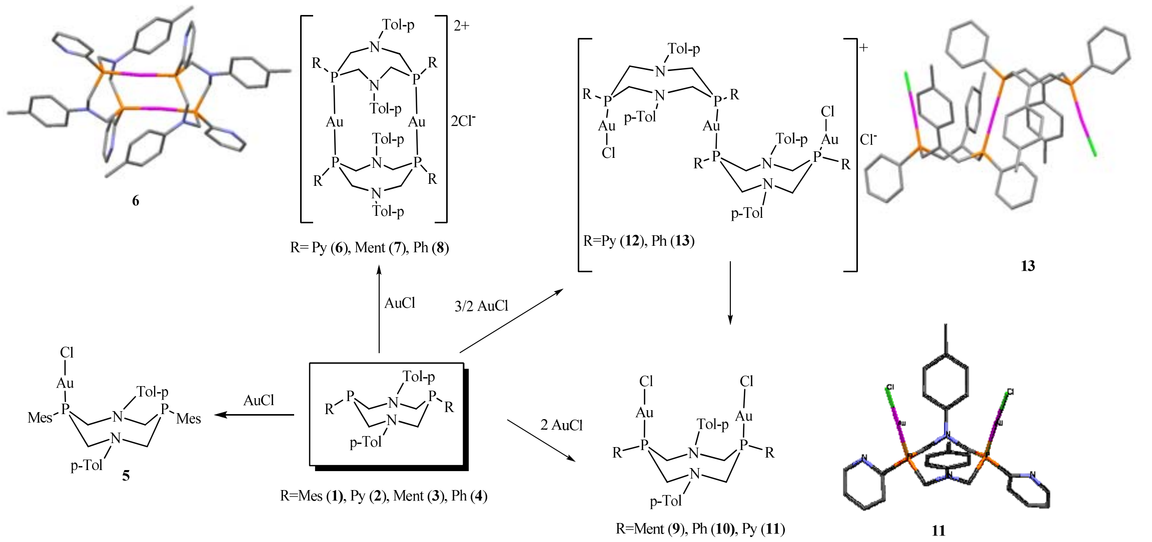
Gold (I) complexes of diphosphines attract an attention due to their biological activity (in particular as anticancer drugs) [1] and the ability to form systems with metal-metal bonds, which have useful physical properties (e.g. luminescence, fluorescence etc.) [2,3]. It has been shown [4a,b], that cyclic aminomethylphosphines coordinate transition metals of 10 group to give P,P-chelate complexes, but complexes with metals 11 group were poorly investigated. Ligands were prepared by the Mannich condensation in system primary phosphine–formaldehyde - primary amine [4]. Reaction of **1** with one equiv. of AuCl led to mononuclear complex **5** whereas **2-4** with less bulky substituents on phosphorus formed unusual binuclear charged macrocyclic structures **6-8.** Complex **6** demonstrated a noticeable water-solubility due to the presence of additional pyridyl groups. Reaction of **2-4** with two equiv. of AuCl gave binuclear compounds **9-11**. The addition of **2** or **4** to gold (I) chloride in molar ratio 2 : 3 led to the formation of trinuclear complexes **12** and **13**, which were isolated in good yield.



X-ray data of compounds **6**, **11** and **13** showed that in all cases gold (I) has a typical linear configuration but heterocycle has “crown” conformation for **11** and **13**, and slightly twisted “chair – boat” conformation for **6**.

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SYNTHESIS AND STRUCTURE OF PYRAZOLATE- AND PYRAZOLATE-CARBOXYLATES COMPLEXES OF 3D-TRANSITION METAL ANALOGUES 1,10 PHENANTHROLINE OR 2, 2'-DIPYRIDINE

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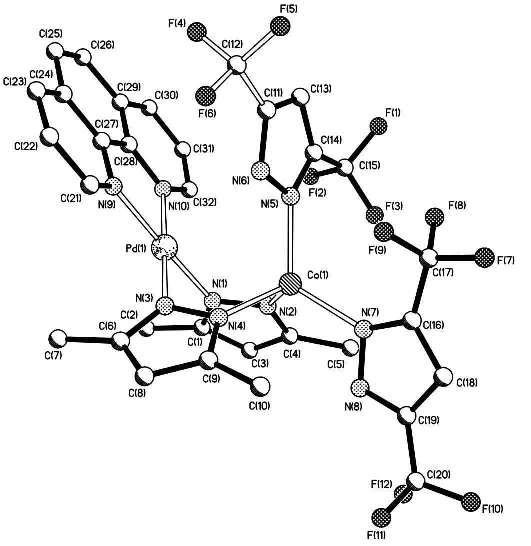
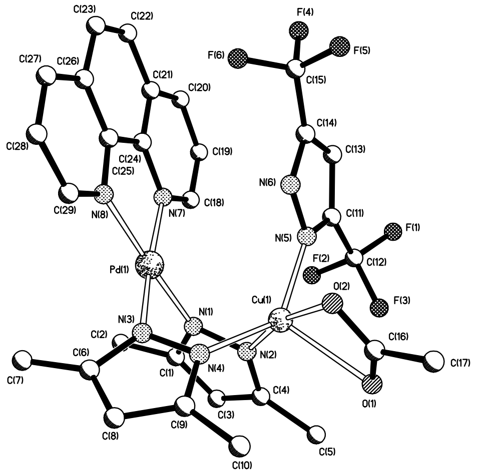
Using transition metal carboxylates as deprotonating agents to coordinated pyrazole molecules leads to the formation bi-, homo trinuclear - heterometallic complexes. It was found that interaction PhenPd(OOCMe)$_2$ (**1**) with Cu(Hdmpz)$_2$(OOCR)$_2$ or M$_2$(μ-dmpz)$_2$(Hdmpz)$_2$(OOCR)$_2$ (M = Zn, Co, R = Bu^t, Me, Ph, Hdmpz -3,5-dimethylpyrazole) formed complexes with metallocore Pd-Cu, Pd-Co, Pd-Zn$_2$. These complexes contain a fragment PhenPd (dmpz $_2$ which is an analogue of the chelating Phen or dipy, which was donates 4 electrons. Despite the fact that these fragments find in a free state has not been possible, their analogue, - complex PhenPd[(CF$_3$)$_2$pz]$_2$ was obtained by reacting 1 with 3,5-trifluoromethylpyrazole (**2**).

Similar reactions PhenM(OOCR)$_2$ (M = Zn, Cu, Co) leads depending on the nature of the transition metal, R, pyrazoles and reaction conditions to form *bis*-pyrazolate PhenM(pz)$_2$ or pyrazolate -carboxylates PhenM(pz)(OOCR) complexes. Thermolysis of the acetates of zinc, copper and cobalt in the presence Hdmpz (120C) are formed compounds are insoluble in organic solvents. Their protonation of the **2** gives pyrazole-pyrazolate mononuclear complexes M (Hdmpz)$_2$[(CF$_3$)$_2$pz]$_2$ (M = Zn, Cu (**3**), Co (**4**)). Reaction of **1** with **3** and **4** under mild conditions lead to pyrazolate-bridged complexes with the cores Pd-M:





Thus, these complexes can be used as building blocks to obtain more complex homo - heterometallic complexes and clusters as analogues Phen or dipy.

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QUANTUM CHEMICAL STUDY OF Au-CATALYZED REACTIONS OF SELECTIVE H-D EXCHANGE WITH THE SOLVENT IN QUERCETIN AND ITS OXIDIZED FORM

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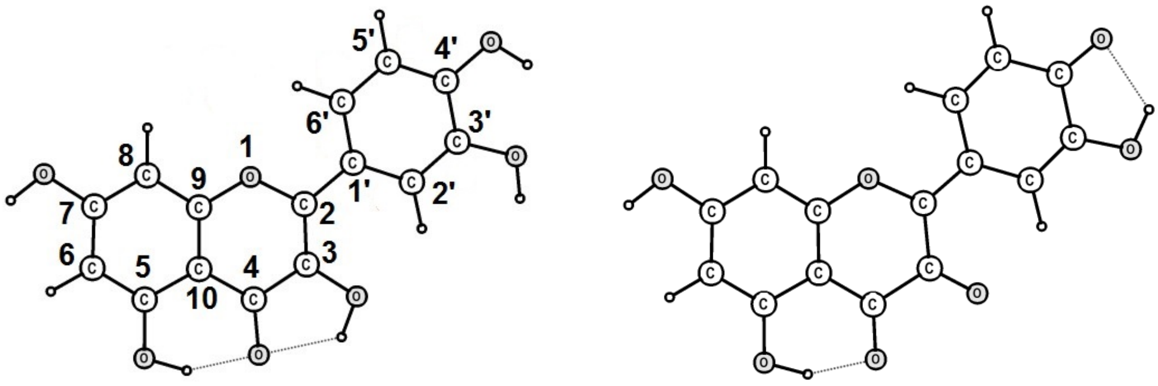
Experimental data [1] show that H–D exchange in solution D_2O – DMSO-d_6 (1:4) of quercetin QcH_2 and its oxidized form Qc occurs in 8-, 6- and 2’-positions (see *Fig.*). The exchange in the 2’-position takes place only in the presence of Au compounds. To understand the mechanism of reactions quantum chemical modeling was applied. All calculations have been performed by means of PRIRODA program using the nonempirical PBE functional and the extended basis set for SBK pseudopotential. It has been done using the facilities of Joint Supercomputer Center of the Russian Academy of Sciences. Calculation of the free energy of solvation was carried out in the Gaussian’03 program.



QcH_2 Qc

Figure

We investigated the energy profiles H–D exchange reactions in 8-, 6-, 2’-positions of QcH_2 and Qc without gold complexes by the relayed mechanism involving water molecules (mechanism **I**) and the mechanism of electrophilic substitution involving Au complex (mechanism **II**). The activation energy of reaction by mechanism **II** is significantly reduced (~10 kcal/mol) when compared with that of the mechanism **I** in both cases. Thus, the most probable mechanism of H–D exchange in QcH_2 and Qc with the solvent is **II**. The activation energy of reactions in the most favourable 8-position for QcH_2 is 8.5 kcal/mol and for Qc is 7.9 kcal/mol. All the results obtained for the relative yield of H–D exchange products are in agreement with experiment.

[1] A.F. Shestakov, A.V. Chernyak, N.V. Lariontseva, S.A. Golovanova, A.P. Sadkov, L.A. Levchenko, *Mendeleev Comm ,* **2013***, 23*, 98-100.

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Pd-POLYMER CATALYTIC SYSTEMS FOR CYANATION OF ARYL HALIDES WITH $K_4Fe(CN)_6$: ADAVANTAGES AND LIMITATIONS.

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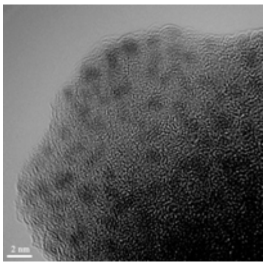
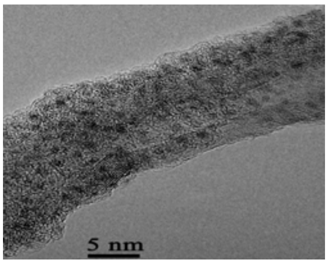
Catalytic cyanation of aryl halides with $K_4Fe(CN)_6$ is very efficient and convenient due to low toxicity of cyanation agent. However, it requires Pd catalyst. Three types of catalytic system for cyanation of aryl halides using $K_4Fe(CN)_6$ were investigated:

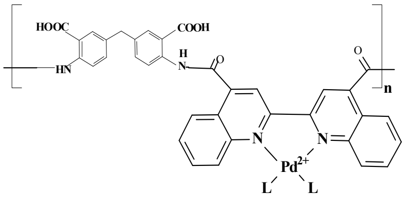
- Pd-polypyrrole nanocomposites (Pd/PPy) which were obtained via direct redox reaction between $Pd(NH_3)_4Cl_2$ and pyrrole;
- Carbon nanotubes with immobilized Pd nanoparticles covered with PPy matrix (Pd/PPy@CNt)
- Pd-polymer complexes (based on polyamic acids containing biquinolyl coordinating units).



Pd/PPy
d(PPy) = 28 nm, 34wt.% of Pd
d(Pd) = 1.4 nm,



Pd/PPy@CNt
d(Pd) = 1.6 nm 26 wt. % of Pd
thickness of PPy layer = 10 nm



L = NMP, CH_3CN

Pd-polymer complex based on polyamic acids

All three systems turned out to be active in cyanation of aryl halides with the use of $K_4Fe(CN)_6$ Pd/PPy can catalyze cyanation of a wide range of aryl halides, including arylchlorides. The reaction can be carried out with good to excellent yields of benzonitriles both in organic solvents (CH_3CN, NMP), and in water. In the latter case the catalyst was immobilized on the graphite felt, to facilite its separation from the reaction mixture.

Pd/PPy@CNt composites were less active in cyanatoin, probably due to fast sedimentation of their dispersion. However, prolonged heating of the reaction mixture (100°C, 20-25 hours) allowed to receive good yields for aryl iodides. Activation using microwave irradiation facilitates the reaction and allows to reduce reaction time up to 10-20 minutes. Due to the presence of nanotubes, the catalyst can be easily separated from the reaction mixture.

The Pd polymer (based on polyamic acids) complexes were obtained via Pd anode dissolution in the presence of polymer ligand. This system can be used as in organicsolvents and water. The yield of benzonitriles was 70-90%. MW irradiation, as well as thermal activation, can be used to speed up of reaction the former being more efficient

Acknowledgements. This work was supported by Russian Foundation for Basic Research (Project № 012-03-00797) and Russian President Foundation (Project № MK-7093.2012.3)

THE REVEAL OF REGULARITIES OF ORIENTATION EFFECT OF SUBSTITUENT ON THE SUBSEQUENT SUBSTITUTION IN POLYHEDRAL $[B_{12}H_{12}]^{2–}$ CLUSTER

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Reactions of the following monosubstituted derivatives of dodecahydro-*closo*-dodecaborate (2–) anion were studied.

♦Reaction of $[B_{12}H_{11}I]^{2–}$, $[B_{12}H_{11}OH]^{2–}$, $[B_{12}H_{11}OC(O)CH_3]^{2–}$ and $[B_{12}H_{11}SCN]^{2–}$ with acetic acid in the presence of oxygen and atmospheric moisture. The single-stage procedure of the hydroxy group introduction into monosubstituted $[B_{12}H_{12}]^{2–}$ anion derivatives without the formation of acetoxo derivatives was developed.

♦Reaction of $[B_{12}H_{11}I]^{2–}$, $[B_{12}H_{11}OH]^{2–}$, $[B_{12}H_{11}OC(O)CH_3]^{2–}$ and $[B_{12}H_{11}SCN]^{2–}$ with formic acid in an inert atmosphere.

♦Reaction of $[B_{12}H_{11}I]^{2–}$, $[B_{12}H_{11}OH]^{2–}$ and $[B_{12}H_{11}OC(O)CH_3]^{2–}$ with $(SCN)_2$ solution in dichloromethane in an inert atmosphere.

♦Reaction of $[B_{12}H_{11}I]^{2–}$, $[B_{12}H_{11}OH]^{2–}$, $[B_{12}H_{11}OC(O)CH_3]^{2–}$ and $[B_{12}H_{11}SCN]^{2–}$ with dimethyl sulfoxide in the presence of acetic anhydride in an inert atmosphere.

It was found for the reactions under consideration that substituents have the electron-seeking effect and decrease the reactivity of monosubstituted anions as compared to that of $[B_{12}H_{12}]^{2–}$.

The reactions under consideration were shown to have the regioselective character. The I, OH, $OC(O)CH_3$ and SCN substituents are *meta*-orientants with respect to the introduced OH, OC(O)H and $S(CH_3)_2$ groups and the OH, $OC(O)CH_3$ substituents are *meta*-orientants with respect to the introduced SCN group. In the case of the reaction of thiocyanogenation of monoiodosubstituted derivative of $[B_{12}H_{11}I]^{2–}$, the 1,12-$[B_{12}H_{10}I(SCN)]^{2–}$ *para*-isomer is formed.

It was found that the introduction of hydroxyl group into monosubstituted derivatives of $[B_{12}H_{12}]^{2–}$ increases substantially their water solubility as compared to that of non-substituted anion.

Data on the synthesis of disubstituted derivatives of cluster $[B_{12}H_{12}]^{2–}$ boron anion and on the orientation effect of substituents can be used in developing BNCT preparations in the case of two biologically active substituents introduced into the boron skeleton of molecule.

Acknowledgements -
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THE RESEARCH OF HYDROCARBON FRACTIONS COMPOSITION COMBUSTIONS UNDER THE ACTION OF CATALYSTS WITH ACTIVE METALOOXIDE ASSOCIATES

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The activity of zeolite catalysts modified with nine-nuclear pivalates of transition metals (Ni, Co, Fe) with heat treatment was studied. The presence of the oxygen (μ_3-O) and hydroxyl groups coordinated with metals in the structure of initial complexes promotes active metalooxide associates formation on the zeolite surface during termodestruction.

The catalyst modified with nine-nuclear pivalate complex of nickel was studied in low-temperature light naphtha elevation process. The reaction was carried out at 200°C in inert gas atmosphere. It is studied that desulphurization process with hydrogen sulphide gassing take place during the reaction. It is established that amount of total sulphur decrease from 1040 wppm to 89 wppm. The same results were obtained in case of cobalt and iron complexes. Experiments at high temperatures (300-500 ^{0}C) shows that naphtha undergoes catalytical combustions show in increased amount of liquid yield, decreased quality of total sulphur and cox.

