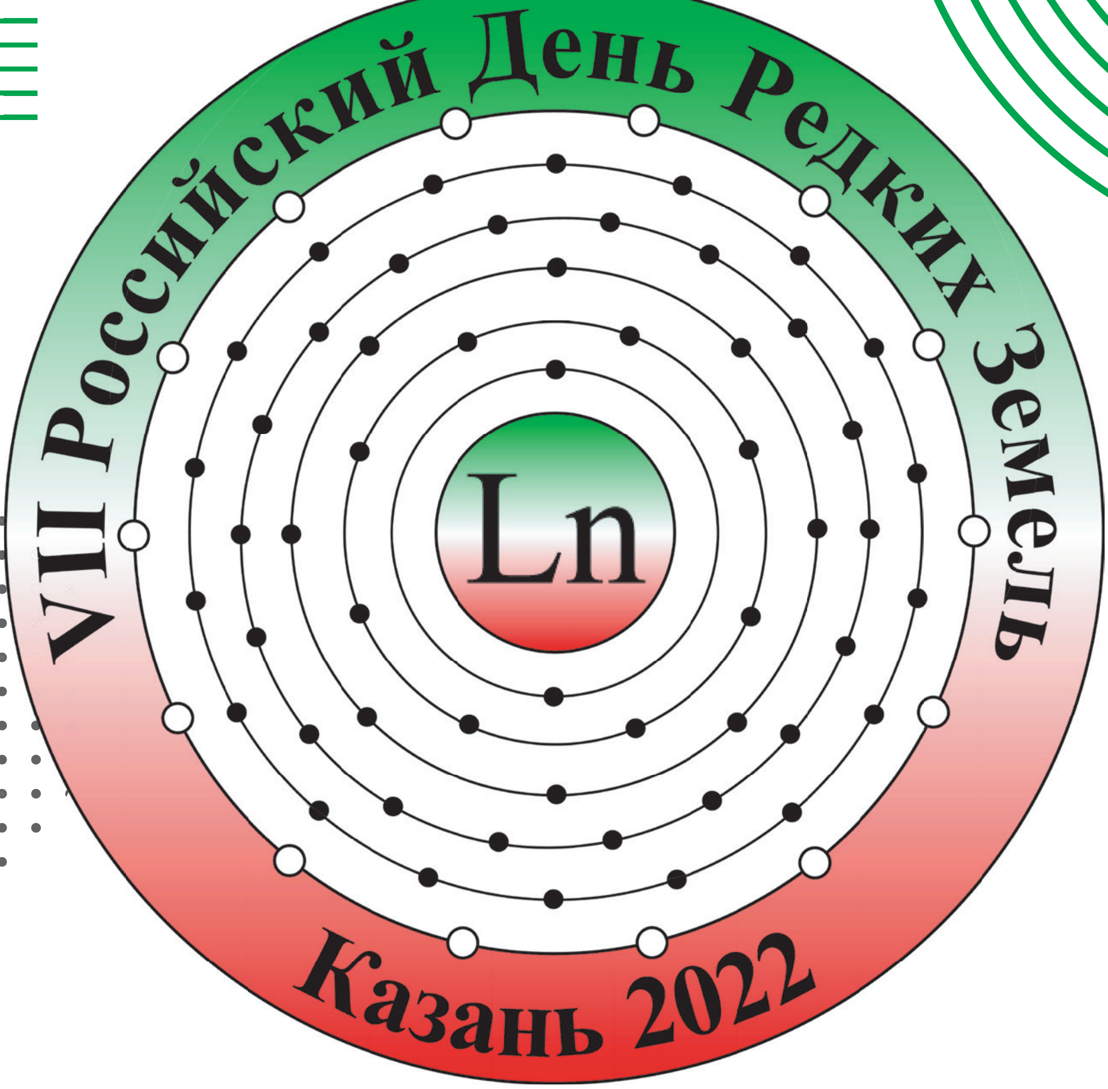


Всероссийская конференция
с международным участием

«VII Российский день редких земель»

ТЕЗИСЫ ДОКЛАДОВ

Казань, 14-16 февраля 2022 года

Всероссийская конференция
с международным участием
«VII Российский день редких земель»

РДРЗ-2022

Тезисы конференции

14–16 февраля 2022 года

г. Казань

Казань, 2022

УДК **546.6**

Тезисы Всероссийской конференции «VII Российский день редких земель» Ответственный за выпуск д.х.н. Н.Г. Наумов. Новосибирск: ИНХ СО РАН, 2022, 139 с.

ISBN 978-5-90168-848-9

Конференция «Российский день редких земель» (РДРЗ) охватывает все важнейшие аспекты и общемировые тенденции в химии редкоземельных металлов (РЗМ), включая органические, неорганические, координационные и гибридные производные, а также неорганические материалы на основе РЗМ. Основная задача конференции — сплотить ряды российских ученых, занимающихся фундаментальными аспектами химии РЗМ.

Традиционно РДРЗ собирает ведущих ученых в области редкоземельных металлов со всей России. Ранее встречи проходили в Нижнем Новгороде (ИМХ РАН, 2015, 2016 и 2019 гг.), Новосибирске (ИНХ СО РАН, 2017 и 2020 гг.) и Москве (ИНЭОС РАН, 2018 г.). В 2022 году Российский день редких земель впервые проходит в Казани 14—16 февраля.

В программу конференции включены устные, стендовые и заочные доклады ученых, работающих в области химии редкоземельных элементов.

ОРГАНИЗАТОРЫ

Министерство науки и высшего образования Российской Федерации
Российская академия наук
Институт неорганической химии им. А.В. Николаева СО РАН
Федеральный исследовательский центр
«Казанский научный центр Российской академии наук»
Институт органической и физической химии им. А.Е. Арбузова
Республиканское химическое общество им. Д.И. Менделеева Татарстана

СОПРЕДСЕДАТЕЛИ КОНФЕРЕНЦИИ

Бочкарев М.Н., д.х.н., проф. (Нижний Новгород)
Федюшкин И.Л., член-корр. РАН (Нижний Новгород)

ПРОГРАММНЫЙ КОМИТЕТ

Еременко И.Л., академик РАН (Москва)
Трифонов А.А., член-корр. РАН (Москва)
Горбунова Ю.Г., член-корр. РАН (Москва)
Карасик А.А., д.х.н., проф. (Казань)
Конченко С.Н., д.х.н. (Новосибирск)
Грачева Е.В., д.х.н. (Санкт-Петербург)
Мустафина А.Р., д.х.н. (Казань)
Кискин М.А., д.х.н. (Москва)

ОРГАНИЗАЦИОННЫЙ КОМИТЕТ

Карасик А.А., д.х.н., проф. (Казань) - председатель
Андреева О.В., к.х.н. (Казань)
Ахмадеев Б.С., к.х.н.(Казань)
Бочкова О.Д., к.х.н. (Казань)
Бурилов О.А. (Казань)
Галимова М.Ф. (Казань)
Гафуров З.Н., к.х.н. (Казань)
Даянова И.Р. (Казань)
Загидуллин А.А., к.х.н.(Казань)
Елистратова Ю.Г., к.х.н. (Казань)
Иванова Н.И. (Казань)
Кагилев А.А. (Казань)
Кантюков А.О. (Казань)
Карасик А.И. (Казань)
Конченко С.Н., д.х.н. (Новосибирск)
Мустафина А.Р., д.х.н.(Казань)
Наумова О.Е. (Казань)
Пушкаревкий Н.А., к.х.н. (Новосибирск)
Сахапов И.Ф., к.х.н. (Казань)
Тригулова К.Р. (Казань)
Трифонов А.В., к.х.н. (Казань)
Фазлеева Р.Р., к.х.н. (Казань)
Файзуллин Б.А. (Казань)
Федоренко С.В., к.х.н. (Казань)
Якупов А.М. (Казань)

Lanthanide Phthalocyanines: Yesterday, Today, Tomorrow

Yu.G. Gorbunova

Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, RUSSIA
Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, RUSSIA

Chemistry of lanthanide phthalocyanines started since 1965, when Kirin and Moskalev reported seminal work on template reaction between rare earth acetates with melted phthalonitrile [1]. The authors isolated surprisingly stable green and blue complexes, where metal ions were sandwiched between two Pc ligands – $M(Pc)_2$. Later the electronic structure and the nature of redox behaviour of such complexes were widely investigated and mono-, double and triple-decker structure of these complexes were established (Fig.1).

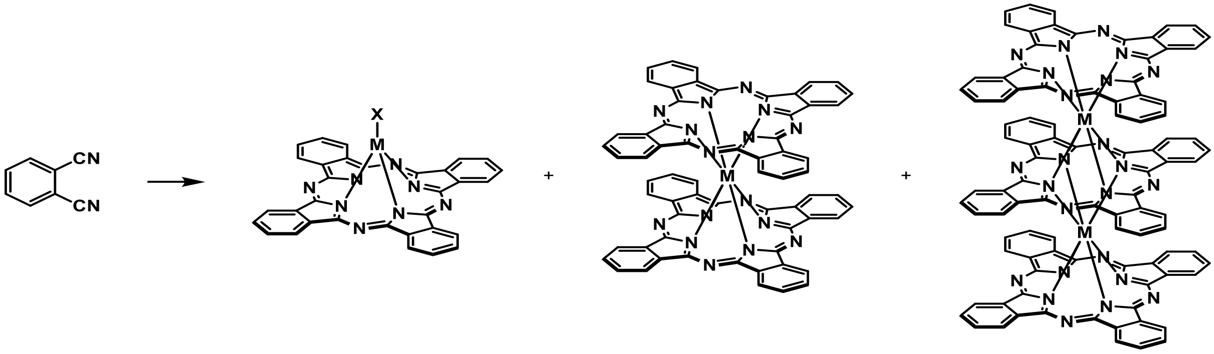


Fig.1.

Today, complexes of lanthanides with phthalocyanines (mono- and sandwich structures) attract great attention of researchers as basis of SMM, organic-field transistors, redox- and photoactive materials, sensors *etc* [2–4]. Recently our group have found new interesting properties of this class of compounds using supramolecular approach [5,6], developing the hybrid materials [7] as well as NMR temperature sensing probes [8].

The future aspects of this intriguing chemistry will be also discussed in the talk.