Acknowledgements -

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10 GROUP PINCER HYDRIDES (^{t}BuPCP)MH (M=Pd, Ni): DIHYDROGEN BONDING AND PROTON TRANSFER REACTIONS

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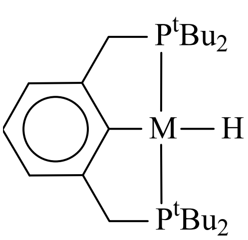
Over the last decades there is a great interest to protonation of transition metal hydrides. Both classical polyhydrides and complexes with molecular hydrogen have been established to be the products of the proton transfer process. Yet, protonation is the most convenient way to obtain η^2-H_2 complexes. However, most of these complexes of the Group 10 metals are very unstable. The key role of dihydrogen bonded intermediates (MH···HX) in formation of non-classical cationic hydrides was shown [1]. But still there is no enough information about the intermediates of the 10 group metal hydrides protonation [2].



In this work the interaction between tridentate pincer 10 group metal hydride complexes L_3MH (M = Ni, Pd, L_3 = 2,6-$(CH_2P(t\text{-}C_4H_9)_2)_2C_6H_4$ (PCP, and proton donors of different strength and nature (R^FOH = $(CF_3)_nCH_{3-n}OH$, n = 1÷3, indole, *p*-nitrophenols, $CpM(CO)_3H$) was studied by IR (ν_{MH}, ν_{CO} and ν_{OH}) and NMR (^1H, ^{31}P, ^{195}Pt) and UV-vis spectroscopy in a wide temperature range (190-290 K). The products and intermediates of the interaction were established. The peculiarities of their structure are revealed by DFT calculations. Kinetic and thermodynamic parameters of hydrogen bonding and proton transfer accompanied by H_2 evolution will be compared. Remarkable finding is the difference in the structure of the protonated reaction intermediate, which is the “traditional” η^2-H_2 species in case of ROH acids, but the unconventional $\mu,\eta^{1:1}$-H_2 species featuring an end-on coordination of dihydrogen between the two transition metals in case of MH acids.

Acknowledgements - this work was supported by the Division of Chemistry and Material Science of RAS and RFBR (11-03-01210, 12-03-33018), and CNR-RAS bilateral agreement.

[1] N. V. Belkova, E. S. Shubina, and L. M. Epstein, *Eur. J.Inorg. Chem.,* 2010, 3555.
[2] V. A. Levina, A. Rossin, N. V. Belkova, M. R. Chierotti, L. M. Epstein, O. A. Filippov, R. Gobetto, L. Gonsalvi, A. Lledós, E.S. Shubina, F. Zanobini, and M. Peruzzini, *Angew. Chem. Int. Ed.*, 2011, **50**, 1367.

CHEMICAL DESIGN OF CHALCOGEN-CONTAINING ORGANOMETALLIC CLUSTERS

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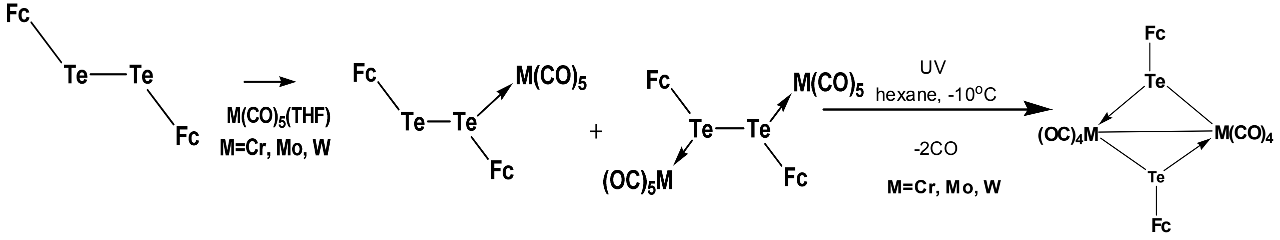
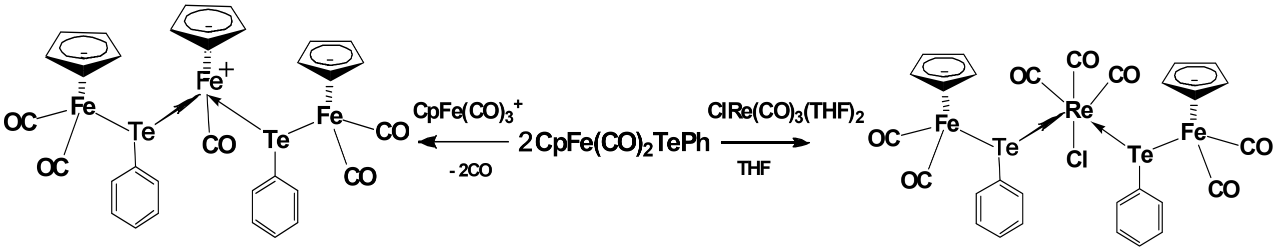
The chalcogen-containing organometallic complexes were used as ligands to complexes of different transition metals (M). X-Ray analyses data showed the common features: a) sharp shortening (from 0.15 to 0.3 A) of formally ordinary M-E bonds (E = S, Se, Te) and M-P bonds[1] compared to the covalent radii sum (CRS) [2] ; b) electron-compensating rearragment of clusters.

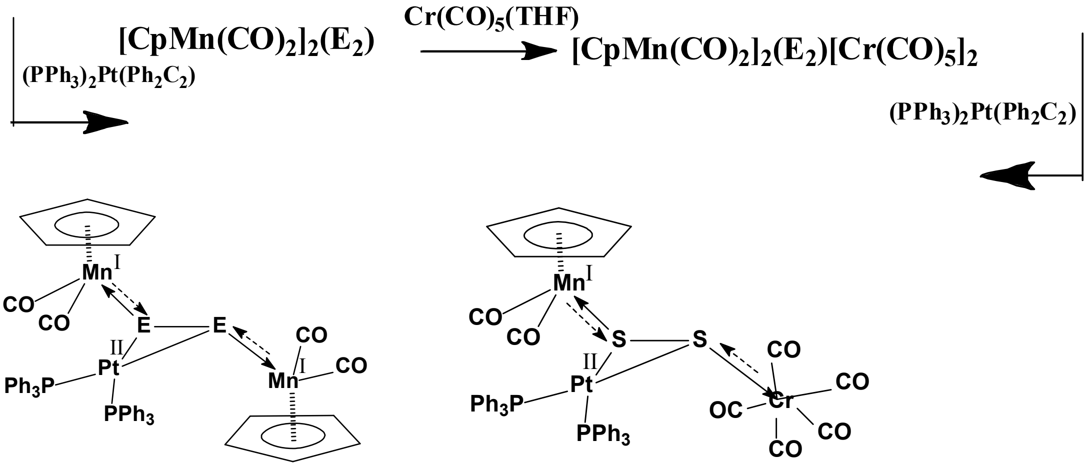
1. The coordination of Fc_2Te_2 (Fc – ferrocenyl) and dissociation of Te-Te bond:



2. The coordination of $CpFe(CO)_2TePh$.



3. The coordination and transmetallation of $[CpMn(CO)_2]_2E_2$ (E = S, Se, Te)



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[1]. A.A. Pasynskii , *Russ. J. Coord. Chem.*, 2011, Vol. 37, No. 11, p. 801
[2]. Cordero, B., Gomez, V., Platero-Prats, A.E., et al., *Dalton Trans.,* 2008, p. 2832

ORGANOTELLURIUM METALLILIGANDS AS A BUILDING BLOCKS

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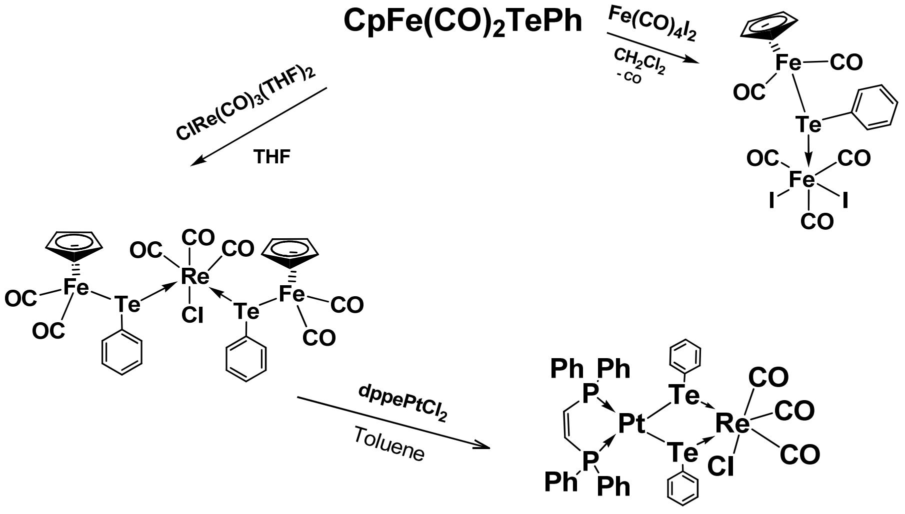
In this work we investigate the approaches to the directed synthesis of metal carbonyl-chalcogenide complexes as a precursors of inorganic materials using organotellurium metalliligands as a building blocks.



$CpFe(CO)_2TePh$ gives bimetallic complex $CpFe(CO)_2(\mu\text{-}TePh)Fe(CO)_4I_2$ on interaction with $Fe(CO)_4I_2$ and trimetallic 5-membered chain cluster $(CpFe(CO)_2(\mu\text{-}TePh))_2Re(CO)_3Cl$ on interaction with $Re(CO)_3(THF)_2Cl$.

In the homo-metallic $CpFe(CO)_2(\mu\text{-}TePh)Fe(CO)_2I_2$ both Fe-Te distances are shortened but not equal. $Fe_{(Cp)}$…Te distance (2.569 Å) is shorter than 2.612Å for Fe-Te distance of $Fe(CO)_3I_2$ fragment (and as compared to 2.617Å Fe-Te in the starting $CpFe(CO)_2TePh$ [2]. This results from the different back-donative ability of $\{CpFe(CO)_2\}$ vs $\{Fe(CO)_3I_2\}$ fragments.

Hetherometallic $(CpFe(CO)_2(\mu\text{-}TePh))2Re(CO)_3Cl$ reveals the same shortening of Te…Re (2.816 Å) (r(Re/Te)=2.89 Å),and Te…Fe (2.571 Å) distances.

Further treatment of $(CpFe(CO)_2(\mu\text{-}TePh))_2Re(CO)_3Cl$ with $dppePtCl_2$ eliminates $CpFe(CO)_2TePh$ ligand giving Pt/Re complex with two PhTe bridges.

The distance Te…Re (2.784 Å) is shorter than the sum of the covalent radii (r(Re/Te)=2.89 Å) and Pt…Te distance (2.632 Å) is shorter too compared with the sum of the covalent radii (r(Pt/Te)=2.74 Å).

[1] . B. Cordero, V. Gromez, A. E. Platero-Prats, M, Revres, J. Echeverrıa, E. Cremades, F Barragran and S. Alvarez // Dalton Trans., 2008, 2832–2838.

[2] Torubaev Yu.V., Pasynskii A.A., Skabitskii I.V.// Russian Journal of Coordination Chemistry. 2009. T. 35. № 5. C. 341-346.

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(CO)POLYMERIZATION OF VINYL MONOMERS IN THE PRESENCE OF IRON COMPLEXES

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Novel polymer materials are demanded in different areas of modern technology and industry. The synthesis of block-, graft- and brushed copolymers significantly increases the range of polymer properties and opens novel applications. The use of organometallic compounds for precise polymer synthesis is perspective division in modern polymer chemistry.

In this work the peculiarities of vinyl chloride (VC) polymerization in the presence of iron carbonyl complexes with different ligand environment ([$CpFe(CO)_2]_2$, $CpFe(CO)_2Br$, $CpFe(CO)_2Cl$] were investigated. Different organic halides (carbon tetrachloride, isoamyl iodide and ethyl-2-isobutyrate) were used as co-initiators. It was established that binuclear iron complex in conjunction with carbon tetrachloride act as initiator-regulator of VC polymerization. The poly(vinyl chloride) obtained in mentioned conditions may be further used as a macroinitiator for synthesis of copolymers with methyl methacrylate, styrene and vinyl acetate.

The graft-copolymers are perspective materials as their properties strongly demand on main and side chains length, composition and so on and thus may be changed in wide range. The graft copolymers of polystyrene with poly(methyl methacrylate) and poly(vinyl acetate) were synthethised in the presence of iron carbonyl complexes ([$CpFe(CO)_2]_2$, $CpFe(CO)_2Br$, $CpFe(CO)_2Cl$]) and with the use of Fe(0) with PPh_3 as a catalytic system. A brominated polystyrene obtained by Fridel-Krafts reaction was used as a macroinitiator. The efficiency of monomer graft and yield were measured and compared. It was shown that the most effective system for methyl methacrylate graft polymerization was one based on $CpFe(CO)_2Br$. The best results for synthesis of poly(vinyl chloride) – polystyrene and polystyrene – poly (vinyl acetate) were obtained in the presence of binuclear iron complex.

The molecular weight parameters, composition and some physico-chemicals properties of obtained copolymers were measured.

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THE REACTIVITY OF NON-TRANSITION METAL O-AMIDOPHENOLATE COMPLEXES TOWARDS ALKYL HALIDES

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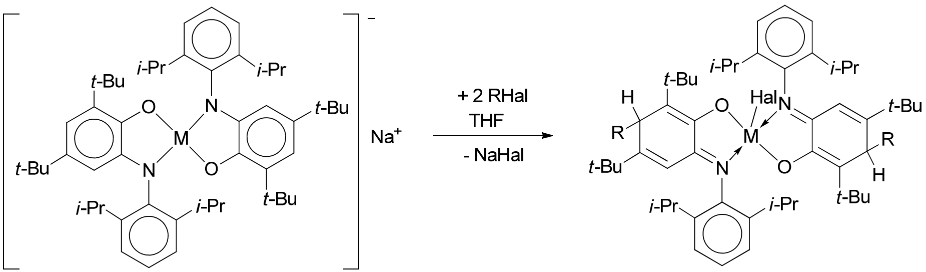
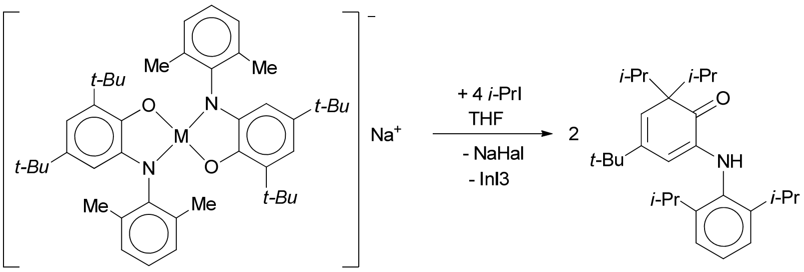
The search of new highly selective reactions of C-C bond formation is one of the primary goals in the organic chemistry. In present time it is achieved quite effectively by using of metal complex catalysis. The noble transition metal (Pd, Rh, Pt, etc.) derivatives play a dominant role in catalytic carbon-carbon (or carbon-heteroatom) bond formation. It can be explained by the ability of such compounds to participate readily in one-step two-electron transfer processes which are elementary steps of numerous transition metal catalyzed transformations. The complexes of the first-row transition metals are mostly characterized by one-electron transformations and have a less application in homogeneous catalysis. It is true for main group metal compounds for which the processes of electron transfer are unusual at all. The problem of inactivity of these elements in multiple electron transformations may be solved by means of the insertion of redox active ligands in their coordination sphere.

The present work is the investigation of potential participation of non-transition metal complexes containing redox active ligands in the cross-coupling reactions, in particular the possibility of alkyl halides activation by such type compounds. The non-transition metal complexes of the type [AP_2M]Na were found to react readily with different alkyl halides (Scheme). The reaction proceeds at mild conditions and leads to new metal derivatives containing iminocyclohexa-1,4-dienolate ligands. The reaction involving indium complexes with less hindered o-amidophenolate ligands leads to deeper alkylation of the forming redox active ligand.



[AP_2M]Na

M = Ga, In
R = Me, Et, i-Pr, Bn, All
Hal = Cl, Br, I



Acknowledgements - We are grateful to the FSP ‘‘Scientific and Scientific-Pedagogical Cadres of Innovation Russia’’ for 2009–2013 years (GK 8465), Russian Foundation for Basic Research (grant 13-03-97048-r_povolzh’e_a), Russian President Grants (NSh-1113.2012.3) for financial support of this work.

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NORBORNENE-BASED SILICON-CONTAINING POLYMERIC MATERIALS. SINTHESIS, LUMINESCENT PROPERTIES

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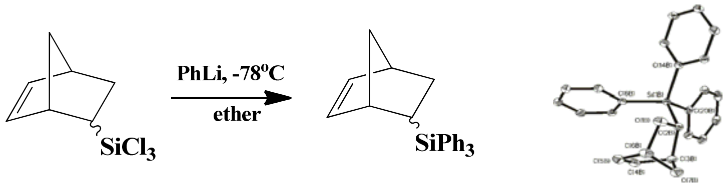
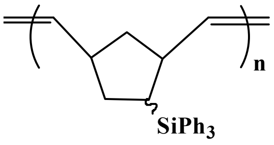
The norbornene derivative with Ph_3Si functional group was synthesized and structurally characterized.