(1) Kirin, I. S.; Moskalev, P. N.; Makashev, Y. A. *Russ. J. Inorg. Chem.* **1965**, *10*, 369–372.
(2) Katoh, K.; Kagesawa, K.; Yamashita, M. Magnets. In *Materials and Energy*; **2018**; pp 271–344.
(3) Wang, H.; Wang, B. W.; Bian, Y.; Gao, S.; Jiang, J. *Coord. Chem. Rev.* **2016**, *306* (P1), 195–216.
(4) Chan, W. L.; Xie, C.; Lo, W. S.; Bünzli, J. C. G.; Wong, W. K.; Wong, K. L. *Chem. Soc. Rev.* **2021**, *50* (21), 12189–12257.
(5) Zvyagina, A. I.; Aleksandrov, A. E.; Martynov, A. G.; Tameev, A. R.; Baranchikov, A. E.; Ezhov, A. A.; Gorbunova, Y. G.; Kalinina, M. A. *Inorg. Chem.* **2021**, *60* (20), 15509–15518.
(6) Shokurov, A. V.; Yagodin, A. V.; Martynov, A. G.; Gorbunova, Y. G.; Tsivadze, A. Y.; Selektor, S. L. *Small* **2021**, 2104306.
(7) Oluwole, D. O.; Yagodin, A. V.; Mkhize, N. C.; Sekhosana, K. E.; Martynov, A. G.; Gorbunova, Y. G.; Tsivadze, A. Y.; Nyokong, T. *Chem. Eur. J.* **2017**, *23* (12), 2820–2830.
(8) Babailov, S. P.; Polovkova, M. A.; Kirakosyan, G. A.; Martynov, A. G.; Zapolotsky, E. N.; Gorbunova, Y. G. *Sensors Actuators A Phys.* **2021**, *331*, 112933. https://doi.org/10.1016/j.sna.2021.112933.

e-mail: yulia.gorbunova@gmail.com

Некоторые аспекты координационной химии ионов лантаноидов с полиоксометаллатами

V.S. Korenev, M.N. Sokolov

Nikolaev Institute of Inorganic Chemistry SB RAN, Novosibirsk, RUSSIA

Polyoxometalates (POMs) are a class of inorganic metal oxo complexes in their high oxidation states (mainly Mo, W, V, Nb and Ta). POMs can be versatile inorganic building blocks for the construction of molecule-based materials. In particular, they bind lanthanide (Ln) cations, resulting in a family of lanthanide substituted polyoxometalates (LSPs) that exhibit interesting luminescence and magnetic properties. Considerable attention has been focused on exploring the reaction of Ln cations with lacunary polyoxoanions because (1) Ln^{3+} cations have strong affinity for the basic oxygen atoms at the defect sites in lacunary; (2) owing to their multiple coordination requirements and stronger oxophilicity, Ln^{3+} cations can link different lacunary polyoxoanions together leading to oligomers or larger aggregates with unexpected structures and properties [1].

This report is focused on an overview of our ongoing study devoted to the synthesis of new **POM**-based Ln^{3+} complexes. Two case studies will be presented: coordination of Ln^{3+} to the lacunary $PW_{11}O_{39}^{7-}$ as quasitetradentate ligands and interactions of Ln^{3+} (such as Gd^{3+}) with large spherically-shaped polymolybdates (keplerates). Some representative examples of the ligands and the complexes obtained are shown in the Fig. 1.

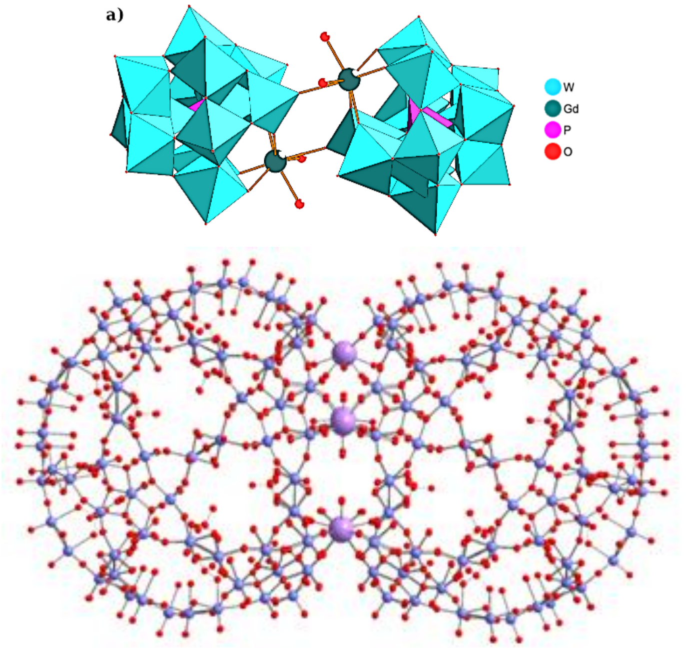


Fig. 1. Top: view of $[\{(PW_{11}O_{39})Gd(H_2O)_2\}_2]^{8-}$.
Bottom: View of $[Gd_5\{Mo_6O_{21}(H_2O)_6\}_{22}\{Mo_2O_4\}_{50}(SO_4)_{54}]^{117-}$.

[1] J. Niu, K. Wang, H. Chen, J. Zhao, P. Ma, J. Wang, M. Li, Y. Bai, D. Dang. *Crystal Growth & Design*, **2009**, *9*, 4362-4372.

e-mail: caesar@niic.nsc.ru

Peculiarities of lanthanide chelates in colloidal state

R.R. Zairov[a,b], A.P. Dovzhenko[b], S.N. Podychev[a], A.R. Mustafina[a]

[a] *A.E. Arbuzov Institute of Organic and Physical Chemistry KSC RAS, Kazan, RUSSIA*
[b] *Kazan (Volga region) Federal University, Kazan, RUSSIA*

Great efforts nowadays have been made to develop non-invasive thermometric methods that use all types of physical signals (optical, electric, magnetic, etc.) in the construction of nanothermometers. In our work, we have fabricated a new nanomaterial (Fig. 1), synthesized by solvent-induced nanoprecipitation [1-4]. The application for the use of thermal sensing in physiological range is discussed as well as insight into colloidal state of lanthanide complexes and their perspectives in chemistry, biology and interdisciplinary directions.

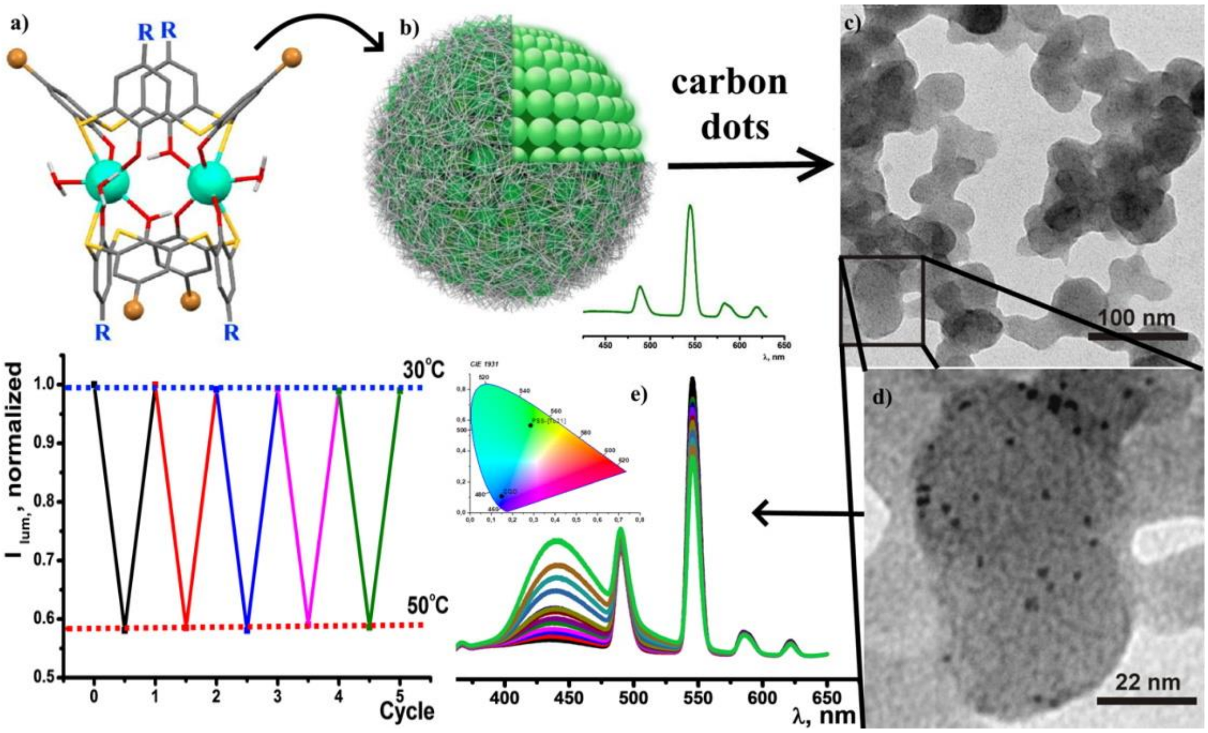


Fig. 1. (a) Structure of Tb2(TCAn)2 complex. (b) Schematic illustration of the PSS-[Tb2(TCAn)2] nanoparticle. (c,d) TEM images of PSS-[TbL-CD] nanoparticles in a dry state. (e) TbL-CD titration in DMF. (inset) Color coordinates of PSS-[Tb2(TCAn)2] and CDs. (f) I/I0 (545 nm) during six “heating-cooling” cycles within the range of 30-50 °C.

[1]. S.N. Podyachev,R.R. Zairov, A.R. Mustafina. Molecules **2021**, 26(5), 1214.
[2]. R.R. Zairov, A.P. Dovzhenko, A.S. Sapunova, A.D. Voloshina, K. Sarkanich, A. Daminova, I.R. Nizameev, D. Lapaev, S.N. Sudakova, S.N. Podyachev, K.A. Petrov, A. Vomiero and A.R. Mustafina. Scientific Reports. 10, Art.num. 20541 (2020).
[3]. Zairov, R.R., Dovzhenko, A.P., Sapunova, A.S., Voloshina, A.D., Tatarinov, D.A., Nizameev, I.R., Gubaidullin, A.T., Petrov, K.A., Enrichi, F., Vomiero, A., Mustafina, A.R. Materials Science and Engineering C. – 2019. Vol. 105 – art. num. 110057.
[4]. Zairov, R.R., Dovzhenko, A.P., K.A. Sarkanich, I.R. Nizameev, A.V. Luzhetskiy, S.N. Sudakova, S.N. Podyachev, V.A. Burilov, I.M. Vatsouro, A.Vomiero, A.R. Mustafina. Nanomaterials 2021, 11, 3080.

Acknowledgement – The authors thank the Russian Science Foundation (grant 21-13-00115) for financial support.
e-mail: rustem@iopc.ru

Coordination polymers based on rhenium cluster complexes and rare earth metal cations

Y.M. Gayfulin, Y.M. Litvinova, K.A. Brylev, Y.V. Mironov

Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA

Coordination polymers are a large class of compounds displaying structures formed by metal centers connected to each other by organic or inorganic bridging ligands. The study of the structure and properties of coordination polymers is a significant part of modern inorganic chemistry due to the diversity of their structures and a number of functional physicochemical properties, which are determined by the properties of individual building blocks. Currently, there is a growing interest in the use of voluminous metal centers as a basis for obtaining polymers with complex framework topologies or specific properties. In this work, study of chalcocyanide tetrahedral and octahedral rhenium cluster complexes as a basis for obtaining coordination polymers and metal-organic frameworks with rare-earth cations is presented. In these clusters, rhenium atoms are linked by covalent bonds forming the polyhedron with corresponding geometry. The faces of the polyhedron are coordinated by “inner” chalcogenide ligands, while the apical ligands are represented by cyanide anions (Fig. 1). The rigid bulk cluster core, high chemical stability and ambident nature of cyanide ligands make such clusters convenient anionic building blocks that are structural analogues of mononuclear cyanometalates. In addition, cluster complexes exhibit functional properties such as luminescence and redox activity, which is of interest for the preparation of functional coordination polymers.