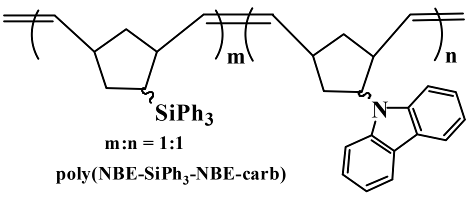


The obtained functionalized norbornene monomer was found to enter into ROMP reactions and produce the silicon-containing polymeric materials.



poly(NBE-SiPh$_3$)

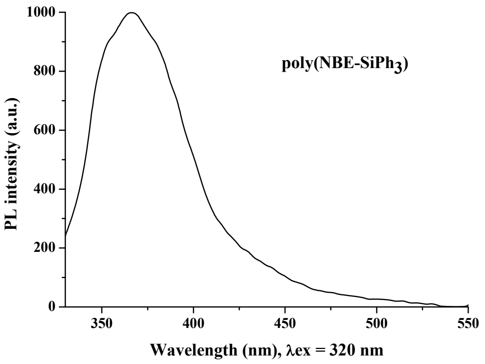
M_w = 41000
PDI = 2.2
T_g = 170°C

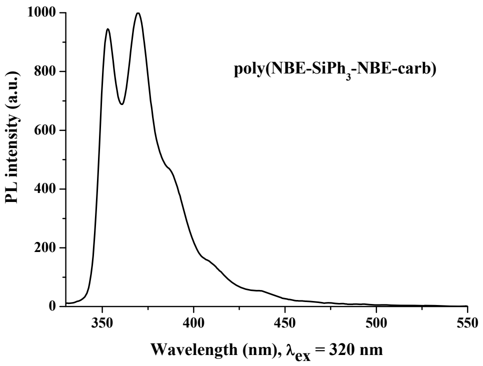


m:n = 1:1
poly(NBE-SiPh$_3$-NBE-carb)

M_w = 31100
PDI = 1.8
T_g = 158°C

Photophysical properties of the synthesized compounds were investigated. The monomer compound and polymeric materials were found to reveal photoluminescence (PL) of blue color.





The relative PL quantum yields of NBE-SiPh$_3$ (6%), poly(NBE-SiPh$_3$) (7%) and poly(NBE-SiPh$_3$-NBE-carb) (14%) were determined in CH_2Cl_2 at room temperature (reference - anthracene in EtOH (Ø =27%)).

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THE COMPLEXES OF MAIN GROUP METALS BEARING REDOX ACTIVE LIGANDS: THE REVERSIBLE BINDING OF O_2 AND NO

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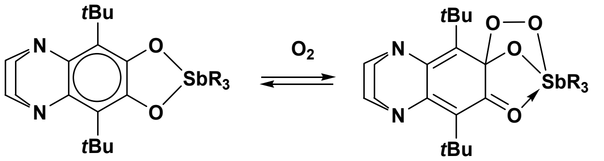
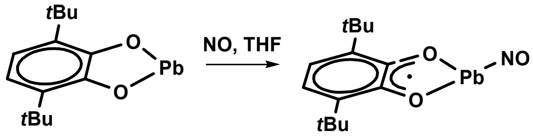
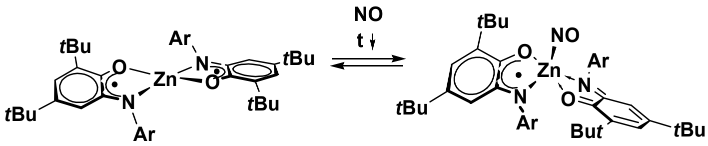
It is well known that both molecular oxygen and nitrogen oxide(II) play an important role in chemical and biochemical processes. Until recently, the range of compounds capable of fixing these small molecules was limited almost completely to transition metal compounds. Until recently main group metal complexes capable to reversible binding of O_2 and NO were not known. The combination of nontransition metal with redox-active ligand allows to construct the system which will be able to model the chemical behaviour of transition metal complexes. We have found that antimony(V) o-amidophenolates and some catecholates react reversibly with molecular oxygen in mild conditions to yield spiroendoperoxides [1]. This ability is affected by the redox-properties of O,O- or O,N-chelating redox-active ligands as well as the acceptor/donor/shielding properties of substituents at the central antimony atom [1,2].

The II group metal catecholates are easily oxidized by NO to corresponding o-semiquinonato-nitrosyl derivatives which are detectable by EPR [3]. At low temperature zinc(II) and cadmium(II) bis-o-semiquinolates/o-iminosemiquinolates react reversibly with NO in toluene/hexane solution to give corresponding (SQ)(Q)M(NO) complexes.







[1] A.I. Poddel’sky, I.V. Smolyaninov, Yu.A. Kurskii, G.K. Fukin, N.T. Berberova, V.K. Cherkasov, G.A. Abakumov, *J. Organomet. Chem.*, **2010**, *695*, 1215-1224.
[2] G.K. Fukin, E.V. Baranov, A.I. Poddel´sky, V.K. Cherkasov, G.A. Abakumov, *ChemPhysChem*, **2012**, *13*, 3773-3776.
[3] E.V. Ilyakina, A.I. Poddel’sky, V.K. Cherkasov, G.A. Abakumov, *Mendeleev Commun.*, **2012**, *22*, 208-210.

Acknowledgements - We are grateful to the Russian Foundation for Basic Research (grants N 13-3-01022, 11-03-00389, 12-03-31367, 12-03-31026, 13-03-97048 r_povolzh’e_a), President of Russian Federation (grants NSh-1113.2012.3) for financial support of this work. This work was made according to FSP “Scientific and scientificpedagogical cadres of innovation Russia” for 2009e2013 years (Contract 8465 from 31.08.2012).

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SEMIQUINONATE AND CATEHOLATE METAL COMPLEXES WITH FORMAZAN LIGANDS

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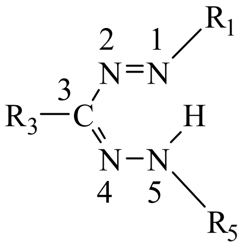
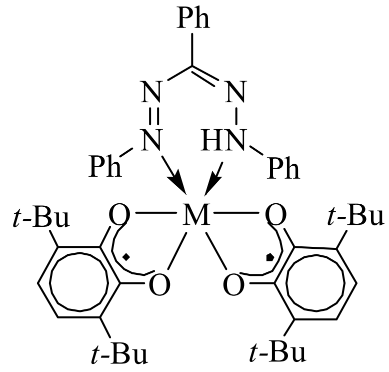
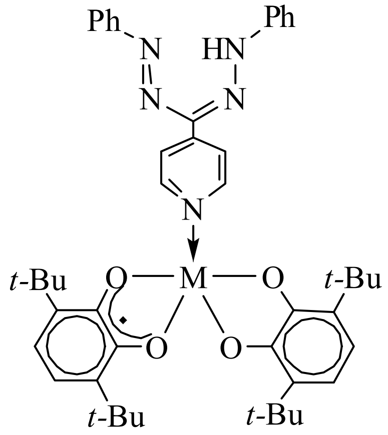
Formazanes are the compounds which contain the characteristic azo-hydrazone bond system. They are known as the chelating π-conjugated N-donor ligands. The denticity of those ligands may be controlled by means of variation of substituents (R_1, R_2, R_3) and inclusion of additional complexing groups. Owing to this fact formazanes hold promise in the preparation of molecularly designed metal complex systems. Formazanes and their metal complexes are widely used in chemistry as analytical reagents, environmentally-friendly colorants, solar cells and thermosensitive elements.



Formazane



M = Co^{II}, Mn^{II}, Fe^{II}



M = Co^{III}, Mn^{III}

In the present work we have synthesized a series of 3,6-di-*tert*-butyl-*o*-benzosemiquinonato cobalt and manganese complexes with formazan ligands (such as 1,3,5-triphenylformazane, 3-(4'-pyridyl)-1,5-diphenylformazane, 1-(2,6-dimethylphenyl)-3-(4'-pyridyl)-5-phenylformazane, 5-(4'-fluorophenyl)-1,3-diphenylformazane, 5-(4'-iodophenyl)-1,3-diphenylformazane). Complexes were characterized by IR, NIR spectroscopy and elemental analysis. Magnetic susceptibility measurements carried out for cobalt and manganese complexes with 1,3,5-triphenylformazane and 3-(4'-pyridyl)-1,5-diphenylformazane have shown that cobalt complexes contain the metal in low-spin state, whereas it is in the high-spin state in the corresponding manganese compounds.

Acknowledgements - We are grateful to RFBR (N 2013-3-01022, 13-03-00891 and 12-03-31367 mol_a), President of Russian Federation (Grant NSh-1113.2012.3) for financial supporting of this work. This work was performed in the accordance with FSP (contract N8465 from 31.08.2012).

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COMPLEXES OF REDOX-ACTIVE RIGID QUINONEIMINE LIGAND (DPP-QIAN)

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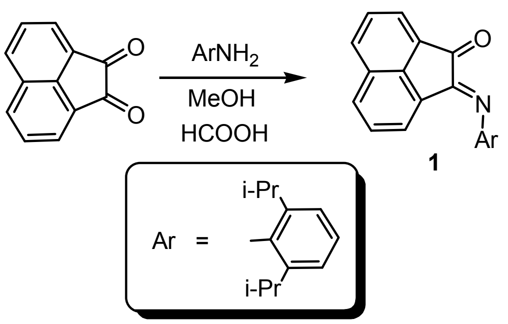
Acenaphthene-1,2-quinoneimine (dpp-QIAN, **1**) was obtained by partial condensation of 2,6-diisopropylaniline with acenaphthenequinone (Scheme 1).



Scheme 1. Synthesis of acenaphthene-1,2-quinoneimine (**1**).

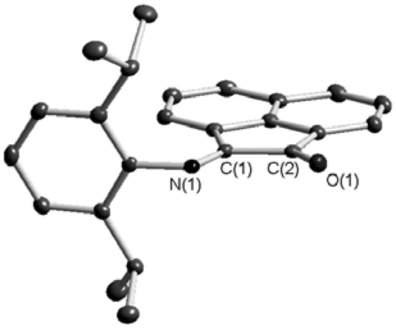


Fig. 1 The crystal structure of compound **1**

Crystals of compound **1** suitable for X-ray diffraction were obtained from Et_2O. Due to steric constraints of i-Pr-groups there is no rotation of aryl substituent along C_{ipso}–N bond. Therefore, the most favourable orientation of the aryl substituent is an orthogonal orientation relative to the acenaphthene plane (Fig. 1).

Magnesium complexes with 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-BIAN) are the most studied. Similarly we have carried reduction dpp-QIAN with magnesium metal in THF. The reaction product (dpp-QIAN)Mg$(THF)_3$ (**2**) was isolated as blue-green crystals with the yield of 80%. Complex **2** reacts with allyl bromide with the formation of the adduct which structure was proved clearly by ^1H-^1H COSY NMR spectroscopy. In contrast to (dpp-BIAN)Mg$(THF)_3$ the complex **2** does not react with phenylacetylene and benzophenone. The product of the reaction of dpp-QIAN with the metallic europium was isolated as deep-green crystals. X-ray diffraction studies proved the tetrameric structure of aimed complex $[(QIAN)Eu]_4(THF)_4(DME)$.

The reduction of the dpp-QIAN with excess of sodium and potassium accompanied with change of color of the reaction mixture. Complexes (dpp-QIAN)$Na_4(THF)_n$ and (dpp-QIAN)$K_4(THF)_n$ were isolated as orange and brown crystals. The attempts of reducing of dpp-QIAN with calcium and samarium led to the formation of intensively coloured solutions, but no crystalline products were isolated. Also, we carried the reactions with various chlorides, i.e. $ZnCl_2$, $GaCl_3$. The reaction of dpp-QIAN with zinc chloride (II) give [(dpp-QIAN)$ZnCl_2]_2$ which was isolated as orange crystals stable in air. For one's turn gallium chloride (III) reacts with dpp-QIAN with the formation of bisligand complex [(dpp-QIAN)$_2GaCl_2]^+[GaCl_4]^-$. It is known that symmetrical dpp-BIAN and gallium chloride (III) forms an ionic complex [(dpp-BIAN)$GaCl_2]^+[GaCl_4]^-$.

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SYNTHESIS AND LUMINESCENCE PROPERTIES OF POLYMERIC TERBIUM COMPLEXES WITH PYRAZOLONATE LIGANDS

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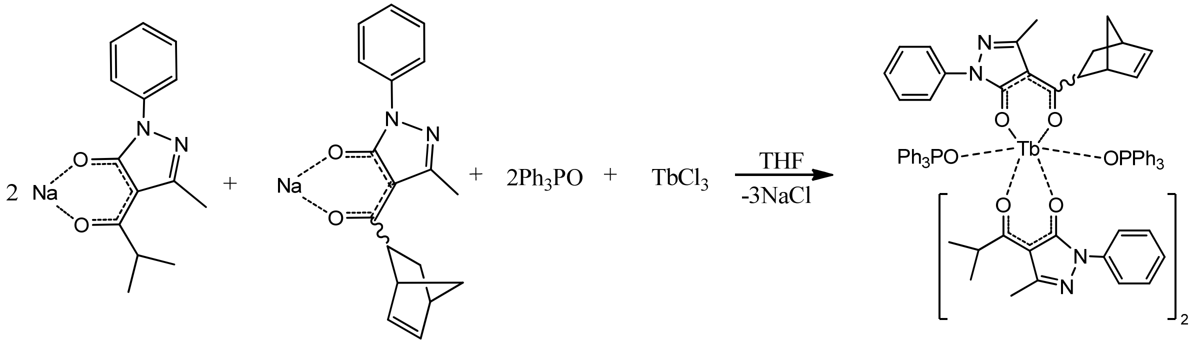
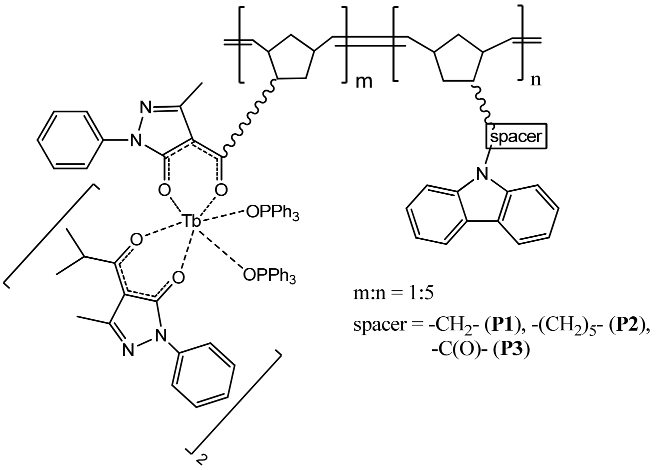
The new heteroligand terbium complex Tb(PMIP)$_2$PyrNBE·2Ph$_3$PO was prepared by reaction of terbium chloride with sodium salts of PMIP (4-isobutyryl-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one) and PyrNBE (4-(bicyclo[2.2.1]hept-5-ene-2-carbonyl)-3-methyl-1-phenyl-1H-pyrazol-5(4H)-one) in the presence of triphenylphosphine oxide:



Tb(PMIP)$_2$PyrNBE·2Ph$_3$PO

The resulting compound was isolated in yield 91% and characterized by IR spectroscopy and elemental analysis. Photoluminescence (PL) spectra of the complex in solution and thin film consist of emission bands of Tb^{3+} ion. The polymeric terbium complexes **P1**-**P3** was prepared by metathesis copolymerization of Tb(PMIP)$_2$PyrNBE·2Ph$_3$PO with carbazole-functionalized norbornene monomers:



m:n = 1:5
spacer = -CH$_2$- (**P1**), -(CH$_2$)$_5$- (**P2**),
-C(O)- (**P3**)

The copolymerization reactions were carried out at room temperature and completed in 6-8 hours. Polymeric complexes were isolated in high yields (83-92%) and characterized by elemental analysis, IR, GPC, DSC (M_w= (2.1-3.8)·10^4, PDI = 1.29-1.80, Tg = 156-172°C). They exhibited metal-centered emission in PL and electroluminescent spectra. The OLED device with the configuration of ITO/**P1**/BATH/Alq$_3$/Yb produced green light with the maximum brightness of 70 cd/m^2.

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SYNTHESIS, STRUCTURES AND SOME PROPERTIES OF LANTHANIDE 4-ACYLPYRAZOLONATE COMPLEXES

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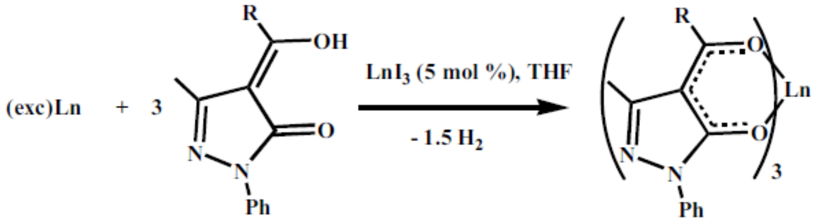
It was found that 4-acylpyrazolones R-PMPH (R = Pr^i, Bu^t, $CHEt_2$) react with metallic lanthanides in THF solution in the presence of catalytic amount of LnI_3 and form lanthanide pyrazolonates $Ln(R\text{-}PMP)_3$ in almost quantitative yields:



Ln = Y, Pr, Nd, Gd, Tb, Ho, Er, Tm

The compounds $Ln(R\text{-}PMP)_3$ (R = Pr^i, Bu^t, $CHEt_2$) were found to sublime in vacuum (10^{-3} Torr) without decomposition in the temperature range of 230-270°C. Single crystal X-ray analyses of the sublimed complexes $Ln(R\text{-}PMP)_3$ (R = Pr^i, Bu^t) revealed dimmers $[Ln(R\text{-}PMP)_3]_2$ in which rare-earth metals are bridged by pyrazolonate units. The coordination environment of the metal atoms can be described as distorted monocapped trigonal prism.

Novel 4-perfluorobenzoylpyrazolone Ph^F-PMPH was synthesized in 80% yield by the reaction of 1-phenyl-3-methyl-5-pyrazolone with pentafluorobenzoyl chloride in THF solution in the presence of calcium hydroxide. The 4-acylpyrazolone Ph^F-PMPH reacts with lanthanide amides $Ln[(Me_3Si)_2N]_3$ (Ln = Eu, Tb, Yb) and forms the lanthanide pyrazolonates $Ln(Ph^F\text{-}PMP)_3$ in high yields.

All the synthesized compounds were characterized by elemental analysis and IR spectroscopy. The diamagnetic yttrium and lutetium derivatives have been also studied by NMR.

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BIVALENT IRON, COBALT AND NICKEL COMPLEXES OF 1,10-PHENANTHROLINE AND 2,2′-BIPYRIDYL WITH THE *CLOSO*-BORATE ANIONS $B_nH_n^{2-}$ (n = 10, 12)

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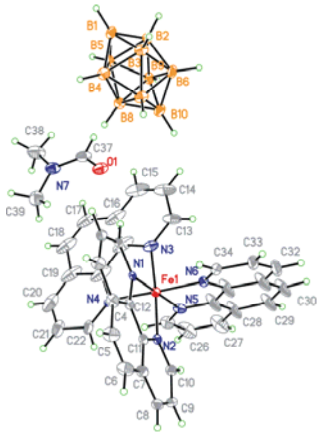
Complexes of general formula $[M^{II}L_3]B_nH_n \cdot xH_2O$ (M^{II} = Co or Ni; L = *phen* or *bipy*; n = 10, 12; x = 1, 2) identified by elemental analysis and IR-spectroscopy are known [1-3]. Thus, nickel(II) complexes $[NiL_3]B_nH_n$ was obtained by interaction of water solutions of $NiCl_2$ with $Cs_2B_nH_n$ (n = 10, 12) with azaheterocyclic ligands L solved in ethanol [1]. The same cobalt(II) complexes $[CoL_3]B_nH_n$ was obtained when $(H_3O)_2B_nH_n$ was allowed to react with $Ba(OH)_2$ and the obtained barium *closo*-borate interacts with sulfates of the corresponding metals and then with ligands [2-3]. All the mentioned complexes were obtained as precipitates from H_2O / C_2H_5OH solutions and could not be prepared in crystalline form. This procedure for synthesis of the complexes is not convenient because it requires preparation of the corresponding acids $(H_3O)_2B_nH_n$ from $(Et_3NH)_2B_nH_n$ by anion exchange column and then isolation of the corresponding cesium or barium salts. At the same time, syntheses from $(Et_3NH)_2B_nH_n$ are preferable because in this form the *closo*-borate anions are obtained from decaborane-14.

In this work we prepared a number of M(II) complexes (M = Fe, Co, Ni) with the *closo*-borate anions and *phen* or *bipy* $[M^{II}L_3]B_nH_n$. The obtained complexes were investigated by elemental analysis, IR- and UV-spectroscopy, X-ray crystallography. We broadened the list of complexes by preparation of iron(II) complexes that had not been mentioned in the literature. The complexes were prepared in CH_3CN or DMF solutions by the simple one-step reactions when $(Et_3NH)_2B_nH_n$ was allowed to react with MCl_2 (M = Fe, Co, Ni; n = 10, 12) in the presence of 3 equiv. of *phen* or *bipy*. In this case, the obtained complexes formed as monocrystals useful for X-ray diffraction analysis. Structure of $[Fe\textit{phen}_3]B_{10}H_{10} \cdot DMF$ is presented in the picture.



According to the obtained data, all the compounds contain cationic complexes $[ML_3]^{2+}$ (M = Fe, Co, Ni) and *closo*-borate anions as counterions. In some cases, BH-groups form specific interactions wih H-atoms of the solvent molecules presented in crystals. The obtained complexes are interesting from the point of view both of inorganic and bioorganic chemistry.

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[2] A. Kayumov, K. Solntsev, L. Goeva, et al., *Russ. J. Inorg. Chem.*, **1988**, *33*(*8*), 1936-1942.

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REVERSIBLE BINDING OF MOLECULAR OXYGEN TO CATECHOLATE AND AMIDOPHENOLATE COMPLEXES OF SB(V): ENERGY ASPECTS

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Recently, it was found that catecholate and amidophenolate complexes Sb(V) can reversibly binding of molecular oxygen [1, 2]. We have shown, that ability of these complexes to bind oxygen depends on electronic (-5.09 эВ (inert) <E_{HOMO} < -5.06 эВ (inert)) and steric factors (G< 90%) [3, 4]. Herein we would like to focus out attention to energy aspects reactions of such type. DFT calculations have been performed for Sb(V) (1) (*p*-F-Ph)$_3$Sb(3,6-Bu^t-Cat), (2) (*p*-Me-Ph)$_3$(6-Br-3,5-Bu^t-Cat)Sb, (3) (*p*-Me-Ph)$_3$(6-Cl-3,5-Bu^t-Cat)Sb, (4) Ph$_3$SbCat, (5) Ph$_3$(3,6-Bu^t-Cat)Sb, (6) (*o*-Me-Ph)$_3$(3,6-Bu^t-Cat)Sb, (7) (*p*-Me-Ph)$_3$(3,6-Bu^t-Cat)Sb, (8) Ph$_3$(3,6-Bu^t-4,5-N$_2$C$_4$H$_6$-Cat)Sb, (9) Ph$_3$(3,6-Bu^t-4-OMe-Cat)Sb, (10) Ph$_3$(3,6-Bu^t-4,5-OMe-Cat)Sb, (11) Ph$_3$(2,6-Pr^i-Ph-AP)Sb, (12) (*o*-Me-Ph)$_3$(2,6-Pr^i-Ph-AP)Sb, (13) Ph$_3$(2,6-Me-Ph-AP)Sb, and $[R_3SbCat\cdot O_2]_{vdw}$, $[R_3SbCat\cdot O_2]_{ts}$, $[R_3SbCat\cdot O_2]_{sp}$ complexes (Figure 1). It was shown, that evaluation of ΔE_{A1}, ΔE_{A2}, ΔE_{R1}, ΔE_{R2}, allows to explain behavior the complexes relative to oxygen (-7.023(act.) < ΔE_{R1} < -4.365(in.), -4.962(act.) < ΔE_{R2} < -2.278(in.) kcal / mol). Besides we have analyzed the energy of intramolecular interactions for $[R_3SbCat\cdot O_2]_{vdw}$ complexes according R. F. W. Bader theory. These criteria allow to evaluate the activity of Sb(V) complexes in reactions reversible binding of molecular oxygen.

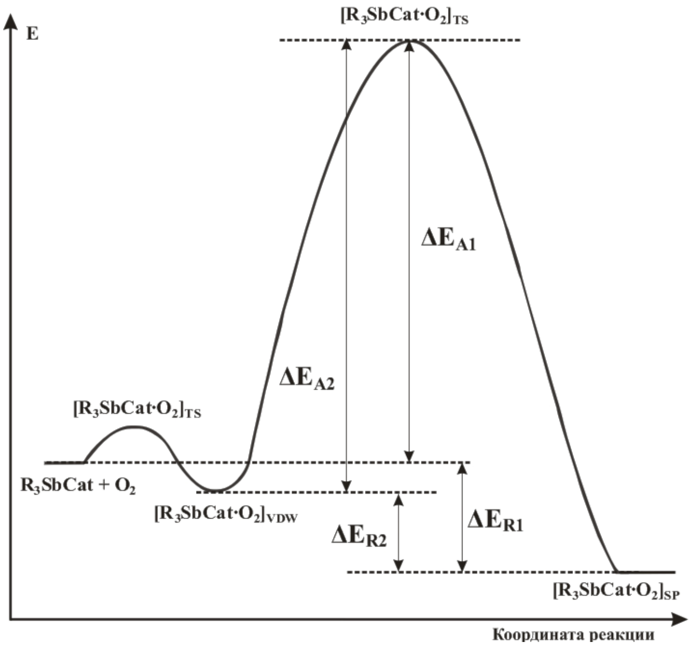

Figure 1. Reaction scheme
vdw и sp – van der Waals and spiroendoperoxide complexes , ts – transition state

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SYNTHESIS AND PROPERTIES OF 2-HETARYL-3-HYDROXYBENZOIC ACID ESTERS

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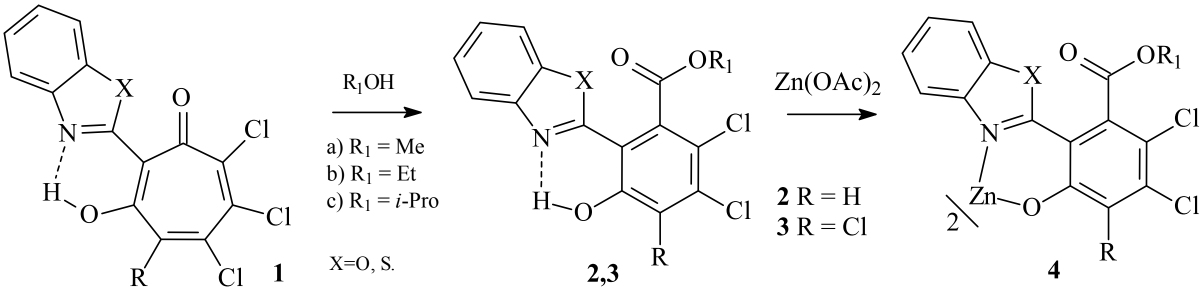
The interaction of 2-methylbenzoxo(thia)zoles with *o*-chloranyl leads to 2-hetaryl-2-yl-substituted 1,3-tropolones **1**. The structural peculiarity of 1,3-tropolones **1** is the presence of a strong intramolecular hydrogen bond in the six-membered chelate ring. In most of the cases the proton signal of the OH group in the ^{1}H NMR spectra is present in the weak field (18-20 ppm in the form of a broad singlet), that correlates with the strength of the O-H···N hydrogen bond. According to the X-ray data the distance O – N comprises 2.480 - 2.534 Å. As a result, the classic complex formation reactions of the compounds **1** with transition metal ions are virtually impossible.

We determined that boiling of 1,3-tropolones **1** in alcohols (MeOH, EtOH, *i*-PrOH) is accompanied by isomerization with formation of derivatives of 3-hydroxybenzoic acid esters **2**,**3** (**Scheme** 1).

Scheme 1



The solutions of compounds **2**,**3** demonstrate an intensive luminescence and we determined the spectral absorption and fluorescent properties of 2-(2'-hydroxyphenyl))benzoxazoles **2**,**3**. Under irradiation of 2-(2'-hydroxyphenyl))benzoxazoles **3a-f** in heptane (λ_{irr}=365 nm) at T=293 K there occurs an excited-state intramolecular proton transfer (ESIPT) O−H…N → O…H−N (from enol form to keto form), which results in formation of an emitting NH-structure in the excited state. The quantum yields of fluorescence are 0.18 – 0.20 for **2**,**3**. We are synthesized Zn(II) complexes on the base of 2-(2'-hydroxyphenyl))benzoxazol ligands **2**,**3**. The structures of the obtained compounds **1**-**4** are confirmed by elemental analysis, and NMR ^{1}H, IR-spectroscopy, and mass-spectrometry data. The molecular structures of the key compounds are determined by x-ray methods.

Acknowledgements – The work was financially supported by the grants of the President of the Russian Federation (grant Nos. MK-4215.2012.3 and NSh-927.2012.3), by the Russian Foundation for Basic Research (project no. 12-03-31491-mol-a, 12-03-31285-mol-a) and by the RAS presidium programme “Development of the methods of obtaining new chemical substances and creation of new materials”.

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PGSE NMR STUDY OF TRIPHENYLANTIMONY(V) CATECHOLATES INTERACTION WITH SMALL MOLECULES IN SOLUTION

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Pulsed Gradient Spin Echo (PGSE) Nuclear Magnetic Resonance is the method for determining mobility of molecules in liquid by NMR. Using Pulsed Field Gradients (PFG) in conjunction with specific NMR pulse program leads to attenuation of NMR signals proportionally to molecules mobility in a solution. This mobility relies on diffusion coefficient which is dependent on hydrodynamic radius of molecule, viscosity of solvent and temperature - the properties of dissolved molecule and its surrounding environment. The analysis of resulting PGSE and Diffusion Ordered SpectroscopY (DOSY) NMR spectra isn’t straightforward but processing the series of obtained spectra lets to quantitatively determine molecules interactions in solution.

Triphenylantimony(V) catecholates attracts considerable interest due to their ability of reversible oxygen binding and some other promising properties. According to X-Ray studies antimony(V) catecholates are often contain small molecules of solvent in crystal phase, but is this interaction observable by diffusion NMR in solution? Is it possible to determine quantity of interacting molecules by NMR? In this work we have applied 1D PGSE and 2D DOSY methods to study the interaction of triphenylantimony(V) catecholates with various small molecules (diethyl ether, THF, pyridine, acetone) in solution. Obtained diffusion coefficients and their dependence on concentration, molecular weight and nature of interacting molecules is discussed.

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NANOMETALLOCARBOSILANES AND ORGANOELEMENTOXANES AS ORGANOMETALLIC PRECURSORS OF PROMISING CERAMIC COMPOSITES COMPONENTS

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One of the most promising approaches to the creation of modern nanostructured ceramic materials with specific properties (high strength, high temperature and oxidation resistant ceramic composites) is to use preceramic oligomers and polymers as starting materials. The authors have developed highly efficient methods of synthesis and studied the characteristics of the molecular structure of preceramic organometallic poly(oligo)mers - nanometallocarbosilanes [1,2] and organoelementoxanes [3-5]. The process of introducing nanoparticles of refractory and magnetic metals, homogeneous distribution of the particles in a nonmagnetic carbosilane matrix was investigated. The processes of thermochemical transformation of the synthesized nanometallocarbosilanes samples into silicon carbide SiC, modified by nanoparticles of refractory compounds (Zr; Hf; Ta) or magnetic metals (Fe; Co); organoalumoxanes in corundum α-Al_2O_3, organoalumoxansiloxanes into mullite $3Al_2O_3{\bullet}2SiO_2$, organoyttriumoxanalumoxanes into the ceramic composition $Al_2O_3{\bullet}Y_2O_3$ (particularly YAG $5Al_2O_3{\bullet}3Y_2O_3$) and organoyttriumoxanalumoxansiloxanes in the ceramic composition: $Al_2O_3{\bullet}Y_2O_3{\bullet}SiO_2$ were studied. It is known that SiC is a very tough, durable material that is thermally and chemically resistant, its sintering requires high temperature and pressure. The use of sintering additive $Al_2O_3{\bullet}Y_2O_3$ or $Al_2O_3{\bullet}Y_2O_3{\bullet}SiO_2$ reduces the sintering temperature and allows us to obtain a dense ceramic material for constructional purposes. The introduction of cobalt ferrite nanoparticles in polycarbosilane space was studied. Calcinating of a composite to 800°C resulted in polycarbosilane transformation in amorphous silica in which volume cobalt ferrite nanoparticles were localized. By means of TEM and XRD methods, we demonstrated that nanoparticles represent cobalt metal with cubic structure. The cobalt ferrite nanoparticles were found to have the average size of 20 nm. Based upon the foregoing data we suggest that the composite has the properties of a weak ferromagnetic [6].

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SYNTHESIS OF A NEW N,N – BINAPHTYL – 1,4 – DIAZA-1,3 – BUTADIENE AND STUDY OF ITS REDOX REACTIONS.

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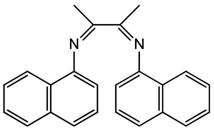
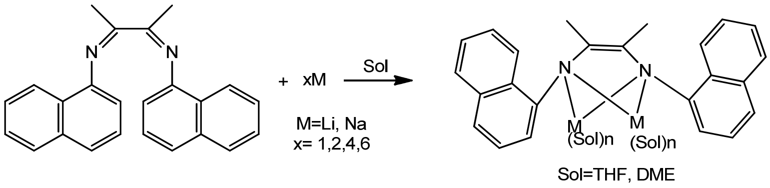
N,N – binaphtyl – 1,4 – diaza-1,3 – butadiene (**1**) was synthesized according to the standard procedure consisting in a condensation reaction between α-naphtylamine and 2,3-butanedione in methanol catalyzed by formic acid in 60% yield.

N, N – binaphtyl – 1,4 – diaza-1,3 – butadiene is an interesting object due presence of naphthalene and NCCN fragments which can accept up to 6 electrons (Scheme 1).



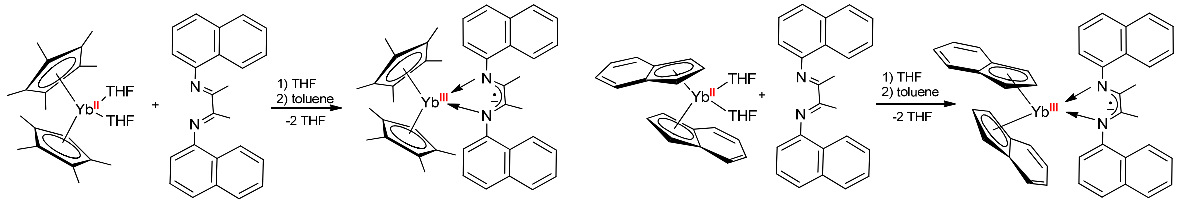
Scheme 1.