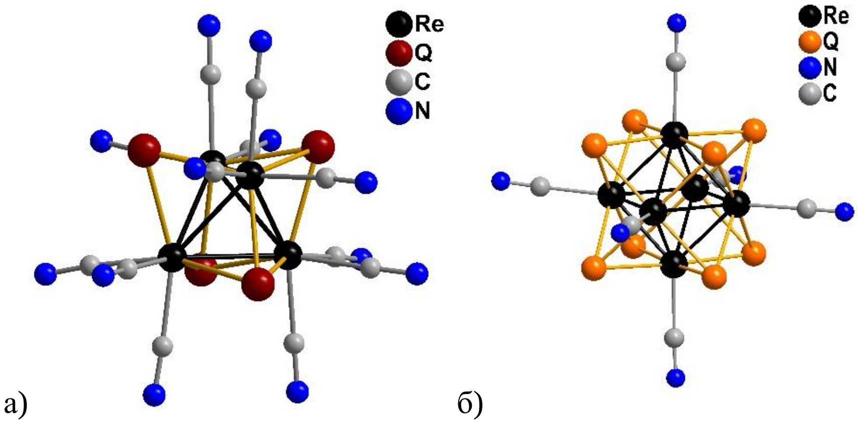


Fig. 1. Structure of cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ (a) and $[Re_6Q_8(CN)_6]^{4-/3-}$ (b).

Over the past few years, the authors have been studying coordination polymers formed by chalcocyanide clusters with different core geometries and complexes of rare earth metal cations with various organic ligands. The study of complexation between these structural fragments showed that the preferred dimensionality of the resulting polymers is determined by the geometry of the cluster anion. Thus, tetranuclear clusters with the general formula $[Re_4Q_4(CN)_{12}]^{4-}$ form mainly low-dimensional structures with chain, oligomeric or ionic structures [1, 2]. At the same time, cluster anions $[Re_6Q_8(CN)_6]^{4-/3-}$ most often form compounds with three-dimensional framework structures, and many of them demonstrate high chemical and thermal stability. This made it possible to obtain the first permanently porous framework polymers based on cluster complexes and to study their sorption properties [3]. It was also shown that the type of cluster anion used determines the physicochemical properties of the resulting polymer compounds. In particular, the luminescence properties of all compounds are determined by the optical properties of cluster anions, while the luminescence of rare earth metal cations is not displayed [4]. This shows that cluster fragments as components of coordination polymers not only play a structure-forming role, but also largely determine their physicochemical properties.

[1] Y.M. Litvinova, Y.M. Gayfulin, D.G. Samsonenko, D.A. Piryazev, Y.V. Mironov, *J. Cluster Sci.*, **2019**, *30*, 1195–1204.
[2] Y.M. Litvinova, Y.M. Gayfulin, D.G. Samsonenko, A.S. Bogomyakov, W.H. Shon, S.-J. Kim, J.-S. Rhyee, Y.V. Mironov, *Polyhedron*, **2016**, *115*, 174-179.
[3] Y.M. Litvinova, Y.M. Gayfulin, K.A. Kovalenko, D.G. Samsonenko, J. van Leusen, I.V. Korolkov, V.P. Fedin, Y.V. Mironov, *Inorg. Chem.*, **2018**, *57*, 2072-2084.
[4] Y.M. Litvinova, Y.M. Gayfulin, K.A. Brylev, D.A. Piryazev, J. van Leusen, P. Kögerler, Y.V. Mironov, *CrystEngComm*, **2020**, *22*, 7935–7943.

Acknowledgements – Authors thank RSF (project 19-73-20196) and Ministry of Education and Science of Russian Federation for financial support.

e-mail: gayfulin@niic.nsc.ru

d/f-Polypnictides derived by non-classical Ln(II) compounds

N. Reinfandt[a], C. Schoo[a], R. Yadav[a], S. Reichl[b], S.N. Konchenko[c], M. Scheer[b], P.W. Roesky[a]

[a]Institut für Anorganische Chemie, Karlsruher Institut für Technologie, Karlsruhe, GERMANY
[b]Institut für Anorganische Chemie. Universität Regensburg, Regensburg, GERMANY
[c]Nikolaev Institute of Inorganic Chemistry SB RAN, Novosibirsk, RUSSIA

The history molecular of *f*-element polypnictide complexes begins from two complexes described by W.J. Evans et al. [1, 2]. Almost 20 years later we have continued it with the first Ln polyphosphide $[(Cp^*{}_2Sm)_4P_8]$ [2], followed by its heavy analogues $[(Cp^*{}_2Sm)_4As_8]$ and $[(Cp^*{}_2Sm)_4As_8]$ as well as a series of mixed-Sm/d-metal polypnictides [e.g. 3-6]. All the compounds were obtained using a reductive approach by reacting appropriate pnictogen containing substrate with the corresponding divalent samarium species. The chemistry and the structure diversity of the compounds, but the limitation to only one 4f-element reduced a brilliance of the chemical story step by step.

An availability of molecular Ln(II) compounds of almost all lanthanides makes this chemistry very interesting again. Herewith we report new d/f-polypnictides – $[K(18\text{-crown-}6)][Cp''_2Ln(E_5)FeCp^*]$ (Ln = La, Ce, Nd; E = P, As) – prepared using a known 3-electron- $([K(18\text{-crown-}6)(thf)_2][(Cp''_2La)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)]$, **A**) [7] as well as two new 4-electron- $([K(18\text{-crown-}6)][(Cp''_2Ln)_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)]$, Ln = Ce (**B**), Nd (**C**) as non-classical reducing agents of the early lanthanides towards $[Cp^*Fe(\eta^5\text{-}E_5)]$.

It was found also that these new d/f-polypnictides react with P_4 resulting in a selective expansion of $\{P_5\}^{3-}$ unit to $P_7{}^{3-}$: $[K(18\text{-crown-}6)][Cp''_2Ln(P_7)FeCp^*]$ (Ln = La, Nd) [2].

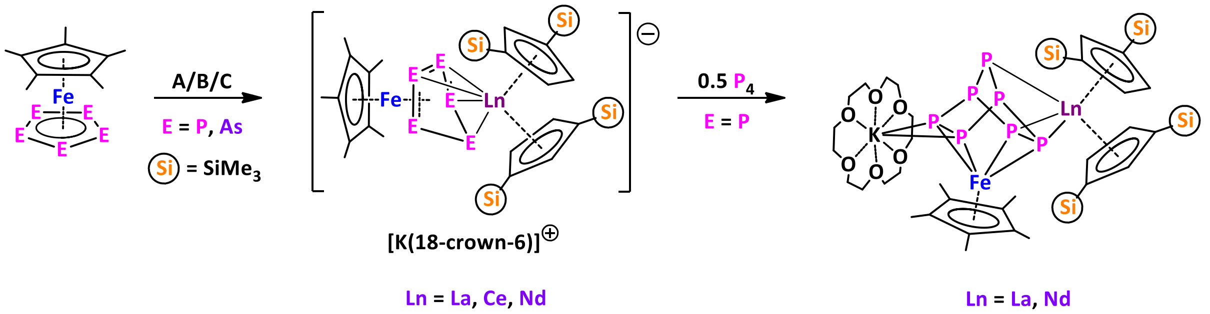


Fig.1. Synthesis of the new d/f-polypnictides and their subsequent reaction with white phosphorus.

Acknowledgements – Authors thank RFBR and Ministry of Education and Science of RF for financial support.

[1] W.J. Evans, S.L. Gonzales, J.W. Ziller, J. Am. Chem. Soc., 1991, 113, 9880.
[2] W.J. Evans, S.L. Gonzales, J.W. Ziller, Chem. Commun., 1992, 1138.
[3] T. Li, M.T. Gamer, M. Scheer, S.N. Konchenko, P.W. Roesky, Chem. Comm., 2013, **49**, 2183.
[4] C. Schoo, S. Bestgen, R. Köppe, S.N. Konchenko, P.W. Roesky, Chem. Comm., 2018, 54, 4770.
[5] C. Schoo, S. Bestgen, A. Egeberg, S.V. Klementyeva, C. Feldmann, S.N. Konchenko, P.W. Roesky, Angew. Chem. Int. Ed., 2018, 57, 5912-5916.
[6] N. Reinfandt, C. Schoo, L. Dütsch, R. Köppe, S.N. Konchenko, M. Scheer, P.W. Roesky, Chem. Eur. J., 2021, 27, 3974.
[7] N. Reinfandt, N. Michenfelder, C. Schoo, R. Yadav, S. Reichl, S. N. Konchenko, A. N. Unterreiner, M. Scheer, P. W. Roesky, Chem. Eur. J. 2021, 27, 7862.

e-mail: konch@niic.nsc.ru

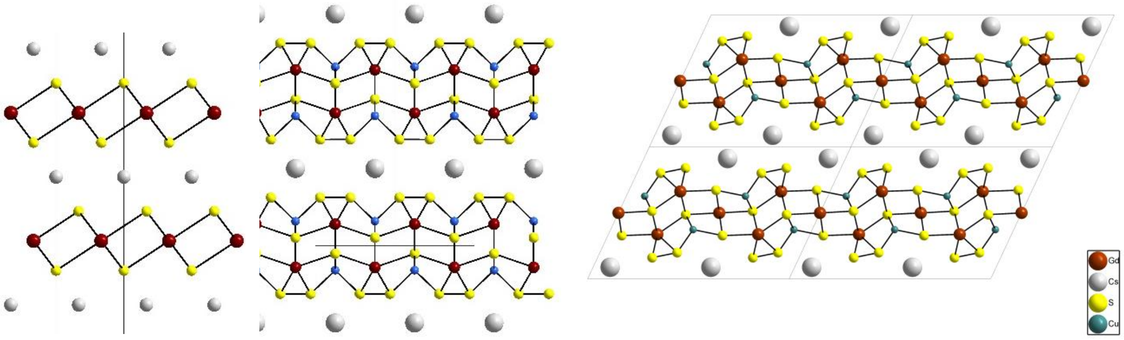
Layered rare earth chalcogenides

N.G. Naumov[a,b], T.A. Pomelova[a], M.S. Tarasenko[a], N.V. Kuratieva[a], S.J. Park[b]

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

The rare earth chalcogenides are the large and intriguing class of inorganic compounds demonstrating promising physical properties: magnetic, charge density waves, thermoelectric, luminescent and non-linear, etc.

This report overviews our recent results and achievements in the synthesis and study of the structure and physicochemical properties of layered rare earth chalcogenides The details of the synthesis, structure, and possibilities of the synthesis of nanoparticles of such materials are widely discussed [1-5].



a) b) c)

Fig. 1. Crystal structures of layered compounds $KLnS_2$ (a), KLn_2CuS_6 (b) and $Cs_2Ln_3CuS_8$ (c)

The synthesis and properties of chalco-orthosilicates Ln_2SiO_4Q, Q=S, Se, Te and oxoselenides Ln_2O_2Se are also reported.

[1] M. S. Tarasenko, A. S. Kiryakov, A. Ryadun, N. V. Kuratieva, P. E. Plyusnin and N. G. Naumov, Mater. Today Commun, **2019**, *21*, 100665.

[2] T. A. Pomelova, T. Y. Podlipskaya, N. V. Kuratieva, A. G. Cherkov, N. A. Nebogatikova, M. R. Ryzhikov, A. Huguenot, R. Gautier and N. G. Naumov, Inorg. Chem., **2018**, *57*, 13594-13605.

[3] T. A. Pomelova, V. K. Muraveva, T. Y. Podlipskaya, S. E. Khandarkhaeva, N. A. Nebogatikova, I. V. Yushina, E. Y. Gatapova, S. Cordier and N. G. Naumov, Mater. Sci. Eng. B, **2018**, *228*, 261-266.