The reactions of (**1**) with varying amounts of alkali metals were investigated. The complete dissolution of metals occurred in these reactions. However, regardless the molar ratio of the reactants (1:2, 1:4, 1:6) only dianionic species has been isolated $[C_{10}H_7NC(CH_3)C(CH_3)NC_{10}H_7]^{2-}M_2^{+}(Sol)_n$ (M = Li, Na; Sol = THF, DME). Furthermore, the trials to obtain a monoanionic form of **1** afforded a mixture of dianionic species and neutral **1** (Scheme 2).



Scheme 2.

At the same time reactions of ytterbocenes $(\eta^5\text{-}C_5Me_5)_2Yb(THF)_2$ and $(\eta^5\text{-}C_9H_7)_2Yb(THF)_2$ with **1** proceeds with the one-electron oxidation of the metal atom and lead to the formation of sandwich complexes Yb(III) containing monoanionic diazabutadiene ligand (Scheme 3).



Scheme 3.

Thus, reactions of N,N – binaphtyl – 1,4 – diaza-1,3 – butadiene with alkali metals in various ratios lead to the formation of dianionic form of diazadiene, while the reactions of ytterbocenes $(\eta^5\text{-}C_5Me_5)_2Yb(THF)_2$ and $(\eta^5\text{-}C_9H_7)_2Yb(THF)_2$ with **1** proceed with the one-electron oxidation of the metal atom and lead to the formation of a sandwich complex Yb(III) containing monoanion diazabuthadiene ligand.

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CARBORANE TUNING PHOTOPHYSICAL PROPERTIES OF PHOSPHORESCENT IRIDIUM(III) COMPLEXES

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Phosphorescent iridium(III) complexes have been intensively studied for more than 10 years because of their remarkable photophysical properties and various optoelectronic applications[1-3]. To date, they have been widely applied in organic light-emitting diodes (OLEDs), light-emitting electrochemical cells, chemosensors, and bioimaging. Considerable efforts have been devoted to synthesis of highly performed neutral and cationic iridium(III) complexes with tuneable and improved phosphorescent properties through the proper choice of the coordinated ligands.

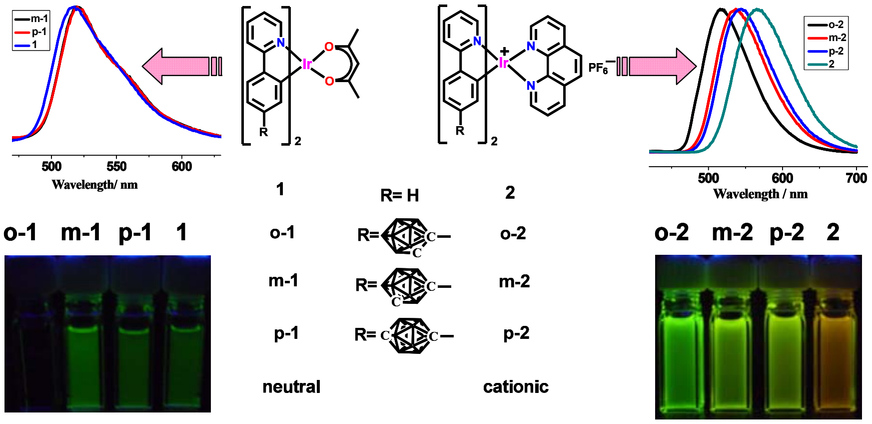

Fig. 1 The structures of neutral and cationic iridium(III) complexes containing carboranes and the model complexes **1** and **2** (middle), and **PL** spectra of neutral complexes for **m-1**, **p-1** and **1**(left) and cationic complexes for **o-2**, **m-2**, **p-2** and **2** (right) in degassed CH_2Cl_2.

We have synthesized both neutral and cationic iridium(III) complexes containing *o*-, *m*- and *p*-carborane in the cyclometalated C^N ligand, named as **o-1**, **m-1** and **p-1** for neutral complexes and **o-2**, **m-2** and **p-2** for cationic complexes. As a result, *o*-carborane was observed to quench phosphorescent emission in neutral complexes, but *m*- and *p*-carboranes can strongly enhance emission both in solution and solid state. In the case of cationic complexes the three carborane isomers can both increase quantum yields and significantly adjust emission wavethlengths of these complexes. The preliminary results demonstrate that the steric, electronic and structural factors of carboranes can efficiently tune phosphorescent properties of iridium(III) complexes.

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NEW WELL-DEFINED PALLADIUM-BASED CATALYSTS FOR THE AEROBIC OXIDATION OF ALCOHOLS

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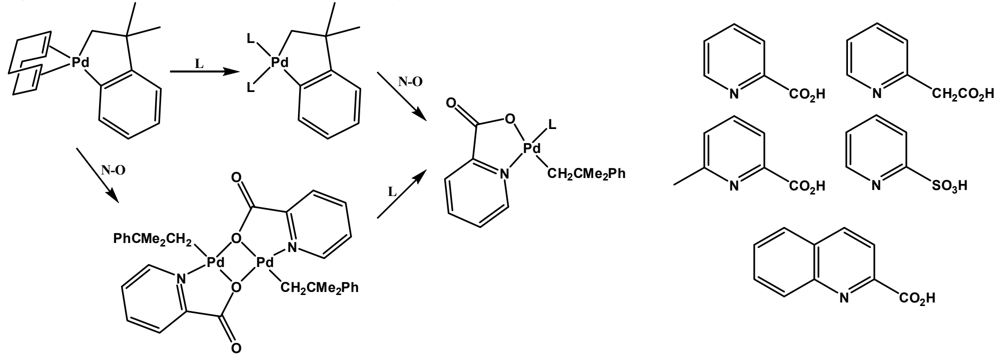
Oxidation of alcohols is one of the most important synthetic operations both in the organic chemistry laboratory and in the industry. Although classic oxidation reactions can be very efficient and selective, they often involve the use of stoichiometric reagents and halogenated solvents, resulting in the generation of large amounts of waste. The urgent need for more sustainable processes has prompted the development of mild and selective oxidation methods based on the use of green reagents and solvents. In this context, direct use of O_2 as an oxidizing reagent is a very desirable feature for modern synthetic methodologies. Therefore, new catalysts for aerobic oxidation of alcohols have received much attention in recent years.

Recently we have synthesized well-defined palladium complexes of the type [Pd(N–O)(X)(L)], in which N–O is an anionic chelate, L is a monodentate base and X is a generic anionic ligand, and tested them in catalytic aerobic alcohol oxidation:



We have developed a versatile synthetic methodology that provides access to a wide variety of neophylpalladium complexes containing different combinations of chelating and monodentate ligands. These complexes were found to promote the aerobic oxidation of benzylic, allylic and aliphatic alcohols by oxygen. Under the catalysis conditions, the Pd–C bond undergoes homolysis, giving rise to the actual active species.

Neophylpalladium pyridinecarboxylate complexes are modular. Their synthesis is straightforward and can be readily extended to other complexes containing different chelates and monodentate ligands. Since the activity and selectivity of these catalysts are ligand-controlled, it is foreseen that the catalyst design can be tuned to improve activity, selectivity and resistance to the aggressive oxidation conditions, or to generate desirable properties such as compatibility with water or other environmentally friendly solvents. Another useful property of this system is that the catalysts perform without additives, facilitating product separation and purification. Also we have been able to come to some relevant mechanistic conclusions.

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SYNTHESIS AND STRUCTURE OF MIXED-METAL DICHALCOGEN COMPLEXES

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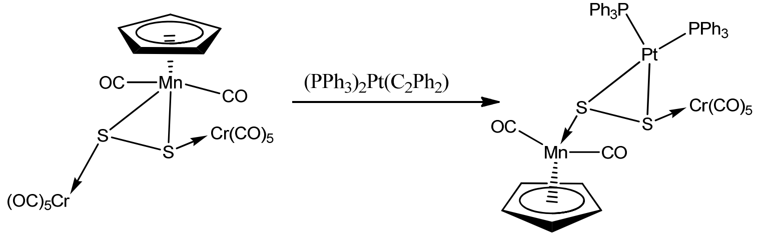
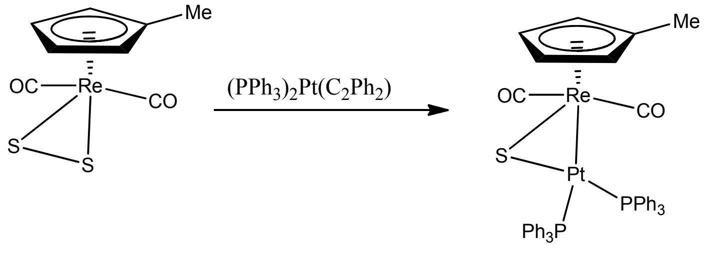
Mixed-metal clusters are of interest as precursors to inorganic materials of complex composition and high homogeneity [1,2].

Recently we have shown that reactions of manganese dimers $[CpMn(CO)_2]_2E_2$ (E = S,Se) bridged by dichalcogen ligand with platinum complex $(PPh_3)_2Pt(C_2Ph_2)$ result in substitution of tolane by coordinated dichalcogen giving $[CpMn(CO)_2]_2E_2Pt(PPh_3)_2$ clusters. Side-on coordination of dichalcogen bridge to platinum results in the rupture of conjugated-bond system in Mn_2E_2 fragment, without chalcogen-chalcogen bond breaking, contrary to usual oxidative additions to dichalcogen bonds. Transmetalation reaction of $[CpMn(CO)_2]_3Te_2$ with $(PPh_3)_2Pt(C_2Ph_2)$ leads to formation of analogous tellurium cluster.

Mixed-metal manganese-chromium disulfur complex $CpMn(CO)_2S_2[Cr(CO)_5]_2$ could also be transmetalated by zero-valent platinum with selective loss of one chromium fragment.



The reaction of new rhenium-chromium $Cp'Re(CO)_2S_2Cr(CO)_5$ complex with $(PPh_3)_2Pt(C_2Ph_2)$ gives analogous product according to IR-spectroscopy. Otherwise reaction of uncoordinated $Cp'Re(CO)_2S_2$ with $(PPh_3)_2Pt(C_2Ph_2)$ results in formation of sulfide bridged complex via unstable intermediate.



Thermal decomposition of some mixed-metal clusters was studied by DSC-TGA.

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ELECTROCHEMICAL TRANSFORMATIONS AND ANTIRADICAL ACTIVITY OF TRIALKYLANTIMONY(V) O-AMIDOPHENOLATES

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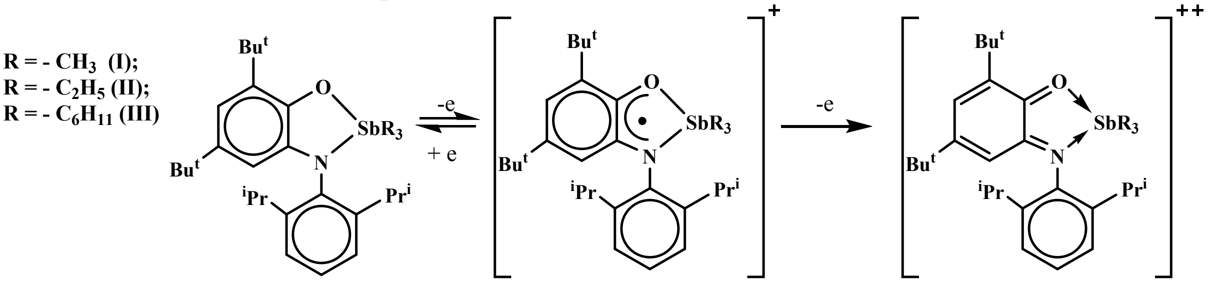
The electrochemical properties of a trialkylantimony(V) *o*-amidophenolates (**I-III**) were studied by cyclic voltammetry. The complexes are undergone two-stage electrochemical oxidation in anodic area: the first redox transfer has one electron quasireversible manner; the second one is the irreversible process.



(AP-H)SbR$_3$ [(ISQ)SbR$_3$]$^+$ [(IBQ)SbR$_3$]$^{++}$

The introduction of donor alkyl groups leads to decreasing redox potential at 0.1 V in comparison with *o*-amidophenolate of triphenylantimony(V) [1]. However the depletion of reversibility redox process points out unstability of the radical cation forms. In course of the second electrochemical transfer, the formation of unstable dicationic species occurs. The particles undergo fast decomposition accompanying of *o*-iminobenzoquinone decoordination. Radical scavenging activity of organoantimony(V) complexes (**I-III**) was considered in assays with DPPH radical and model peroxidation of oleic acid.

N	Compound	EC$_{50}$, μmol	IC$_{50}$, μmol	Inhibiton of oleic acid oxidation, %
I	Me$_3$Sb(AP-H)	18.9±1.2	21.0±0.9	92.7
II	Et$_3$Sb(AP-H)	13.7±0.8	19.5±1.2	94.4
III	(C$_6$H$_{11}$)$_3$Sb(AP-H)	17.6±0.6	21.2±0.7	97.8
IV	Ph$_3$Sb(AP-H)	9.0±1.3	-	97.5

The values of EC$_{50}$ (DPPH test) and IC$_{50}$ (oleic acid peroxidation) for complexes point out that the compounds can act as an efficient antiradical agent. All complexes are displayed inhibition effect on the process of oleic acid oxidation. The compounds (**I-III**) are played the role of effective LOOH destructors, as triphenylantimony(V) *o*-amidophenolate (**IV**) [1]. In conclusion, our results suggest that the combination organometallic fragment containing of antimony with redox-active ligand leads to appear uncommon properties, which are varied from properties the initial trialkylantimony(V) compounds.

[1] I. Smolyaninov, A. Poddel’sky, N. Antonova // *J. Organometallic Chemistry,* **2011**, *696*, 2611-2620.

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REDOX-ISOMERIC TRANSFORMATIONS. ELECTRONIC AND LATTICE CONTRIBUTIONS.

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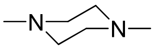
Bis-quinonato cobalt complexes are the promising compounds for studding of regularities of redox-isomeric interconversion. It is actual for intelligible synthesis of redox-isomeric compounds with preprogramed properties.

Here we report the synthesis and investigation of the family of 1,10-phenathroline bis-quinonato cobalt complexes – derivatives of different quinones and phenanthrolines. Recently we have reported synthesis and properties of (1,10-phen)Co(3,6-DBSQ)$_2$ [1]. Using of o-quinonato ligand substituted in 4-position by –OMe group (4-OMe-3,6-DBQ) leads to another redox-isomeric compound. In spite of the difference of redox properties of 3,6-DBQ and 4-OMe-3,6-DBQ the temperature of redox-isomeric transition is practically the same. It is the consequence of the presence of solvate molecule in the lattice. In the case of quinonato ligands modified by annulated cycles: $—O-CH_2-CH_2-O—$ and  in 4,5-position the trigonal-prismatic complexes are formed. No redox-isomeric transformations are observed in these cases. Modification of 1,10-phenathroline ligand also affects the complex properties. Using the 2,9-dimethyl-1,10-phenanthroline slightly distort complex geometry and as the consequence the redox-isomeric transformation is absent.

[1] M. Bubnov et al., *Russ.Chem.Bull., Int.Ed.*, **2011**, *60*, 440-446.

Acknowledgements - We are grateful to the RFBR (grants №№ 13-03-12444, 13-03-97082, 13-03-97070), Russian President Grant supporting Scientific Schools (NSh-1113.2012.3) and Fundamental Research Programm of Presidium of RAS (№ 18) for financial support.

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THE EFFECT OF LIGAND FIELD ON LD LISC

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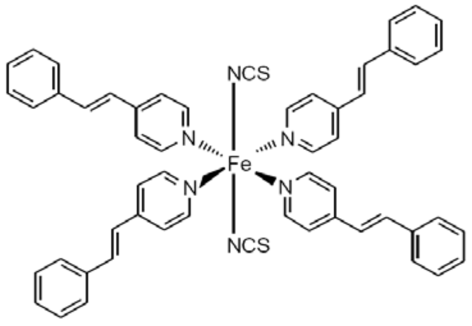
Coordination compounds whose magnetic properties can be controlled by external stimuli (temperature, pressure and irradiation) serve as building blocks for the design of the magnetically responsive molecular switches and magnets [1]. The well-known effects resulting in switching magnetic properties of metal complexes by means of irradiation are LIESST and LD LISC. The latter consists in the change of ligand field caused by light-induced *cis-trans* photoisomerization of photoactive fragments which leads to the manifestation of switchable magnetic properties by one of the forms of the complex. LD LISC effect occurs in solution and thin films of Fe(II) and Fe(III) coordination compounds [2] which fact distinguishes it from the strictly cooperative effect of spin-crossover. The magnetically bistable systems exhibiting LD-LISC effect are based on various types of ligands.



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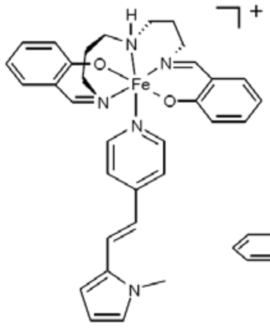

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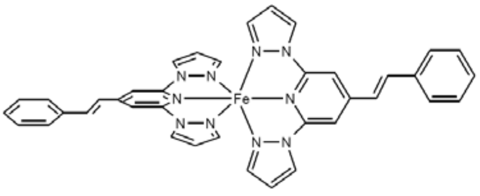

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With the purpose of study of the mechanism of LD LISC effect and the influence of photoinduced isomerisation on the change in the strength of the ligand field the experimentally characterized coordination compounds **1-3** have been theoretically explored. High spin and low spin isomers of the complexes involved and the dependence of the magnetic properties on the packing in the crystals have been studied by the use of the density functional theory B3LYP*/6-311++G(d,p) calculations.

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COORDINATION PROPERTIES OF NOVEL HYBRID LIGANDS BASED ON AMINOMETHYLPHOSPHINES

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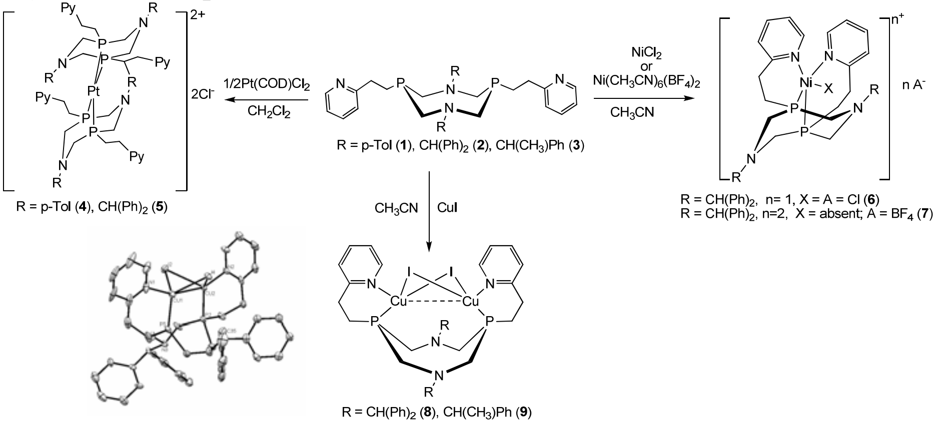
Pyridylphosphines are hybrid ligands which are pre-organized for the design of polynuclear complexes. The metal complexes based on Py-P hybrid ligands are excellent catalysts due to lability of metal-N(Py) bonds. In this work we present a synthesis of novel cyclic aminomethylphosphines with 2-(2-pyridyl)ethyl groups on phosphorus atoms and their coordination properties.

The 1,5-di(R)-3,7-bis(2-(2-pyridyl)ethyl-1,5-diaza-3,7-diphosphacylcooctanes **1-3** were obtained by Mannich-like condensation of 2-(2-pyridyl)ethylphosphine, formaldehyde and primary amines in good yields (70-90%).

The coordination properties of **1-3** are studied toward d^8 and d^{10} metals. Complexes of Ni(II), Pt(II) are potential catalysts and complexes of Cu(I) are able to show luminescence. Ligands **1** and **2** form with $Pt(COD)Cl_2$ in ratio ligand:metal 2:1 desired bis-P,P-chelate complexes **4** and **5**, which are similar to ones described earlier [1]. The interaction of **2** with one equiv. $Pt(COD)Cl_2$) leads to the formation of the mixture of neutral [(κ^2-P,P-**2**)$PtCl_2$] and cationic [(κ^3- P,P,N-**2**)PtCl]Cl complexes.



After the reaction of **2** with $NiCl_2$ or $Ni(CH_3CN)_6(BF_4)_2$ the corresponding bis-P,N-chelate complexes **6, 7** were isolated. Bis-P,P-chelate complex as a minor product was observed in the reaction mixture during the formation of **6**, but after the solvent removal and the washing of crude powder with methanol only one signal of **6** was registered in the NMR ^{31}P spectra.

The reactions of **2** and **3** with copper (I) iodide result in binuclear complexes **8** and **9**, where ligands show a P,N-chelate and P,P-bridge coordination mode together. Due to the rigid framework of eight-membered heterocycle, Cu-Cu distance (2.6 Å) is less than sum of Van der Waals radii. The coordination of pyridyl with Cu(I) and short distance between metal cores is the reason of strong luminescence of complexes **8** and **9**.

[1] A.A. Karasik, R.N. Naumov, A.S Balueva, *Heteroatom Chemistry*, **2006**, *17*, 499-513.

Acknowledgements –
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SYNTHESIS AND INVESTIGATION ORGANIC SOLID STATE ACTIVE MEDIA

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The development of new materials for using as active media for tunable lasers, optical sensors, OLEDs, OSLs has been attracting the attention of researchers in the last years.

The priority in the branch of synthesis of solid-state active media based on organic compounds belongs to A.Costela [1].

We continue investigations [2-4] in the field of synthesis of solid-state active media for tunable lasers aimed at investigations of solid-state active media lasing in a wide spectral range and development of lasers on their basis.

In the present work, results obtained in the field of synthesis of solid-state active media on the modified methylmetacrylate matrices activated by dyes rhodamine 6G, pyrromethene 567 that effectively generate radiation in the visible range of the spectrum are given. The components of hybrid polymer were organic monomers (MMA – methylmetacrylate, HEMA – hydroxy ethyl metacrylate, TEOS - tetraethoxysilane, 8-POSS - polyhedral oligomeric silsesquioxane). Patterns of changing the lasing characteristics depending on composites and excitation conditions are established. It is demonstrated that the solid-state active media with efficiency and lifetime that are not inferiors to solutions can be synthesized on their basis.

[1] A. Costela, I. García-Moreno, R. Sastre, *Physical Chemistry Chemical Physics*, **2003**, *5*, 4745-4763.
[2] T.N. Kopylova, G.V. Mayer et.al.,*Quantum Electronics*, **2003**, *33 (6)*, 498-502.
[3] T.N. Kopylova, G.V. Mayer et.al., *Applied Physics B* , **2004**, *78*, 183-187.
[4] T.N. Kopylova, S.S. Anufrik et.al., *Russian Physics Journal,* **2012**, *55 (10)*, 1137-1142.

Acknowledgements –This work was supported in part by the Russian Foundation for Basic Research (grants Nos. 10-02-90007-Bel-a and 12-02-00694-a) and by grant of RF President (SS-512.2012.2).

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REACTIONS IN COORDINATION SPHERE OF *o*-SEMIQUINONATO NICKEL(II) COMPLEXES

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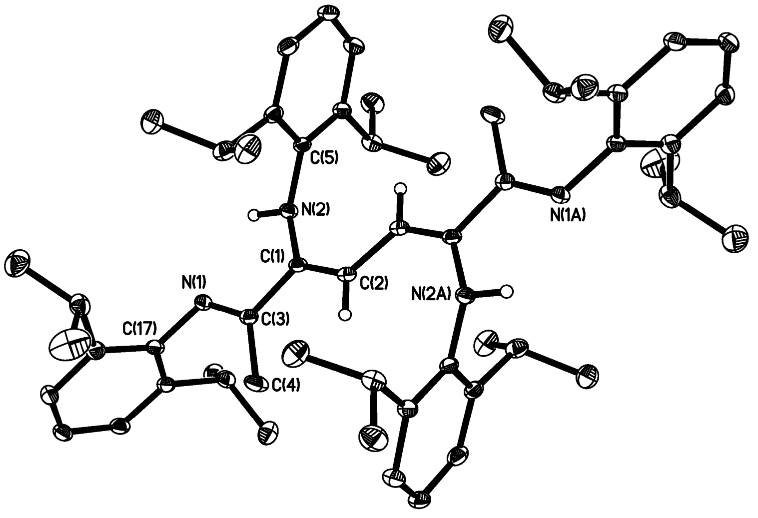
High spin molecules are useful for design of molecular magnets – perspective materials for molecular electronics. Redox active ligands – derivatives of structurally hindered o-quinones - can be used for synthesis of paramagnetic six-coordinate compounds.

Here we report about products of the reaction between bis-o-semiquinonato nickel(II) complex Ni(3,6-DBSQ)$_2$ and sterically hindered diazabutadienes. Square-planar bis-semiquinonato nickel complexes are known to be diamagnetic due to their single diradical nature. Addition of N,N’-dialkyl-1,4-diazabutadiens-1,3 to them leads to formation of stable six coordinate products containing high spin nickel(II) coupled ferromagnetically with two semiquinones: (Alkyl-DAB)Ni(3,6-DBSQ)$_2$. Interaction of Ni(3,6-DBSQ)$_2$ with N,N’-bis-(2,6-dimethylphenyl)-1,4-diaza-2,3-dimethyl-butadien-1,3 also leads to six coordinate product: (2,6-Me$_2$-phenyl-DAB)Ni(3,6-DBSQ)$_2$. However according to ^{1}H NMR spectrum this product in solution is partly dissociated into corresponding catecholate complex and free quinone. Interaction of the same bis-semiquinonato nickel with more sterically hindered N,N’-bis-(2,6-di-iso-propylphenyl)-1,4-diazabutadien-1,3 results in two different crystalline products which were identified as six coordinate complex: (2,6-i-Pr$_2$-phenyl-DAB)Ni(3,6-DBSQ)$_2$ and co-crystallized corresponding nickel catecholate with guest quinone molecule: (2,6-i-Pr$_2$-phenyl-DAB)Ni(3,6-DBCat)+(3,6-DBQ). Further increasing of steric hindrance of diazabutadiene – using of N,N’-bis-(2,6-di-iso-propylphenyl)-1,4-diaza-2,3-dimethyl-butadien-1,3 leads to dimeric catecholate product. Hydrolysis allowed to isolate the dimeric diazabutadiene.



Acknowledgements: We are grateful to the RFBR (grants №№ 12-03-31348, 12-03-31367), Russian President Grant supporting Scientific Schools (NSh-1113.2012.3) and Fundamental Research Programm of Presidium of RAS (№ 18), FSP “Scientific and scientific-pedagogical cadres of innovation Russia” for 2009-2013 years (Agreement 8465) for financial support. Also thanks to I.D.Grishin for MALDI experiments, A. Bogom’akov for magnetic measurements and structural research group of our Institute.

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LANTHANIDE COMPLEXES FOR CATALYTIC FORMATION OF C-N AND C-P BONDS

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Lanthanide complexes proved to be efficient catalysts for a wide range of conversions of unsaturated substrates (polymerization/oligomerization, hydroamination, hydrosilylation, hydroboration etc). Design of new ligand systems suitable for coordination to rare-earth metals and providing control of their reactivity, catalytic activity/selectivity and investigation of the structure-reactivity relationships are in the focus of our studies. The synthesis of alkyl, hydrido and amido lanthanide complexes supported by various N,N-, N,N,N-, N,N,O-, N,N,P(O)-ligands and their catalytic activity in olefin hydroamination, hydrophosphination, aldehyde hydrophosphonylation will be reported.

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REDOX-AMPHOTERIC TIN(IV) COMPLEXES WITH TETRADENTATE LIGANDS

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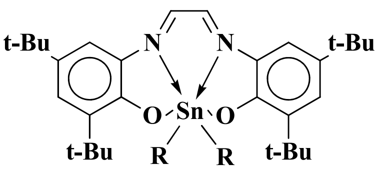
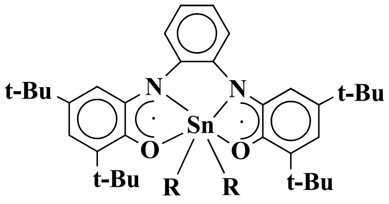
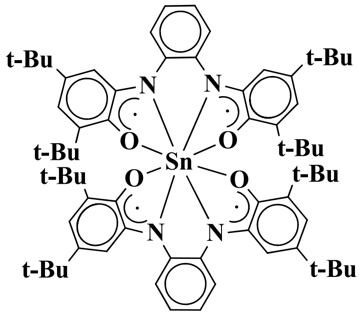
We have been interested in synthesis of tin complexes containing the tetradentate ligands for physicochemical measurements in order to establish the potential of these ligands to be involved in redox transformations. The redox inactive metals make it possible to observe pure redox behavior of the coordinated ligand which is not complicated with oxidation or reduction of the metallic center.



R = Me(1), Et(2),
t-Bu(3), Ph(4)



R = Me(5), Ph(6)



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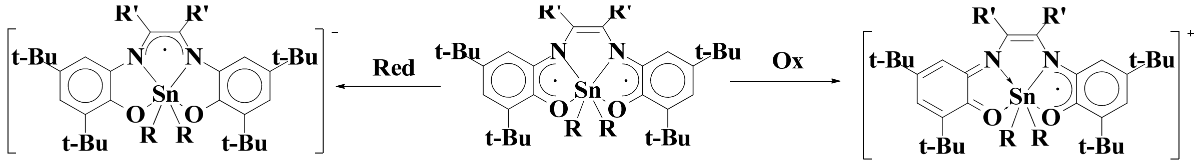
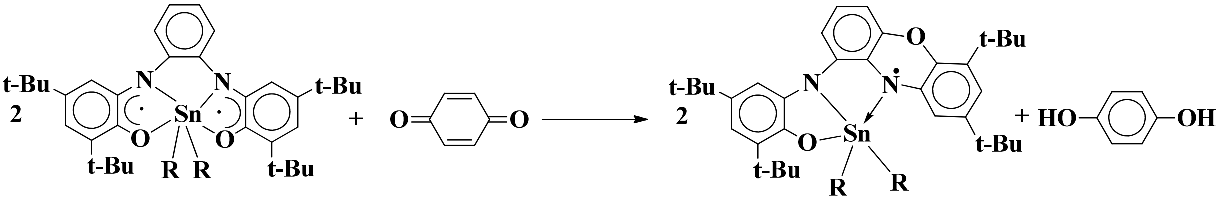
Cations of complexes **1-7** and anions of complexes **1-6** were generated chemically by the oxidation with $AgBF_4$ (or I_2) or reductions with metallic potassium, respectively. The obtained solutions of cations and anions were examined using X-band EPR spectroscopy. The spin distribution in cations and anions of **1** and **5** were investigated with help of DFT calculations.



The oxidation of complexes **5** and **6** with p-quinone results in cyclization of tetradentate ligand with formation of a mixed phenolate/phenoxyl radical.



R = Me(5), Ph(6)

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CATALYTIC SYSTEMS BASED ON RUTHENACARBORANES IN THE CONTROLLED SYNTHESIS OF PERSPECTIVE POLYMER MATERIALS

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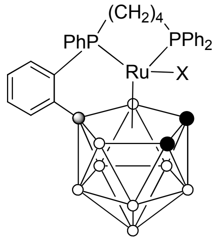
The development of new synthetic ways to the well-defined polymers is one of the most challenging problems of modern polymer chemistry. Atom Transfer Radical Polymerization (ATRP) is one of the remarkable processes by which precise polymer synthesis may be achieved with an efficient use of organometallic catalysts.

In this work the activity of paramagnetic ruthenium complexes with C_2B_9-carborane ligand in ATRP was investigated in the polymerization of methyl methacrylate (MMA), izobornyl metacrilate (IBMA) and tert-butyl metacrylate (TBMA) in the presence amines of different nature.



X=Br, Cl

Our experiments have shown that polymerization of all mentioned monomers in the presence of amines and ruthenacarboranes proceeds without spontaneous acceleration up to high degrees of conversion, even at low catalyst concentrations (0.01 mol.%). The polymers formed had narrow molecular weight distribution. The molecular weight of the samples was in a good agreement with theoretically calculated for ATRP process and dependence of molecular weight of the samples on conversion is linear. At the same time no increase of molecular weight of PIBMA samples is observed. The polydispersity indices remain virtually unchanged at a level of 1.5.

A successful synthesis of diblock- and threeblock-copolymers using PMMA-macroinitiator, synthesized in the same conditions was done. Formation block-copolymers is confirmed by SEC by the shift of curve of block-copolymer into the area greater molecular weights relative to the original macroinitiator. The glass transitions temperatures of the synthethised samples indicate their block-copolymer nature.

It was shown that the polymers formed in the presence of bromine containing catalysts and initiators had lower molecular weights in comparison with their chlorine counterparts.

Thus, systems on the basis of ruthenacarboranes in combination with amines in the presence of halogen-containing catalysts are effective in controlled synthesis of macromolecules.

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SYNTHESIS OF HOMO- AND BLOCK-COPOLYMERS USING *O*-IMINOSEMIQUINONE COMPLEXES OF TIN(IV)

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Germanium(IV) and tin(IV) catecholate complexes reversibly reacts with radicals and therefore can be used as a chain growth regulator in polymerization of styrene (St) [1]. Products of interaction of tin(IV) catecholates and carbon-centered radicals - corresponding *o*-semiquinone derivatives - have been detected by EPR [1].

The paramagnetic compounds of tin(IV) - imSQSnR$_2$Cl, where R = Cl, Me, Et, Bu^t, and Ph and imSQ - anion radical 3,5-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-aminophenol, also may be used as regulators of radical polymerizations of MMA initiated by AIBN at 70ºC [2]. Complex imSQSnBu$^t_2$Cl under given conditions acts as iniferter – the initiator and regulator of radical polymerization of MMA at 70-90°C [2]. To assess the ability of initiating and controlling these complexes, as well as to determine the most probable mechanisms of reactions occurring in the system was studied a number of other features of the polymerization of vinyl monomers.