[4] A. S. Kiryakov, D. A. Piryazev, M. S. Tarasenko and N. G. Naumov, J. Struct. Chem. (Engl. Trans.), **2018**, *59*, 635-640.

[5] T. A. Pomelova, S. E. Khandarkhaeva, T. Y. Podlipskaya and N. G. Naumov, Colloids Surf. A, **2016**, *504*, 298-304.

Acknowledgements – Authors thank RFBR (projects 20-53-00036) and Ministry of Education and Science of Russian Federation for financial support.

e-mail: naumov@niic.nsc.ru

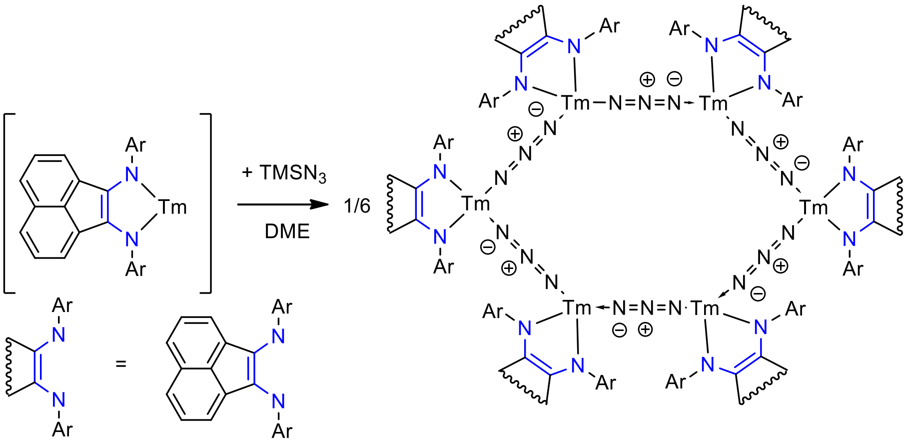
О синтезе бисиминоаценафтеновых производных Tm(II) и Dy (II)

В.А. Додонов, М.Н. Земнюкова, В.М. Макаров, И.Л. Федюшкин

Институт металлорганической химии им. Г.А. Разуваева РАН
603137 Нижний Новгород, ул. Тропинина, 49

Среди новых важных направлений исследований лантаноидов – поисковые работы по производным «неклассических» двухвалентных лантаноидов Dy, Tm и Nd. Эта тема в настоящее время привлекает значительное внимание исследователей.[1-3] Благодаря высокому значению восстановительного потенциала такие соединения чрезвычайно активны и не стабильны, что, однако, может быть использовано для активации органических субстаратов и малых молекул.

В настоящей работе сообщается о попытках синтеза [(dpp-bian)Tm(DME)$_2$] и [(dpp-bian)Dy(DME)$_2$] – аналогов [(dpp-bian)Yb(DME)$_2$] – и изучении их реакционной способности в отношении гетеродиенов и гетерокумуленов.



[1] M. N. Bochkarev, *Coord. Chem. Rev.* **2004**, *248*, 835-851
[2] M. E. Fieser, M. R. MacDonald, B. T. Krull, J. E. Bates, J. W. Ziller, F. Furche, W. J. Evans, *J. Am. Chem. Soc.* **2015**, *137*, 369-382
[3] F. Nief, *Dalton Trans.* **2010**, *39*, 6589-6598.

Благодарности: Работа выполнена при финансовой поддержке гранта РНФ 21-73-20153.

e-mail: dodonov@iomc.ras.ru

Lanthanide complexes of sterically-hindered acenaphthene-1,2-diimines

I.L. Fedushkin

G.A. Razuvaev Institute of Organometallic Chemistry of RAS, Nizhny Novgorod, RUSSIA

Complexes of the rare earth elements – ytterbium, samarium, europium, lanthanum and thulium – stabilized by sterically hindered Ar-bian family ligands (dpp-bian or Ar^{BIG}-bian) have been prepared and characterized. The titled compounds revealed reactivity which is associated with the metal center as well as with the redox-active diimine ligand. Ytterbium complexes reveal two types of thermally induced redox-isomerism depending on the ligand. The bulkiness of the Ar-bian ligand leads to the formation of low-coordinate and solvent-free metal complexes. High electron capacity of ligands allowed formation of their polyanions that form stable sandwich-like complexes with the lanthanides.

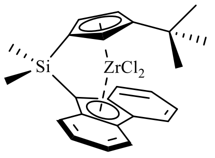
e-mail: igorfed@iomc.ras.ru

Phosphonium-bridged *ansa*-metallocenes of rare-earth metals

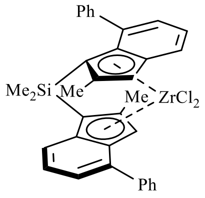
Jasmin J. M. Quentin[a], Konstantin A. Rufanov,[a,b] and Jörg Sundermeyer[a]

[a]*Fachbereich Chemie der Philipps-Universität Marburg, Hans-Meerwein-Strasse, 35032 Marburg, Germany*
[b] *Institute of Living Systems, I. Kant Baltic Federal University, University str., 2, Kaliningrad, 236040, Russian Federation*

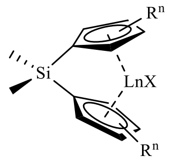
Group 4 *ansa*-metallocenes, in particular *ansa*-zirconocenes, (**A, B**) became one of the most important classes of d-electron poor transition metal catalysts for olefin polymerisation.[1] *Ansa* units, interannular bridging groups prevent free rotation of the cyclopentadienyl rings thus fixing their molecular configuration in a constrained manner, thus increasing both the Lewis acidity of the active metal center and as a result the turnover of a catalytic polymerisation. Although metallocenes of the group 4 metals have been dominated, the advantages of rare-earth *ansa*-metallocenes in catalysis have been already demonstrated. Since the early work of Yasuda,[2] who published a series of mono- (**C**) and bis-Me_2Si-bridged *ansa*-metallocenes (**D**) with high activities in the linear polymerization of PE and block copolymerization of polar and nonpolar monomers, *ansa*-metallocenes of rare-earth metals have been successfully applied in the catalysis of various polymerization and copolymerization reactions.



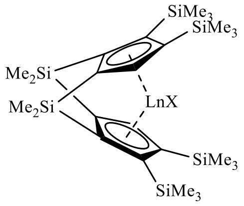
A



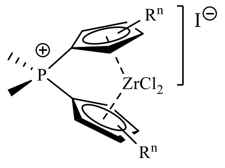
B



C

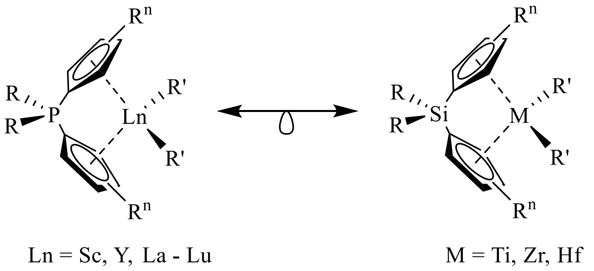


D



E

Heteratom-bridged metallocenes can play an important role in the development of novel catalysts. First attempts to fully establish phosphonium bridges *ansa*-zirconocenes of the type **E** were reported by Parkin[3]. Isolobal relationship between well established R_2Si-bridged *ansa*-metallocenes of group 4 metals and R_2P-bridged *ansa*-metallocenes of rare-earth, i.e. group 3 metals and lanthanides, assumes similarity in both steric and electronic properties for both compound classes and therefore may result in highly variable catalytic properties.



Synthesis of salt-free ligands $[Me_2P(C_5Me_4)C_5Me_4H]$ **1-H** and $[Me_2P(C_9H_6)C_9H_7]$ **2-H** has been achieved by dehydroiodation of corresponding phosphonium salts. Their metallation by different organometallic agents as well as molecular structure and reactivity of the resulted *ansa*-metallocenes will be reported.

[1] W. Kaminsky, K. Külper, H.-H. Brintzinger, F. R. W. P. Wild, *Angew. Chem.*, **1985**, *97*, 507; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 507.
[2] H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, *J. Am. Chem. Soc.* **1992**, *114*, 4908.
[3] J. H. Shin, B. M. Bridgewater, G. Parkin, *Organometallics* **2000**, *19*, 5155

Acknowledgements – *This research was supported from the Russian Federal Academic Leadership Program Priority 2030 at the Immanuel Kant Baltic Federal University*.

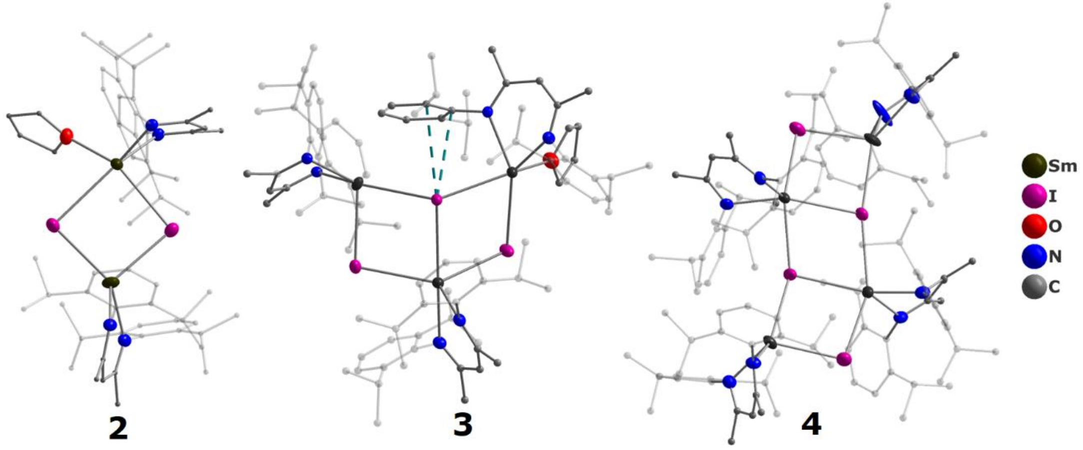
e-mail: kruf@mail.ru, KRufanov@kantiana.ru

Oligomerization and reductive properties of Sm(II) iodo-β-diketiminate complexes

N.A. Pushkarevsky, O.A. Mironova, T.S. Sukhikh, S.N. Konchenko

Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA

Molecular halogenide complexes of lanthanides (Ln) are widely used as starting compounds. Knowing their exact composition and structure is important for the control of reaction stoichiometry, as well as for understanding the reactivity. The type of donor solvent molecules used in the synthesis heavily influence the molecular structures of Ln halogenides. Excess of small molecular donors, such as tetrahydrofurane (thf) or CH_3CN often leads to mononuclear complexes, while in a non-coordinating medium, or as a result of donor solvent loss during storage, di- or polynuclear species can form.



We have been investigating Ln iodide complexes with a β-diketiminate ligand $\{HC(C(Me)N(dipp))_2\}^-$ (Nacnac$^-$; Dipp = 2,6-$C_6H_4{}^iPr_2$) [1,2]. The series [Ln(Nacnac)I_2(thf)$_2$] with Ln^{3+} cations (for Nd, Sm, Gd, Tb, Dy) resist full desolvation upon elevated temperatures. A partially desolvated complex could be obtained only for Nd, [Nd(Nacnac)I_2(thf)], which is still mononuclear. The Sm^{2+} complex [Sm(Nacnac)I(thf)$_2$] [3] can be fully desolvated with the stepwise formation of di-, tri- and tetranuclear complexes (**2**–**4** on the figure), which are composed of {Sm(Nacnac)I} fragments and feature different thf content. The fully desolvated **4** can bind two thf molecules and transform into structurally very similar **4**·2thf (**4***), which is an exact dimer of **2**. The complexes behave as multielectron reductants. The complex **4** is oxidized by iodine to the mixture of a donor-free Sm^{3+} complex [{Sm(Nacnac)I_2}$_2$] and a unique heterovalent Sm$^{2+/3+}$ complex [{Sm(Nacnac)I}$_4$(μ_4-I)], stoichiometrically with respect to the I_2/**4** ratio. The complex **3** is oxidized by $^nBu_3PTe$ which leads to the product [{Sm(Nacnac)I}$_3$(μ_2-Te_2)(thf)] which contains a ditelluride fragment. Structural features and reaction routes will be discussed.

[1] O. A. Mironova, T. S. Sukhikh, S. N. Konchenko, N. A. Pushkarevsky, *Polyhedron*, **2019**, *159*, 337–344.
[2] O. A. Mironova, A. A. Ryadun, T. S. Sukhikh, S. N. Konchenko, N. A. Pushkarevsky, *New J. Chem.*, **2020**, *44*, 19769–19779.
[3] O. A. Mironova, T. S. Sukhikh, S. N. Konchenko, N. A. Pushkarevsky, *Russ. J. Coord. Chem.*, **2020**, *46*(4), 241–250.

Acknowledgements – Authors thank Russian Science Foundation (project No. 22-23-00983) and Ministry of Education and Science of Russian Federation for financial support.

e-mail: nikolay@niic.nsc.ru

Синтез и каталитические свойства церийсодержащих композиций

Е.Ю. Либерман, В.Н. Грунский, Е.А. Симакина, Т.В. Конькова

Российский химико-технологический университет им. Д.И. Менделеева

Церийсодержащие композиции нашли широкое применение в самых разнообразных областях науки и техники: полирующие материалы, твердотельные электролиты, противокоррозионные и оптические покрытия, биомедицинские препараты и др. Однако наибольший интерес вызывает применение данных материалов для использования в качестве катализаторов и их носителей в таких процессах, как очистка промышленных газовых и автомобильных выбросов, дожиг сажи, деструкция органических соединений, получение синтез-газа, PROX, что во многом обусловлено наличием редокс-перехода $Ce^{+3} \leftrightarrow Ce^{+4}$. Увеличению каталитической активности церийсодержащих материалов способствует проведение изо- и гетеровалентного допирования диоксида церия ионами d- и f-элементами, в результате которого происходит образование твердых растворов на основе кристаллической решетки диоксида церия. Свойства образующихся соединений во многом определяются химической природой выбранного иона-допанта. Так, при модифицировании ионами Zr^{+4} происходит увеличение термостойкости диоксида церия, что позволяет улучшить его эксплуатационные свойства.

Синтез твердых растворов проводили путем соосаждения ионов Ce^{+3} и Zr^{+4} гидроксидом аммония с последующим прокаливанием при температуре 500°C. Методом рентгеновской дифракции показано, что при содержании Zr, не превышающим 20 мол.%, происходит формирование твердого раствора на основе кристаллической решетки диоксида церия. При более высоком содержании циркония происходит образование бифазной системы: флюоритоподобного твердого раствора и диоксида циркония. Образование твердых растворов, согласно результатам проведенных дериватографических исследований, протекает уже на стадии осаждения, но окончательное формирование происходит только на стадии прокаливания. Существенным недостатком данного метода, является образование труднофильтруемых гелеподобных осадков. Проведенные исследование влияния параметров синтеза на такие характеристики, как коэффициент фильтрации суспензии гидроксидов церия (III) и цирконила и удельную поверхность твердого раствора $Zr_{0,2}Ce_{0,8}O_2$, показали, что оптимальными условиями проведения синтеза являются температура синтеза 40-60˚С и pH 10,5-11 единиц. В данном случае происходит формирование материала с величиной удельной поверхности 78 $м^2$/г. Добавление в суспензию 3 об.% раствора водорастворимого полимера полиакриламида (ПАА), имеющего концентрацию 1 мас.%, позволяет не только улучшить фильтрационные характеристики, но и увеличить удельную поверхность до 150 $м^2$/г. Однако при этом происходит ухудшение каталитической активности в реакции окисления CO, что, по-видимому, связано с эффектом «зауглероживания» поверхности, которая приводит к блокировке активных центров.

Флюоритоподобная структура сохраняется и при дальнейшем модифицировании ионами Me^{+3}, где Me = Pr – Lu, в количестве 10 мол.%. Отмечено наличие корреляции между параметром решетки и ионным радиусом допанта: с увеличением порядкового номера допанта наблюдается уменьшение параметра решетки. Синтезированные системы обладают высокой дисперсностью. Допирование редкоземельными элементами сопровождается развитием пористой структуры: удельная поверхность синтезированных катализаторов увеличивается до 81-85 м^2/г, суммарный объем пор возрастает до 0,102-0,109 см^3/г. Активность твердых растворов в реакции окисления CO (условия проведения каталитических измерений: состав газовой смеси: CO – 3,6 об.%, O_2 – 8,0 об.%, N_2 – баланс, объем катализатора 1 см^3, объемная скорость 3600 ч$^{-1}$) зависит от природы иона-допанта: наиболее активным является катализатор $Pr_{0,1}Zr_{0,18}Ce_{0,72}O_{2-\delta}$: $T_{50\%}$ 205°C, $T_{90\%}$ - 290°C, наименее - $Lu_{0,1}Zr_{0,18}Ce_{0,72}O_{2-\delta}$: $T_{50\%}$ - 345°C, $T_{90\%}$ - 386°C. Так, средний размер частиц составляет порядка 8 нм. Согласно результатам спектроскопии КР, образец $Pr_{0,1}Zr_{0,18}Ce_{0,72}O_{2-\delta}$ имеет наиболее дефектную структуру. Исследования приповерхностного слоя, проведенные методом РФЭС, показали наличие сегрегации ионов Pr^{+3} на поверхности катализатора.

Перспективным является проведение допирования ионами Bi^{3+} и Gd^{3+}. Проведенные исследования влияния природы редкоземельного допанта на каталитические свойства синтезированных материалов $M_{0,05}Bi_{0,05}Zr_{0,18}Ce_{0,72}O_{2-\delta}$, где M – Nd, Sm, Gd, показали, что наиболее активным в реакции окисления CO (условия проведения каталитических измерений: состав газовой смеси: CO – 1,0 об.%, O_2 – 8,0 об.%, N_2 – баланс, масса катализатора 0,3 г, объемная скорость 3600 ч$^{-1}$) является образец, допированный ионами Gd^{3+}, для которого температура 50%-конверсии составляет 150˚C. Так, анализ активности $Gd_{0,1}Zr_{0,18}Ce_{0,72}O_{2-\delta}$ и $Gd_{0,05}Bi_{0,05}Zr_{0,18}Ce_{0,72}O_{2-\delta}$ показал значительное увеличение активности при введении ионов висмута. Повышение каталитической активности вызвано тем, что, во-первых, модифицирование Zr0,2Ce0,8O2 ионом Gd^{3+}, имеющего более низкий заряд, приводит к возникновению анионных вакансий и образованию иона Ce^{3+}, что способствует росту каталитической активности вследствие повышения мобильности кислорода в кристаллической решетке и редокс-превращениям Ce^{3+}/Ce^{4+}. Во-вторых, ион Gd^{3+} усиливает искажения кристаллической решетки $Zr_{0,2}Ce_{0,8}O_2$, т.к. обладает значительно большим ионным радиусом по сравнению с ионами Ce^{4+} и Zr^{4+}. Вероятно, что в случае совместного допирования ионами Bi^{3+} и Gd^{3+} происходит формирование наиболее дефектной структуры, способствующей повышению активности. Для четырехкомпонентных систем $M_{0,05}Bi_{0,05}Zr_{0,18}Ce_{0,72}O_{2-\delta}$, где M – Nd, Sm, Gd наблюдается противоположная тенденция: активность уменьшается с увеличением ионного радиуса допанта. Вероятной причиной этого является формирование структуры, снижающей мобильность кислорода вследствие пространственных ограничений.

Таким образом, проведенные исследования показали перспективность использования многокомпонентных композиций на основе кристаллической решетки диоксида церия для их использования в качестве катализаторов окисления CO.

e-mail: el-liberman@muctr.ru

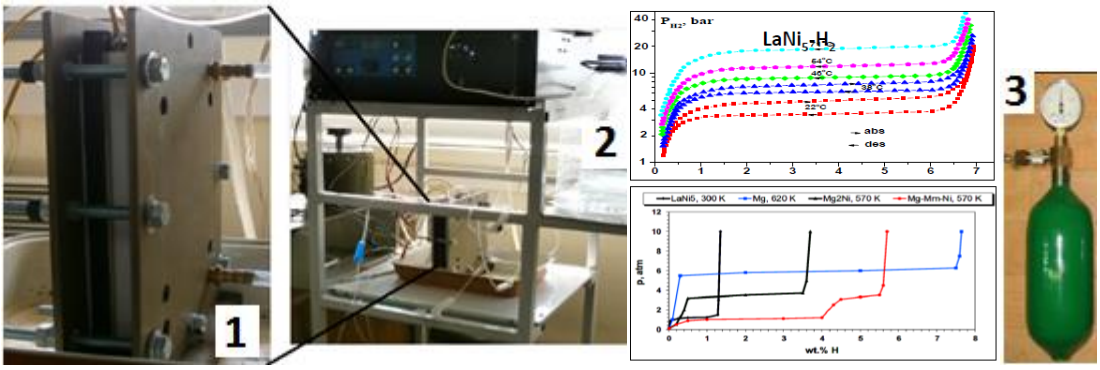
Techno-economic feasibility of producing hydrogen by electrolysis using rare-earth metals

S.A. Sosnovskiy

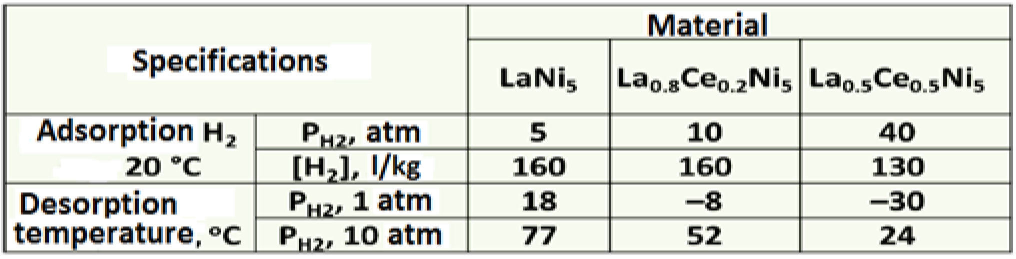
Tomsk State University, Tomsk, RUSSIA

As an alternative fuel, hydrogen has been regarded as one of the promising clean energies with the advantage of abundance (generated through water splitting) and pollution-free emission if used in fuel cell systems. However, some key problems such as finding efficient ways to produce and store hydrogen have been hindering the realization of the hydrogen economy. Here from the scientific perspective, variousmaterials including the nanostructures and the bulk hydridescontaining, rare earth metals, have been examined in terms of their crystal and electronic structures, energetics, and different properties forhydrogen generation or hydrogen storage applications.