It was shown that complex imSQSnBu$^t_2$Cl can be the effective initiator for the synthesis of poly(meth)acrylates. In the case of St, the introduction of this complex leads to a reduction autopolymerization rate at 70-90ºC. The initiation of polymerization of St by imSQSnBu$^t_2$Cl was observed only at 110°C. However, the linear increase MW with conversion and low polydispersity of polymers, an example, ~1.6-2.1 for polyBMA and ~ 1.4-1.9 for polySt, is retained. Conversions of acrylates, acrylonitrile (in monomers weight) or vinyl chloride using imSQSnBu$^t_2$Cl does not exceed ~ 5-10%. Formation of high MW product polymerization of vinyl acetate in the presence of imSQSnBu$^t_2$Cl in the range of 50-110°C does not fixed.

It was found that polymers prepared in the presence of imSQSnBu$^t_2$Cl at 70-110ºC capable to reinitiation of polymerization various vinyl monomers. PolyMMA prepared in the presence of AIBN and each of the imSQSnR$_2$Cl at 70-90ºC also can act as a macroinitiators. Based on these polymers possible to obtain block-copolymers of polyMMA-*b*-polySt, polySt-*b*-polyBMA and polyBMA-*b*-polyMMA a broad range of compositions. Copolymers of polyMMA-*b*-polyAN may be synthesized in strongly polar solvents.

Thus, complexes of tin(IV) with redox-active *o*-iminosemiquinone ligand can act as regulators of chain growth in polymerization of various vinyl monomers initiated by AIBN and without it.

[1]. Vaganova, L.B., Maleeva, A.V., Piskunov, A.V., and Grishin, D.F., *Izv. Akad. Nauk, Ser. Khim.*, 2011, №8, P.1594–1601. [2]. L.B. Vaganova, A.A. Shchepalov, I.N. Meshcheryakova, M.G. Chegerev, A.V. Piskunov, D.F. Grishin*, 2012, Doklady Chemistry,* 2012, V. 447, №12, P.286–292.

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SYNTHESIS AND CRYSTAL STRUCTURE CHARACTERIZATION OF METAL COMPLEXES OF ACYCLIC CHEALTING LIGANDS HAVING CARBOXAMIDE FUNCTIONALITY

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The pyridine monocarboxamides, such as pyridine-3-carboxamide and pyridine-4-carboxamide apart from having medicinal importance are also versatile ligands from crystal engineering point of view. These ligands have the structural adaptability to self assemble into 1D, 2D or 3D frameworks either using hydrogen bonding or coordination polymerization or a combination of both. The coordination geometry of metal ion along with the nature of bridging ligand decides the direction of extension of these architectures.

In this presentation, we will report the synthesis and structural characterization of $M^{II}X_2$-N,N-dialkylisonicotinamide (alkyl = ^{i}Pr and ^{i}Bu) complexes, M(II) = Zn(II), Cu(II) and Co(II); and X = Cl^-,NO_3^-,OAc^-. X-ray crystal structures of some of these complexes are used to demonstrate the formation of coordination polymers.

[1] Ajay Pal Singh Pannu, Pratibha Kapoor, Geeta Hundal, Ramesh Kapoor, Martin Martinez-Ripoll, Rayond J. Butcher and Maninder Singh Hundal, *Polyhedron*, **2011**, *30*, 1691-1702.

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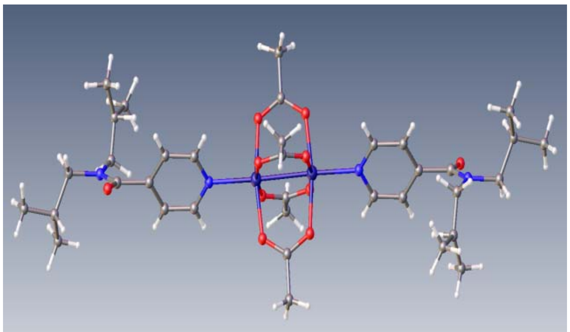
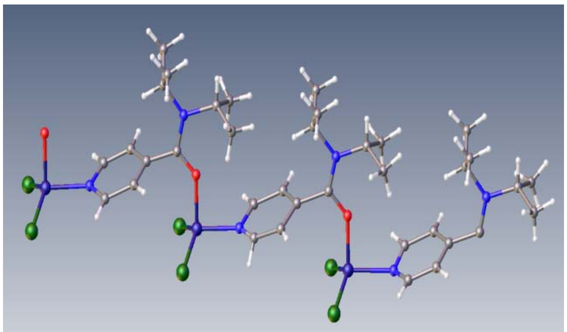


Paddle wheel structure hown by $[Cu(OCOCH_3)_2(L')]_2$
(L' = diisobutylisonicotinamide)



1D Coordination polymer of $[ZnCl_2(L)_2]_n$.
(L = diisopropylisonicotinamide)

COPPER(I) COMPLEXES WITH 4-(1*H*-PYRAZOL-1-YL)PYRIMIDINES: SYNTHESIS, STRUCTURES AND LUMINESCENCE

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Synthesis of luminescent metal complexes is an interesting and important field of coordination chemistry. Cu(I) complexes and clusters are currently one of main classes of luminescent metal compounds based on a relatively abundant and non-toxic element showing interesting photophysic properties. Unfortunately Cu(I) complexes usually show weak emissions (quantum yield (φ) < 1 %) and short lived excited states. The effective Cu(I) emitters are rather scarce. The aim of this study is to synthesize effective Cu(I)-containing emitters.

A series of Cu(I) halide complexes, [CuL^{n}X] (n = 1, 2; X = Cl, Br), [CuL^{n}PPh$_3$X] (n = 1, 2; X = Cl, Br, I; n = 3; X = I), [Cu$_2$(L^n)$_2$I$_2$] (n = 1, 2, 3, 4) and [Cu$_2$L^{4}X$_2$] (X = Cl, Br), based on 4-(1*H*-pyrazol-1-yl)pyrimidines have been synthesized. The pyrazolylpyrimidine ligands differ by a substituent in the C6 position of the pyrimidine ring (Fig. 1).

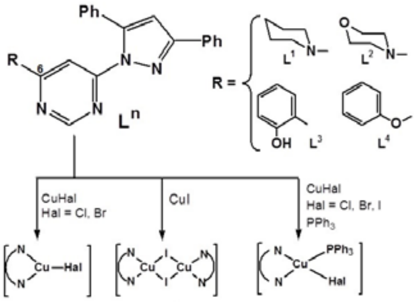

Fig. 1. Structures of the complexes and the ligands.

The emissive properties depend on the structure of heteroaromatic ligands and halide ions. All complexes display luminescence in the visible region, the color of the emission changes from yellow-green to red. Halide ions show strong effect on the luminescent properties of the complexes: the emission intensity increases in the order: $Cl^- < Br^- < I^-$. The complex [Cu$_2$(L^3)$_2$I$_2$] has more expanded conjugated π-system of the ligand in comparison with complexes [Cu$_2$(L^n)$_2$I$_2$] (n = 1, 2, 4) and its emission is red-shifted.

In the solid state the mononuclear [CuL^{1}PPh$_3$X] complexes demonstrate a ^{3}MLCT luminescence in yellow-red region. The degree of distortion of pseudo-tetrahedral CuN$_2$PX core determined from X-ray single crystal data and the Stokes shift being an indicator of the degree of excited state distortion decrease in the order: [CuL^{1}PPh$_3$Cl] > [CuL^{1}PPh$_3$Br] > [CuL^{1}PPh$_3$I]. The constants of non-radiation decay decrease in the same sequence with synchronous low frequency shift of the bands in IR spectra. The luminescence quantum yield and excited state lifetimes increase in the reverse order: [CuL^{1}PPh$_3$Cl] (φ = 1.7%) < [CuL^{1}PPh$_3$Br] (φ = 6.3%) < [CuL^{1}PPh$_3$I] (φ = 29.4%).

Thus, suppression of vibrational quenching and more symmetrical coordination core lead to improvement of Cu(I) photoluminescence quantum efficiency.

Acknowledgements - the work was financially supported by Russian Foundation for Basic Research (Projects 11-03-00268 and 12-03-31266 mol_a).

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POLYCONDENSATION OF $[Mo_2S_2O_2(H_2O)_X]^{2+}$ TO A CYCLIC CLUSTERS IN PRESENCE OF SOME BIBASIC ACIDS

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Polyoxothiometalates – a new branch of sulfur-containing polyoxometalates (POTMs) as a subclass of the polyoxometalate family. The richness and diversity of POTMs open great opportunities and prospects of this field in fundamental and applied aspects. [1]

In this work we represent the results of self-condensation of $[Mo_2S_2O_2]^{2+}$ oxothiocation to cyclic clusters in the presence of amino acids and diphosphonic acids, which are supposed to act as structure templates.

In the case of L-aspartic acid, the compound, $(NMe_4)_3[Mo_{10}S_{10}O_{10}(OH)_{10}(C_4H_5O_4N)H_2O]Cl\cdot 21,5H_2O$, was obtained. Five $\{Mo_2S_2O_2\}$ building blocks are connected through double hydroxo bridges to give Mo_{10}-ring and acid residue is located within molybdenum ring (fig. 1).

In the case of 2, 5 – thiophenphenylenediphosphonic acid a supramolecular assembly $[N(CH_3)_4]_4[Mo_{10}S_{10}O_{10}(OH)_{10}(H_2O)_5]Cl_2(C_4O_4H_4P_2S)\cdot 17H_2O$ was obtained, in which Mo_{10}-rings and the acid residues form polymeric chains *via* hydrogen bonds (fig. 2).

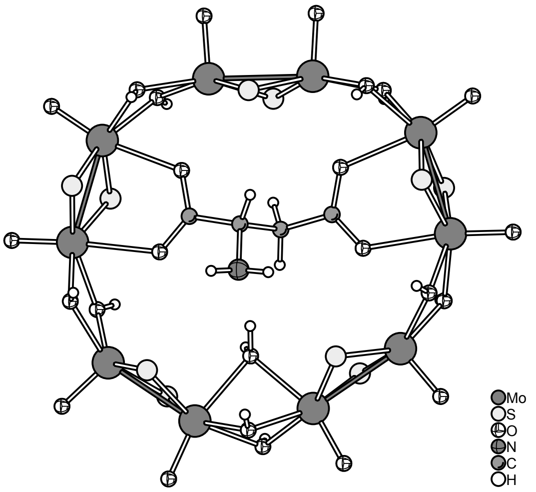

Fig. 1

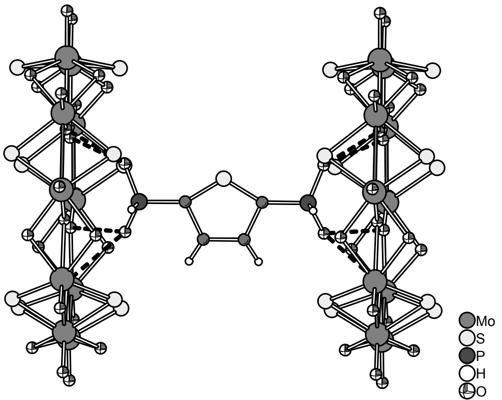

Fig. 2

[1] Lemonnier J.-F., Duval S., Floquet S., Cadot E. *Isr. J. Chem.*, **2011**, *51*, 290 – 302.

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NEW LANTHANIDE BIS(AMIDINATE) AMIDO COMPLEXES AS EFFECTIVE CATALYSTS FOR THE RING-OPENING POLYMERIZATION OF RAC-LACTIDE AND HYDROPHOSPHONYLATION OF ALDEHYDES

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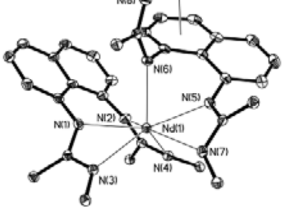
Amido rare-earth complexes supported by N- donor ligands demonstrated catalytic potential in ring-opening polymerization of cyclic esters, olefin hydroamination and hydrophosphination. We attempted synthesis of new amido complex supported by bulky ansa bis(amidinate) ligand system via one-pot reaction of [1,8-$C_{10}H_6${NC(tBu)N-2,6-Me_2-C_6H_3}$_2$]Na_2, $NdCl_3$ and $LiN(SiMe_3)_2$ (THF, 25°C). However, this procedure led to the heterobimetallic complex, containing two bis(amidinate) ligands [1,8-$C_{10}H_6${NC(tBu)N-2,6-Me_2-C_6H_3}$_2$]Nd[1,8-$C_{10}H_6${NC(tBu)N-2,6-Me_2-C_6H_3}{NC(tBu)N-Li(DME)-2,6-Me_2-C_6H_3}]·Et_2O (**1**). When $NaN(SiMe_3)_2$ was used instead of $LiN(SiMe_3)_2$ in a one-pot reaction amido complexes [1,8-$C_{10}H_6${NC(tBu)N-2,6-Me_2-C_6H_3}$_2$]$YN(SiMe_3)_2$ (**2**), [1,8-$C_{10}H_6${NC(tBu)N-2,6-Me_2-C_6H_3}$_2$]$NdN(SiMe_3)_2$THF (**3**), [1,8-$C_{10}H_6${NC(tBu)N-2,6-Me_2-C_6H_3}$_2$]$SmN(SiMe_3)_2$THF (**4**) were successfully isolated in 43-54% yields. The complexes **1-4** were characterized by elemental, spectroscopic analyses. Structures of the complexes **1**, **2** and **3** were determined by X-ray diffraction studies.

Amido complexes **2-4** proved to be efficient initiators for the ring-opening polymerization (ROP) of racemic lactide (rac-LA), which allow to obtain polymers with high molecular weights (M_n up to 79780 g·mol^{-1}), and moderate molecular weight distributions (M_w/M_n=1.35-2.12) Effective immortal ROP of rac-LA was feasible by combining complexes **2-4** with 3-5 eguiv. of isopropanol, effording PLAs whith well controlled molecular weights and narrow polydispersities (M_w/M_n = 1.13-1.29).

All these lanthanide amido complexes displayed high catalytic activities in hydrophosphonylation of aldehydes. Addition of diethyl phosphite to benzaldehydes bearing in para position various substituents *p*-$RC_6H_4C(O)H$ (R = Me, OMe, Cl) afforded the products in quantitaive yields by employing low loadings of the catalysts (1 mol %) at room temperature in a very short time (15 min). When the reaction was carried out with benzaldehyde or aliphatic aldehydes RC(O)H (R = Pen, Bu, Pr, iPr) longer reaction times were required (24 h) to reach 84-93% yields of products.



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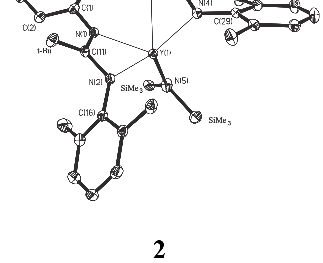

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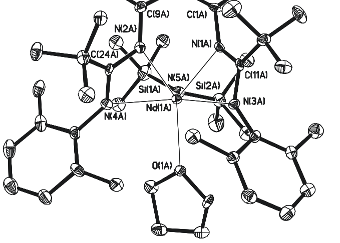

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Acknowledgements: This work is supported by the Russian Foundation of Basic Research (Grant Nos. 11-03-00555-a).

SPECTROSCOPIC STUDY OF HYDRIDOTRIS(PYRAZOLYL)BORATE RUTHENIUM HYDRIDES INTERACTION WITH ACIDS AND BASES

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Proton transfer processes are of fundamental importance in a number of (bio)chemical and catalytic systems. Our recent mechanistic studies of the protonation reaction of half-sandwich diphosphine ruthenium hydride complexes Cp’RuH(dppe) (Cp’ = C_5Me_5 [1], C_5H_5 [2], dppe = $Ph_2P(CH_2)_2PPh_2$) showed the dramatic ligand effect on the direction of the process. Continuing this line of investigation we carried out the detailed variable-temperature IR and NMR spectroscopic studies of protonation of the analogous complex supported by hydridotris(pyrazolyl)borate ligand TpRuH(dppe) (**1**, Figure 1).

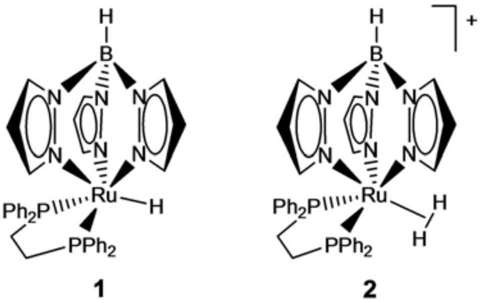

Figure 1. Complex **1** and its protonation product **2**.

The interaction of complex **1** with weak proton donors, e.g. trifluoroethanol, was shown to give the dihydrogen bonded complex TpRu(dppe)H···HOR. The thermodynamic parameters of this process were determined from the temperature dependence of the equilibrium constant and the H···H distance was calculated from the T_1 relaxation measurements. Dihydrogen complex **2** can be obtained by protonation of **1** with stronger proton donors and is stable toward further structural transformations. The study of hydrogen bonding of **2** with neutral bases is the main task of our work because of its importance in many processes, e.g. dihydrogen activation in the coordination sphere of metals. There is only single published paper really focused on the $M(\eta^2\text{-}H_2)\cdots B$ hydrogen bonds (B = base) [3]. The first results of the spectroscopic studies of the interaction of **2** with a number of neutral bases of different strength (pyridine, Et_3N, Oc_3PO, etc.) will be presented and discussed.

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[3] N. K. Szymczak, L. N. Zakharov, D. R. Tyler *J. Am. Chem. Soc.*, **2006**, *128*, 15830.

Acknowledgements – This work was financially supported by the Russian Foundation for Basic Research (projects No. 11-03-01210 and 13-03-00604) and by the German-Russian Interdisciplinary Science Center (G-RISC) funded by the German Federal Foreign Office via the German Academic Exchange Service (DAAD) (project No. C-2012a-4).