Among the techniques required to realize the hydrogen economy, hydrogen storage isone major challenging barrier to introduce hydrogen in the transportation area. One of the key parameter is the hydrogen storage capacity. Water electrolysis are seen as potential technologies to achieve GHG emission reductions and limit the global warming to 1.5 °C above pre-industrial levels. Moreover, are also seen as a solution to balance electricity grid in the case of higher share renewable energy production which would increase the intermittent energy production. One technology cannot solve all problems but hydrogen has already versatile end-use applications and potential to make significant reductions in CO_2-emissions in energy sector, limiting the global temperature rise. On scheme 1 presents hydrogen storage systems based on rare earth metals, as well as the author's electrolysis production of hydrogen at an asymmetric current under conditions of resonant interaction.



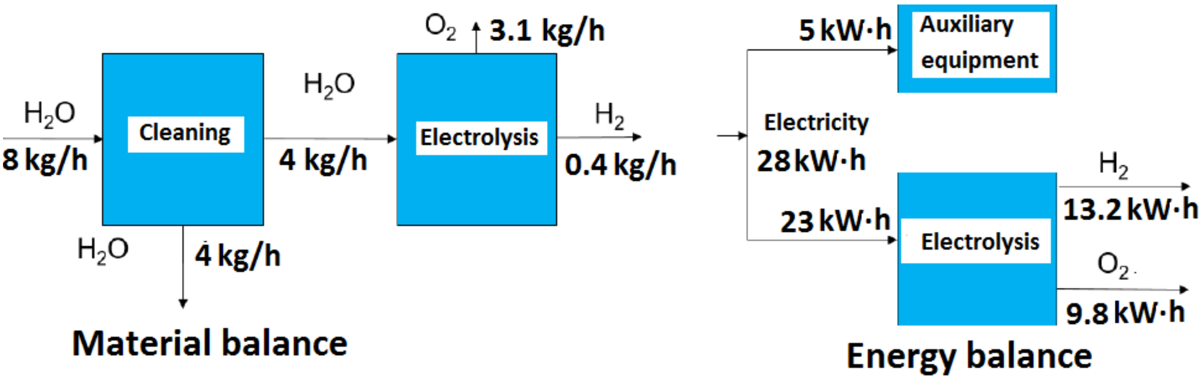
Scheme. 1 Hydrogen storage systems based on rare earth metals, as well as the author's electrolysis production of hydrogen at an asymmetric current under conditions of resonant interaction.
1- electrochemical module for hydrogen production; 2- source of electrical asymmetric and frequency current; 3- cylinder with hydrogen and metal hydride inside.



Specifications		Material		
		$LaNi_5$	$La_{0.8}Ce_{0.2}Ni_5$	$La_{0.5}Ce_{0.5}Ni_5$
Adsorption H_2 20 °C	P_{H2}, atm	5	10	40
	$[H_2]$, l/kg	160	160	130
Desorption temperature, °C	P_{H2}, 1 atm	18	−8	−30
	P_{H2}, 10 atm	77	52	24

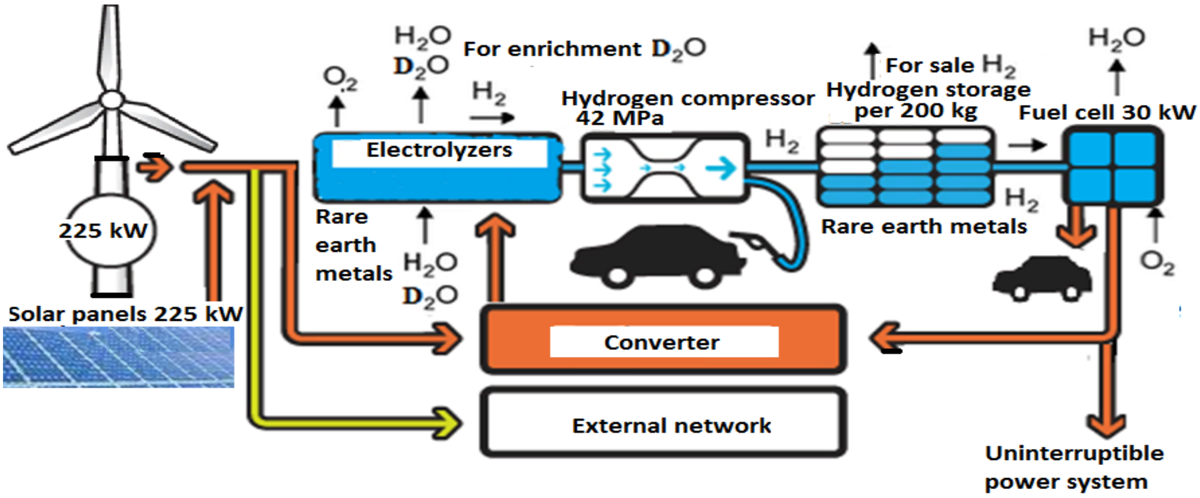
Scheme. 2 Metal hydride chemical compounds for hydrogen storage, based on rare earth metals.

Scheme 3 shows the material and energy balances of the electrolysis production of hydrogen using an asymmetric current under conditions of electrochemical resonance.



Scheme. 3 The material and energy balances of the electrolysis production of hydrogen.

Scheme 4 presents an environmentally friendly technology for the production of hydrogen and the production of deuterium in the process of electrolysis using asymmetric current in resonant conditions.



Scheme. 4 Scheme for obtaining environmentally friendly hydrogen and deuteriumusing rare earth metals in the form of metal hydride compounds for hydrogen storage.

e-mail: ssa777@mail.ru

Amine-boranes dehydrogenation – a new challenge for rare earth metal complexes

O. A. Filippov[a], V. A. Kirkina[a], A. A. Kissel[a], A. N. Selikhov[b], Y. V. Nelyubina[a], N. V. Belkova[a], E. S. Shubina[a], A. A. Trifonov[a,b]

[a]*A.N.Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia*
[b]*G. A. Razuvaev Institute of Organometallic Chemistry RAS, Nizhniy Novgorod, Russia*

The dehydrocoupling of amine-boranes is not only an efficient way to produce hydrogen but also to obtain new molecules and tailored new materials with B–N bonds [1]. The intensive exploration resulted in the development of many efficient systems for catalytic amine–boranes dehydrogenation which are mainly based on transition-metal complexes, however the principles of sustainable development call for the use of cheaper earth-abundant metals like Fe, Ni, Co, Mn etc. Known for their Lewis acidity and variety of coordination behavior, lanthanides can also be a promising class of metals for use as amine borane dehydrogenation catalysts; however, they have hardly been explored from this point of view [2,3].

Here we present our latest results of the mechanistic and catalytic studies of amine-boranes ($Me_2NH{\cdot}BH_3$, $t$$BuNH_2{\cdot}BH_3$) dehydrogenation by rare earth metal complexes $(TBDM)_2ML_n$ (M = Sm, Yb; TBDM = (p-$t$$Bu$-$C_6H_4)_2CH$; L = TMEDA (n = 1), DME (n = 2)) by IR, NMR (^1H, ^{11}B) and X-Ray spectroscopies [4]. It was shown that formation of amido-borane lanthanide complexes (**2** and **3** at Fig. 1) precedes catalytic dehydrogenation of aminboranes. The intermediates of the pre-catalytic reaction, kinetics of the subsequent amine-borane dehydrogenation, as well as the difference between Sm and Yb complexes will be discussed.

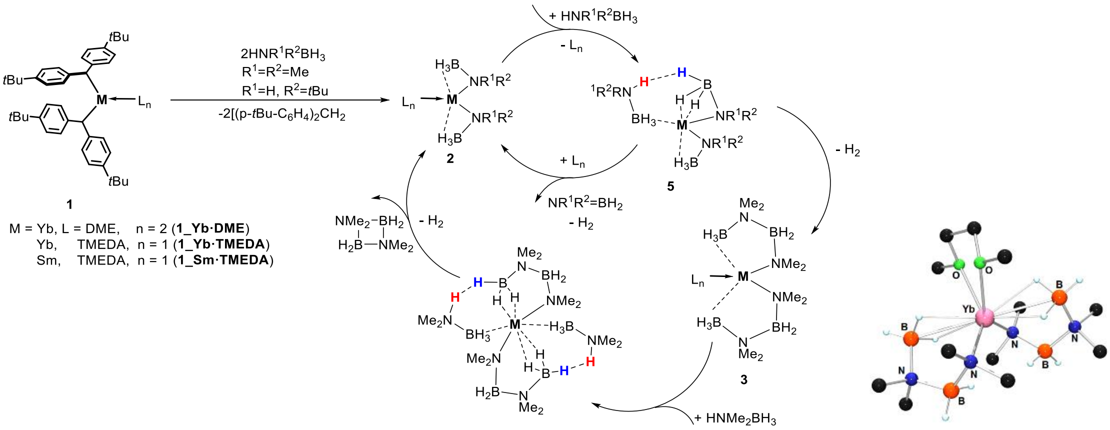


Fig. 1. Amine-borane dehydrogenative coupling catalyzed by lanthanide(II) species.

[1] A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.*, **2010**, *110*, 4079 – 4124
[2] M. S. Hill, G. Kociok-Kohn, T. P. Robinson, *Chem. Commun.*, **2010**, *46*, 7587−7589
[3] P. Cui, T. P. Spaniol, L. Maron, J. Okuda, *Chem. Eur. J.*, **2013**, *19*, 13437 – 13444
[4] V. A. Kirkina, A. A. Kissel, A. N. Selikhov, Y. V. Nelyubina, O. A. Filippov, N. V. Belkova, A. A. Trifonov, E. S. Shubina, *Chem. Commun.*, **2022**, Advance Article

Acknowledgements – this work have been financially supported by RFBR project № 19-03-00524 and CNR–RFBR project №18-53-7818.

e-mail: H-Bond@ineos.ac.ru

The effect of Lu^{3+} and Gd^{3+} co-doping on the morphology and luminescence of $NaYF_4$: Eu^{3+}/Sm^{3+} phosphors

A.A. Betina, A.A. Vidyakina, A.S. Mereshchenko

Saint-Petersburg State University, Saint-Petersburg, RUSSIA

Microcrystalline β-$NaYF_4$: Eu^{3+}/Sm^{3+} particles co-doped with Gd^{3+} and Lu^{3+} ions were synthesized for the first time by hydrothermal autoclave synthesis. Analysis of XRD patterns demonstrated that all synthesized materials have the same crystalline phase, which corresponds to the hexagonal β-$NaYF_4$. Unit cell parameters were refined using XRD data. It was concluded that the listed lanthanide ions (Eu^{3+}, Sm^{3+}, Gd^{3+}, and Lu^{3+}) are capable of isomorphically replacing the yttrium ion in the crystal lattice, because unit cell parameters linearly depend on the dopant concentration. The resulting particles have the form of hexagonal prisms with a diameter of 40 to 1200 nm, depending on the composition. It was found that the addition of europium and gadolinium ions leads to a decrease, while the addition of lutetium ions leads to an increase in the particle size.