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ABOUT PREVIOUSLY UNKNOWN FEATURES OF OXIDATION OF FERROCENE AND ITS DERIVATIVES BY HYDROGEN PEROXIDE IN WATER AND IN ORGANIC SOLVENTS

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When we studying the mechanism of ferrocene oxidation by hydrogen peroxide recorded previously unknown phenomenon consisting in shifting the absorption band λ_{max} ferricenium cation (a.b.f.c.) to longer wavelengths and it simultaneously broadening the reaction. The amount of displacement $\Delta\lambda_{max}$ increases with excess concentration H_2O_2 relative to the concentration of ferrocene and a ratio up to 90 nm or more. A similar pattern changes a.b.f.c. takes place during the oxidation of a number of derivatives of ferrocene (Fc). At comparable concentrations of the metal complex and H_2O_2 offset a.b.f.c. not observed. The oxidation of ferrocene other peroxides - t-C_4H_9OOH or $(PhCOO)_2$ changes in the spectrum of the ferricenium cation also not recorded at any ratio of reactant concentrations. It is shown that the basis of the observed phenomenon is the formation of the radical cation of { ferricenium cation + $^{\bullet}OH$} at the primary interaction of the metal complex with H_2O_2 and the subsequent reaction between the radicals of the radical pair mechanism for radical substitution, leading to the formation of hydroxy derivatives of ferrocene and their cations. The consistent accumulation of OH-substituents on the metal complexes and related ferricenium cations causes a continuous shift a.b.f.c. at longer wavelengths. Another previously unknown feature ferrocene oxidation is that the resulting ferricenium cations can react with H_2O_2 to restoring the neutral complex. A prerequisite for this reaction is detected in time division stages formation ferricenium cation (Fc^+) and its interaction with the peroxide, which is taken in large excess compared to the original metallocomplexes. Thus, the overall mechanism of the oxidation of ferrocene and its derivatives must include not only the oxidation of ferrocene to ferricenium ions, but the reaction of cations with OH-radicals and hydrogen peroxide. By varying the ratio of the concentrations of H_2O_2 and ferrocene, you can make the contribution of these reactions to the overall process of oxidation of the metal complex to reduce its minimum and only to the formation of the ferricenium cation Fc^+.

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COBALT-INDUCED B-H AND C-H ACTIVATION LEADING TO FACILE B-C COUPLING OF CARBORANEDITHIOLATE AND CYCLOPENTADIENYL

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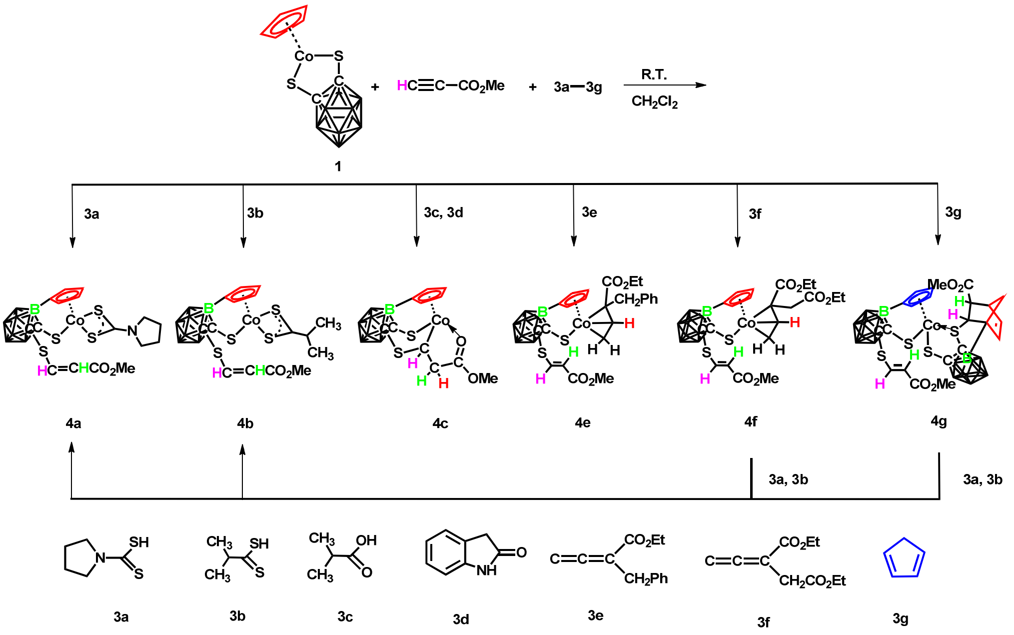
We report the one-pot reactions of the 16e half-sandwich complex CpCoS2C2B10H10 (1), methyl propiolate and 3e-donor ligands which have led to selective B-functionalization at carborane with cyclopentadienyl as a functional group at ambient temperature in good yields. Metal-promoted activations of both B–H bond at carborane and C–H bond at Cp unit have taken place sequentially in the cooperation of organic ligands. The reaction requires a 3e-donor ligand and an activated alkyne, therefore suitable for a broad range of substrates. This investigation provides a simple and efficient synthetic route to B-functionalized carborane derivatives.



[1] R. Zhang, L. Zhu, G. F. Liu, H. M. Dai, Z. Z. Lu, J. B. Zhao and H. Yan*, *J. Am. Chem. Soc.*, **2012**, 134, 10341.
[2] M. Herberhold*, H. Yan, W. Milius and B. Wrackmeyer*, *Angew. Chem., Int. Ed.*, **1999**, 38, 3689.

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METHODS FOR OBTAINING NEW ACTIVE MAGNETIC MATERIALS BASED ON MWCNT AND TRANSITION METAL COORDINATION COMPOUNDS

E. Zharikova[a], L. Ochertyanova, N. Efimov, V. Minin, Zh. Dobrokhotova, M. Kiskin, A. Bogomyakov, V. Imshennik, Y. Maksimov, R. Shub, M. Grishin, A. Ganin, I. Eremenko.

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Multi-walled carbon nanotube (MWNT) is used as modifying agents to various types of materials, for example, to increase strength and heat resistance. MWCNT or composites with MWCNT are used as catalysts for chemical reactions, solar components and fuel elements, electronic and optical devices, chemical sensors, and adsorbing materials [1]. The most promising for the application considered modified MWNTs, nanotubes contain various functional groups, nitrogen or oxygen-containing. This fact encourages the development of various methods of functionalization of MWCNTs and metal-organic fragments of molecules in order to increase the reactivity of the nanotubes and the appearance of unusual physical properties that can expect to receive new types of functional materials [2-4].

Creation of systems that combine magnetic ions on the surface or inside of CNT, is a way to get new types of magnetic materials. It has been shown MWNTs modified with organic groups containing pyridine fragments can interact with transition metal compounds ($FeCl_3$·6H2O (including isotope Fe^{57}), $Fe_2NiO(Piv)_6(HPiv)_3$ (HPiv = HO_2CCMe_3) and $Cu_2(Piv)_4(HPiv)_2$) to form new magnetoactive compounds. Detailed information about the study of composition, structure and properties of the newly prepared compounds M@MWCNT will be presented in the report.

[1] H. Chu, L. Wei, R. Cui, J. Wang, Y. Li, *Coord. Chem. Rev.*, 2010, **254**, 1117.
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NOVEL CHARGE-COMPENSATED NIDO-CARBORANES WITH AMMONIUM SUBSISTUENT.

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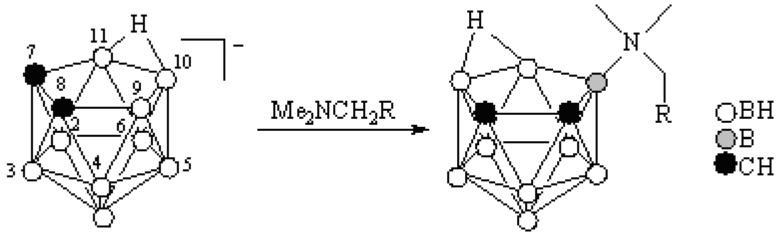
119334, Moscow, Vavilov str., 28, RUSSIA.

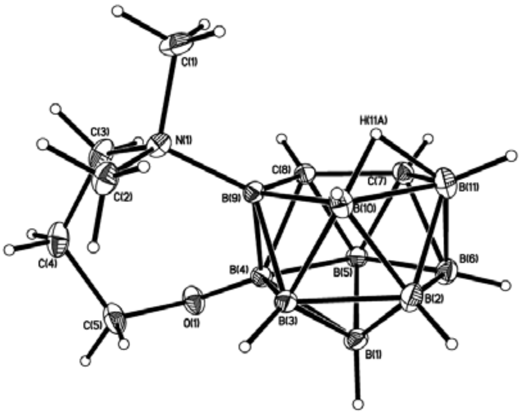
Introduction of ammonium substituents which contains functional group into carborane cage provide wide possibilities both for medical and coordination chemistry. Using different amines we synthesized series of new compounds:



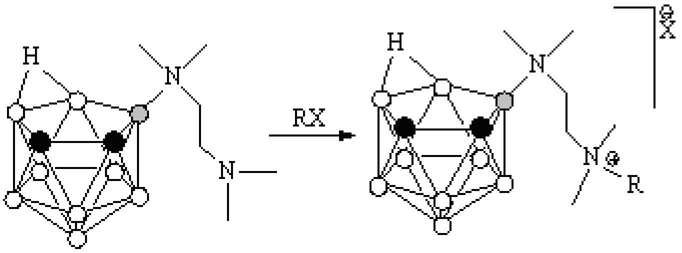
R = Ph, 4-Br-C_6H_4, C≡CH, CH_2OH, CH_2CH_2OH, CN, CH_2NMe_2

Charge-compensated products were isolated in moderate to good yield. Structure of carboranes with Me_2NCH_2Ph, Me_2CH_2CN and $Me_2CH_2C{\equiv}CH$ moieties were confirmed by X-ray diffraction.

In the case of N,N-dimethylaminopropanol, unusual minor seven-member cyclic product was isolated and characterized by NMR ^{11}B-^{11}B COSY and single-crystal X-ray diffraction.



Terminal Me_2N-group of charge-compensated product 7,8-$C_2B_9H_{11}$-9-$Me_2N(CH_2)_2NMe_2$ can be modified by the reaction with alkyl halogenides:



R = allyl, propargyl, ethoxyacetyl, methoxyacetyl

Thus series of ammonium-based charge-compensated nido-carboranes was synthesized. Also possibility of further modification was demonstrated.

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SYNTHESIS AND CHARACTERIZATION OF NOVEL COBALT COMPLEXES CONTAINING 4,5-DISUBSTITUTED *O*-SEMIQUINONE

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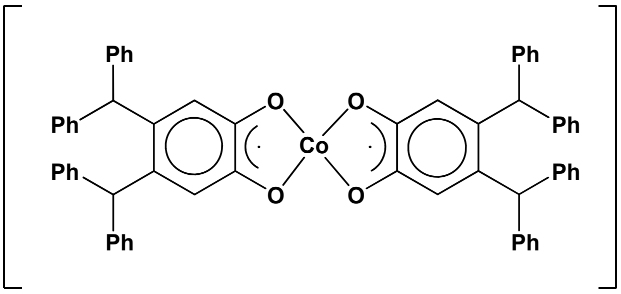
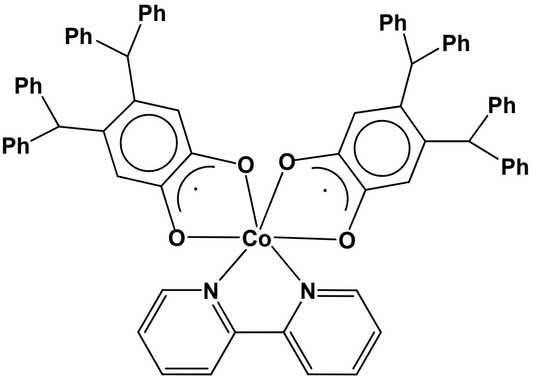
o-Semiquinonic transition metal complexes are the most widely studied objects of research in the field of redox isomerism. Typically, derivatives of sterically hindered 3,5- and 3,6-di-tert-butyl-1,2-benzoquinone are used as a redox active ligand. Compounds based on the *o*-semiquinone ligands with free 3,6-positions of the benzene ring are practically unknown. Two novel cobalt complexes based on sterically unhindered 4,5-bis(diphenylmethyl)-1,2-benzoquinone were synthesized.





The obtained compounds were investigated by such methods of analysis as IR- and EPR spectroscopy, variable temperature magnetic susceptibility measurements and elemental analysis. The presence of the intensive band corresponding to vibrations of sesquialteral C-O bond in the IR spectra of the obtained compounds indicates the semiquinonic type of ligand coordination. However, there is low intensity of absorption at 4000 cm^{-1} corresponding to the catechol-semiquinone LLCT band in the spectrum of the complex with dipyridyl. EPR spectrum of the powder of complex with neutral donor ligand has a typical for redox isomeric complexes of cobalt temperature dependence – line broadening simultaneously with decreasing of signal intensity with increasing temperature. EPR spectroscopy data are generally consistent with the results of magnetic measurements. The value of the effective magnetic moment of the complex with dipyridyl uniformly increases with increasing temperature, but even at 370 K the curve of the temperature dependence does not reach a plateau. These data suggest that the heteroligand complex undergoes redox isomeric conversion in a wide temperature range.

Acknowledgements. The authors are thankful to RFBR (grants: 13-03-97070, 13-03-12444, 13-03-97082), Russian president grant supporting scientific schools (НШ-1113.2012.3) and Program of Presidium of RAS №18 for financial support and A. Bogomyakov for magnetic measurements.

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POLYNUCLEAR COMPLEXES OF Co(II) AND Ni(II) WITH DIMETHYLMALONATE ANIONS, CONTAINING CROWN ETHERS

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The reaction of potassium dimethylmalonate (K_2Me_2Mal) and cobalt(II) carboxylates (pivalate or acetate) resulted in $\{[K_6Co_{36}(H_2O)_{28}(OH)_{20}(HMe_2Mal)_2(Me_2Mal)_{28}]\cdot 58H_2O\}$ (**1**) (where Me_2Mal^{2-} is the dimethylmalonate dianion) [1]. Same reactions of nickel(II) salts (acetate, pivalate, chloride) result in crystals (according to IR spectra the compound contains 36-nuclear anion $\{Ni_{36}\}$) with a high symmetry group, that complicates refinements of crystal structure. An addition of crown ether in reaction mixture would allow binding the part of the potassium atoms to from new surround of 36-nuclear fragment to low symmetry of crystals. The reaction of $\{M^{II}(Piv)_2\}$ (M^{II} = Co, Ni) and K_2Me_2Mal in the presence of 18-crown-6 in a mixture of ethanol-water (10:1) led compounds $\{[K_8Co_{36}(H_2O)_{20}(OH)_{20}(18\text{-crown-}6)_4(Me_2Mal)_{30}]\cdot 14H_2O\}$ (**2**) and $\{[K_6Ni_{36}(H_2O)_{16}(OH)_{20}(18\text{-crown-}6)_2(HMe_2Mal)_2(Me_2Mal)_{28}]\cdot 17H_2O\}$ (**3**), respectively. The structure of 36-nuclear anion $\{M_{36}\}$ in **2** and **3** is similar to the anion of **1**. Two potassium atoms are located inside anion $\{M_{36}\}$ for both complexes. Each potassium atom forms ionic bonds with O atoms of malonate anions (Fig. 1). Anions $\{M_{36}\}$ in **2** and **3** are bound to each other by $\{K(H_2O)_x\}^+$ fragments in chain structure.

Addition of dibenzo-18-crown-6 instead of 18-crown-6 in reaction mixture $\{Co(Piv)_2\}$–K_2Me_2Mal led the formation of complex $\{[K_8Co_{36}(H_2O)_{12}(OH)_{20}(\text{dibenzo-18-crown-}6)_9(Me_2Mal)_{30}]\cdot 18H_2O\}$.

Compound **2** exhibits low magnetic anisotropy and antiferromagnetic interactions between Co^{II} centers. Compound **3** is characterized by ferromagnetic interactions between nickel(II) ions in 36-nuclear fragment.

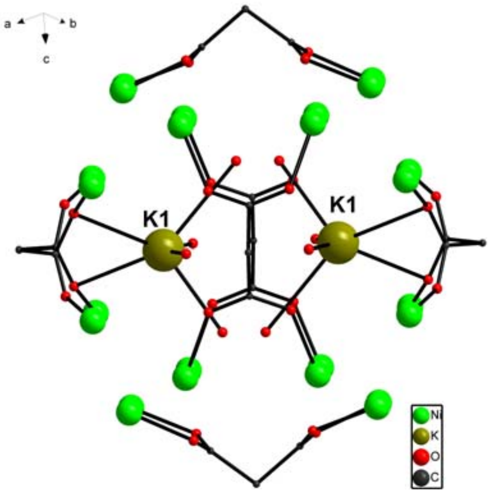

Fig.1 Potassium atoms inside anion $\{Ni_{36}\}$ and six dimethylmalonate dianions

[1] E.N. Zorina, N.V. Zauzolkova, A.A. Sidorov, G.G. Aleksandrov , A.S. Lermontov, M.A. Kiskin, A.S. Bogomyakov , V.S. Mironov, V.M. Novotortsev, I.L. Eremenko, *Inorg. Chem. Acta*, **2013**, *396*, 108-118.

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