Upon 393-nm excitation of β-$NaYF_4$: Eu^{3+}, Gd^{3+}/Lu^{3+} materials, characteristic narrow bands of the europium ion are observed in the emission spectrum; the emission bands have maxima at 591, 615, 650, and 695 nm, corresponding to the electronic transitions $^5D_0$-^7F_J (J = 1–4). It was found that the optimal concentration of europium ions is 30% in the $NaYF_4$ matrix. It is shown that the lifetime of the $^5D_0$ state decreases from 6.7 ms to 2.2 ms as the concentration of europium ions increases from 1 to 50%. The addition of 1% gadolinium or lutetium ions leads to an increase in the luminescence intensity up to 2.5 times [1].

Upon 401-nm excitation of β-$NaYF_4$: Sm^{3+}, Gd^{3+}/Lu^{3+} materials, the characteristic narrow bands of the samarium ion are observed in the emission spectrum; the emission bands have maxima at 561, 595, 643, and 704 nm, corresponding to the electronic transitions $^4G_{5/2}$-^6H_J (J = 5/2 - 11/2). It was found that the optimal concentration of samarium ions is 2% in the $NaYF_4$ matrix. It is shown that the lifetime of the $^4G_{5/2}$ state decreases from 4.0 ms to 0.3 ms as the concentration of samarium ions increases from 0.5 to 20%. The addition of 0.5% gadolinium or lutetium ions leads to an increase in the luminescence intensity up to 2.5 times.

[1] I.E. Kolesnikov, A.A. Vidyakina, M.S. Vasileva, V.G. Nosov, N.A. Bogachev, V.B. Sosnovsky, M.Y. Skripkin, I.I. Tumkin, E. Lähderanta, A.S. Mereshchenko, *New J. Chem.*, **2021**, *45*, 10599-10607.

Acknowledgements – The measurements were performed at the Research Park of Saint-Petersburg State University (‘‘Magnetic Resonance Research Centre’’, ‘‘SPbU Computing Centre’’, ‘‘Cryogenic Department’’, ‘‘Interdisciplinary Resource Centre for Nanotechnology’’, ‘‘Centre for X-ray Diffraction Studies’’, ‘‘Chemical Analysis and Materials Research Centre’’, and ‘‘Centre for Optical and Laser Materials Research’’). This research was funded by Fellowship of President of Russia MD-1191.2022.1.3.

e-mail: a.mereshchenko@spbu.ru

Design of functional molecular systems based on lanthanide complexes

E.V. Grachova

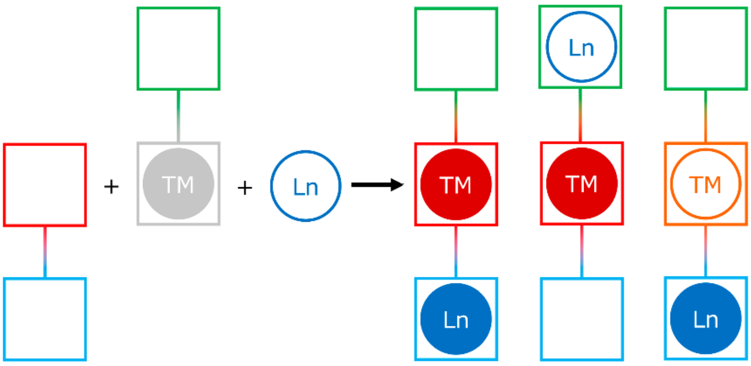
Institute of Chemistry, St Petersburg University, St. Petersburg, RUSSIA

Construction of luminescent compounds demonstrating multiband luminescence due to electronic communication between different chromophore and emission centers followed by partial or blocked intramolecular energy transfer is one of the most exciting trend in the modern coordination chemistry.

Design of emissive heterometal molecular systems or so called polynuclear molecular ensembles is based on ‘building blocks’ strategy where different complexes of transition metals (TMs) are selectively connected together through a suitable linker. Every ‘building block’ in this molecular aggregates plays its own role in resulting emission and can be involved in intramolecular energy transfer, energy exchange or quenching.

The use of Ln(III) complexes as one of ‘block’ has a number of advantages, the main ones is the predictability of the emission colour and of the possibility of direct exciting or exchanging the energy of between different ‘blocks’.

Thus, the design of luminescent polynuclear heterometallic molecular aggregates using Ln(III) complexes as ‘building blocks’ will be discussed, and some general principles of molecular multiband emitter design will be presented as in the framework of the lecture.



Scheme 1. Idealized scheme of different Ln−TM emissive molecular ensemble design.

Acknowledgements – The authors greatly appreciate financial support from the Russian Science Foundation, grant 21-13-00052. The work was carried out using equipment of St Petersburg University Research Park: Centers of Magnetic Resonance, Optical and Laser Materials Research, Chemical Analysis and Materials Research, for Physical Methods of Surface Investigation; and X-ray Diffraction Centre.

e-mail: e.grachova@spbu.ru

Luminescence of divalent europium in novel bimetallic iodides

V.A. Ilichev, A.F. Rogozhin, R.V. Rumyantsev, M.N. Bochkarev

Razuvaev Institute of Organometallic Chemistry of RAS, Nizhniy Novgorod, RUSSIA

The photoluminescence (PL) properties of divalent Eu derivatives significantly differ from those of trivalent ones. This difference is caused by the f–d character of the PL of Eu^{2+} ions resulting in a broadband emission whose energy depends on the ion environment. In contrast, Eu^{3+} exhibits a narrowband emission of f–f transitions whose energies are constant.

In this work, we report on a new brightly luminescent ate-complex consisting of an Eu^{2+} ion, which is coordinated by four DME molecules, and a tetraiododicuprate dianion – $[Eu(DME)_4][Cu_2I_4]$. This substance, which can be considered as a bimetallic iodide of Eu(II) and Cu(I), exhibits intensive double peaked PL and luminescence thermochromism in the temperature range of 180–250 K [1] (Fig. 1), which has a potential application in luminescence thermometry. In order to ascribe these bands to the Eu(II) or iodocuprate emission centers and understand the nature of this PL thermochromism we have studied molecular structures and PL properties of this compound at various temperatures using single crystal X-ray analysis and time-resolved PL spectroscopy.

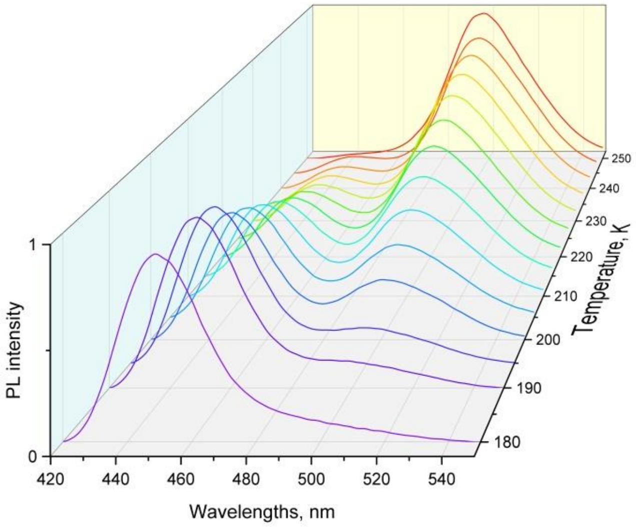


Fig. 1. Steady-state PL spectra of $[Eu(DME)_4][Cu_2I_4]$ at various temperatures.

In addition, novel bimetallic iodide of Eu(II) and Pb(II) - $[Eu(DME)_4][Pb_2I_6]$ was synthesized and structurally characterized. Unlike the copper counterpart, this compound did not exhibit the PL. Possible reasons of such PL behavior are discussed.

[1] V.A. Ilichev, L.I. Silantyeva, A.F. Rogozhin, A.N. Yablonskiy, B.A. Andreev, R.V. Rumyantsev, G.K. Fukin and M.N. Bochkarev, *Dalton Trans.*, **2021**, *50*, 14244-14251.

Acknowledgements – This work was supported by RSF (project 20-73-10115).

e-mail: ilichev@iomc.ras.ru

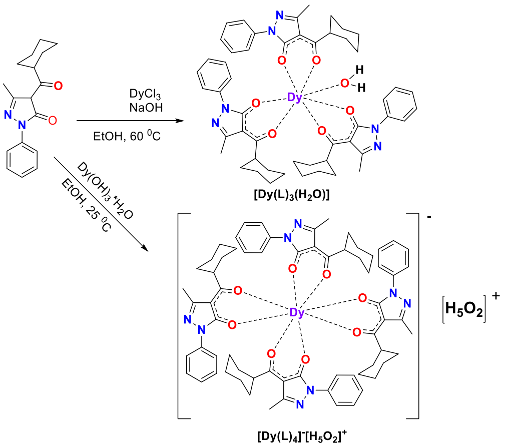
Towards design of bright Dy^{3+}-emitters – effects of coordination environment symmetry, partially deuteration and gadolinium dilution

Ilya V.Taydakov[a], Yury A.Belousov[a,b], Vladislav M.Korshunov[a], Nikolay P. Datskevich[a], Mikhail T.Metlin[a], Daria A.Metlina[a] and Mikhail A.Kiskin[c]

[a]*P.N. Lebedev Physical Institute of RAS, Moscow, RUSSIA.*
[b]*Lomonosov Moscow State University, Department of Chemistry, Moscow, RUSSIA*
[c]*N.S. Kurnakov Institute of General and Inorganic Chemistry of RAS, Moscow, RUSSIA*

Dy^{3+} coordination compounds attract an attention due to their unusual (vis+NIR) luminescence as well as magnetic (SMM) properties. Since Dy^{3+} luminescence is much less intensive that Eu^{3+} or Tb^{3+} one, a rational design of ligands and complexes and subsequent energy transfer optimization are vital for the preparation of highly emissive materials. Among possible ligands 4-acylpyrazolones hold a most unique position among the other1,3-diketones due to their synthetic availability and relatively high energy of triplet level favorable for sensibilization of Dy^{3+} luminescence.

Here we wish to report on design of bright luminescent tris- and tetrakis dysprosium complexes (Scheme 1) based on 4-(cyclohexanecarbonyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (HL) and further fine tuning of their emissive properties by combination of various factors – symmetry of coordination environment, partially deuteration of exchangeable water molecules and dilution of Dy^{3+} by heavy non-luminescent magnetic ion (Gd^{3+})[1]. Single and combined effects of each factor will be discussed as well as utilization of imperfection of ligand-to-ion energy transfer for the creation of white emissive materials.



Scheme 1. Synthesis of tris- and tetrakis dysprosium (III) complexes.

[1]. Belousov, Y. A.; Korshunov, V. M.; Metlin, M. T.; Metlina, D. A.; Kiskin, M. A.; Aminev, D. F.; Datskevich, N. P.; Drozdov, A. A.; Pettinari, C.; Marchetti, F.; Taydakov, I. V. *Dyes and Pigments* **2022**, *199*, 110078.

Acknowledgements – Authors thank RFBR, project number 20-33-70208. The ligand synthesis and analysis were performed with the financial support of the Russian Science Foundation (project No. 19-13-00272).

e-mail: taidakov@gmail.com

Lanthanide-based high temperature luminescent thermometry

V.V. Utochnikova, L.O. Tcelykh, M.B. Vialtsev

Lomonosov Moscow State University, Moscow, RUSSIA

Luminescent thermometry is not only one of the most accurate methods of measuring temperature, but also indispensable for contactless temperature measurements. One of the most important applications of luminescent thermometry is the measurement of high temperatures, i.e. in components of engines and gas pipelines, where contactless luminescent thermometry is practically the only way of measurement. In addition, it allows continuous measurements in real time and even temperature mapping. Despite the clear prospects, research in this area is very scarce.

Inorganic materials are usually used as luminescent thermometers at high temperatures. Despite the low intensity of their luminescence, they are stable up to really high temperatures, while the thermal stability of brightly luminescent coordination compounds (CCs) is insufficient. However, metal-organic frameworks (MOFs) based on lanthanide aromatic carboxylates are often stable up to temperatures of 400-600 °C, which is sufficient for a whole number of thermometric applications, and demonstrate very intense luminescence.

We proposed heterolanthanide aromatic carboxylates as high temperature luminescent thermometers within composite films based on transparent thermally stable amorphous, crystalline and liquid crystalline (LC) polymeric materials [1]. Theoretical aspects, as well as practical results, i.e. the obtaining of the novel highly sensitive composite materials, were investigated.

We proposed the analytical description of the four-level system for luminescent thermometry, which includes one ground and three excited states, to which Tb-Eu complexes with organic ligand belong, and demonstrated the strategy toward the design of such systems to increase the temperature sensitivity [2]. Based on this study, we proposed new approaches to the sensitivity increase through the complex design [3].

We investigated a series of highly stable complexes as emitters for high-temperature luminescent thermometry, studied the complex stability upon simultaneous impact of UV excitation and heating, as well as the peculiarities of the composite film formation with polymers of different classes. As a result, we obtained materials, which can operate up to 200 ^{o}C with both visible and NIR emission [4]. We also demonstrated – both mathematically and practically – that the use of a mixture of monometallic complexes is superior to the use of one bimetallic compound.

These results demonstrated the prospects of the heterolanthanide carboxylates as emitters for high-temperature luminescent thermometry.

1. Bobrovsky A., Kozlov M., Utochnikova V. Eu-doped cholesteric mixtures with a highly thermosensitive circular polarization of luminescence // J. Mol. Liq. Elsevier, 2021. Vol. 341. P. 117431.
2. Popelensky T.Y., Utochnikova V. V. How does the ligand affect the sensitivity of the luminescent thermometers based on Tb-Eu complexes // Dalt. Trans. Royal Society of Chemistry, 2020. Vol. 49, № 35. P. 12156–12160.
3. Vialtsev M.B. et al. New approach to increase the sensitivity of Tb-Eu-based luminescent thermometer // Phys. Chem. Chem. Phys. Royal Society of Chemistry, 2020. Vol. 22, № 44. P. 25450–25454.
4. Vialtsev M.B. et al. Terbium and europium aromatic carboxylates in the polystyrene matrix: The first metal-organic-based material for high-temperature thermometry // J. Lumin. North-Holland, 2021. Vol. 239. P. 118400.

Acknowledgements – Authors thank Russian Science Foundation (grant 20-73-10053).

e-mail: valentina.utochnikova@gmail.com

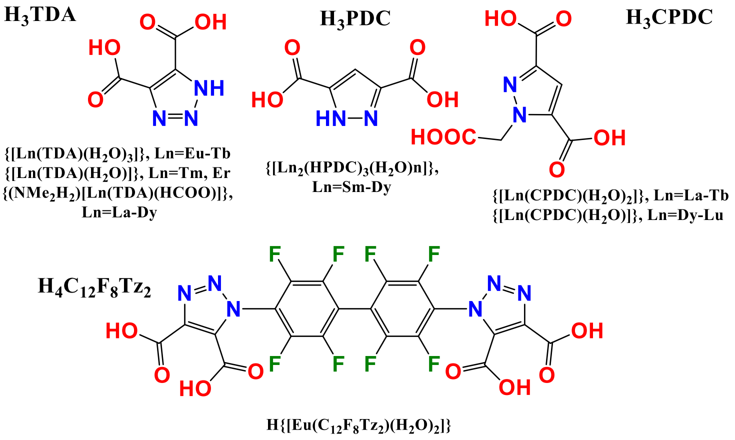
REE azolcarboxylates: synthesis, structure, luminescent and sensoric properties

V.E. Gontcharenko[a], A.V. Sidoruk[a], A.M. Lunev[a], A.I. Ivanova[a] I.V. Taydakov[b],
Y.A. Belousov[a,b]

[a]*Lomonosov Moscow State Universsity, Moscow, RUSSIA*
[b]*P.N.Lebedev Physical Institute of RAS, Moscow, RUSSIA*

Azolecarboxylic acids are a unique class of ligands that usually form with REE cations polymeric complexes with MOF porous structure [1].The structure of various pyrazole-[2] and 1,2,3-triazolecarboxylic acids [3,4] promotes the formation of several metallocycles, which makes the formation of polymeric complexes preferable instead of molecular compounds. The aromatic nature of the ligands, together with the minimization of the number of CH bonds, makes these ligands promising "antennas" for the manifestation of the full potential of the photoluminescent properties of lanthanides. These features make REE azole carboxylates promising luminescent sensor materials for the detection of water [4] and metal cations.

This report is focused on an overview of our ongoing inverstigations devoted to the synthesis new MOF’s based on azolecarboxylic acid ligands, and their use for detection on different analytes.



Scheme 1. The studied azolecarboxylic ligands and the composition of the REE complexes they form.

[1] Belousov, A. A. Drozdov, I. V. Taydakov, F. Marchetti, R. Pettinari and C. Pettinari, *RSC Adv.*, *Coord. Chem. Rev.* **2021**, *445*, 214084
[2] A.M. Lunev, A.V. Sidoruk, V.E. Gontcharenko, M.A. Kiskin, I.V. Taydakov, Y.A. Belousov and A.A. Drozdov, *Inorg.Chim. Acta*, **2022** (article in press)
[3] V. E. Gontcharenko, A. M. Lunev, I. V. Taydakov, V. M. Korshunov, A. A. Drozdov, Y. A. Belousov, *IEEE Sens. J.* **2019**, *19*, 7365–7372.
[4] Y. A. Belousov, V. E. Goncharenko, A. M. Lunev, A. V. Sidoruk, S. I. Bezzubov, I. V. Taidakov, *Russ. J. Coord. Chem. Khimiya* **2020**, *46*, 394–401

Acknowledgements – Authors thank RFBR (projects 19-03-00263).

e-mail: belousov@inorg.chem.msu.ru

Polyfunctional Luminescent Materials Based on Mesogenic Lanthanide Complexes

A.A. Knyazev[a], Y.G. Galyametdinov[a,b]

[a]Federal State Budgetary Educational Institution of Higher Education «Kazan National Research Technological University»
[b]Zavoisky Physical-Technical Instituteis a separate structural subdivision of the Federal State Budget Scientific Institution «Federal Research Centre «Kazan Scientific Centre of the Russian Academy of Sciences»

Coordination compounds of lanthanides (III) are a promising class of substances that can be used as functional luminescent materials and devices: various types of sensors (anions, cations, simple molecules, pH, temperature, viscosity, oxygen, UV radiation), light-transforming materials and coatings, monochromatic light sources, solar concentrators, etc. Their main property and advantage is the effective luminescence provided by the Ln (III) ion, and not by organic ligands. One of the most interesting classes of coordination complexes are lanthanide(III) complexes with aromatic β-diketonate ligands, since they combine intense monochromatic luminescence with attractive physicochemical properties.

Film luminescent materials with high optical quality are topical for modern molecular electronics. The main problem of their application is the rapid degradation of luminescence under the action of UV radiation (especially in the presence of atmospheric oxygen), low thermal stability, poor mechanical properties, and a tendency to aggregation. A known solution is the incorporation of these compounds into host matrices (organic polymers, ionic liquids, zeolites, etc.).

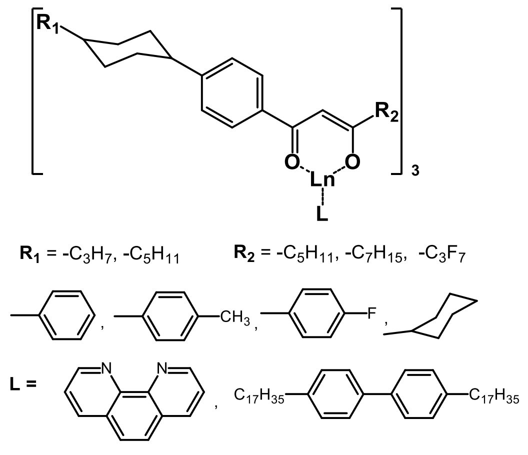


Fig. 1 – The structure of synthesized complexes

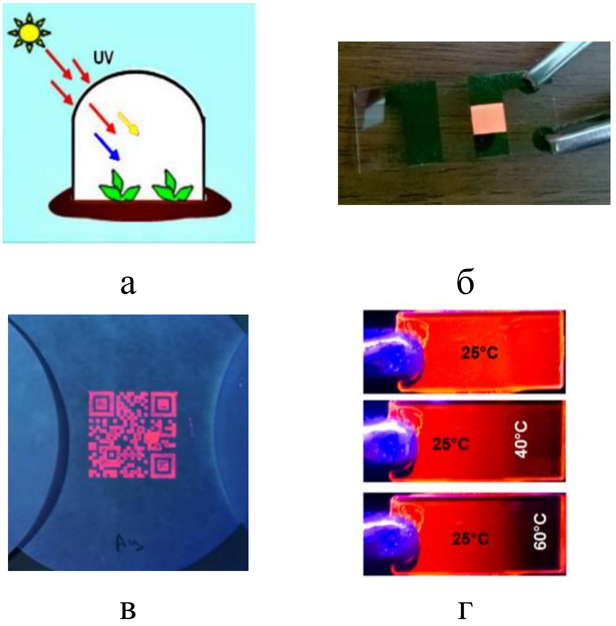


Fig. 2 – Light-transforming coatings (a) OLED based on the Sm(III) complex (b) document marking (c) fluorescent thermometer based on the Eu(III) complex

The paper proposes an alternative approach to solving the above problems - the use of anisometric analogs of β-diketonate compounds of lanthanides (III) (Fig. 1). The main advantage of these compounds is the absence of crystallization due to long hydrocarbon substituents in the structure of the complexes, which makes it possible to obtain thin nano-, micro- and macro-sized homogeneous film materials by melting at relatively low temperatures and by spin-coating. The combination of these properties makes it possible to create luminescent materials from melts of these compounds in the form of glassy films with high optical quality (up to 95%) in visible and near-IR regions. It is important to note that such films cannot be obtained from nonanisometric analogs of lanthanide(III) β-diketonate complexes due to the high tendency to crystallization and high melting points.

Upon excitation with UV light at a wavelength of 365 nm, films of Eu(III) and Tb(III) complexes exhibit monochromatic luminescence at wavelengths of 545 nm and 612 nm, respectively. Moreover, it was found that film materials based on Eu(III) and Tb(III) complexes can reversibly change the luminescence intensity and decay time in the temperature range of 298–348 K and 143–253 K, respectively. It was found that the resulting compounds have high photostability. The intensity of their luminescence does not change even after 10 hours of exposure by UV radiation.

It has been shown that such compounds can be used as components of nanosized light-transforming coatings (Fig. 2a), OLED emitters (Fig. 2b), luminescent markers (Fig. 2c), luminescent thermometers (Fig. 2d), O_2 sensors, dosimeters and molecular filters of UV [1-3].

[1] Knyazev, A.A., Krupin, A.S., Galyametdinov, Y.G. *Journal of Luminescence*, 2022, 242, 118609.

[2] Knyazev, A.A., Karyakin, M.E., Heinrich, B., Donnio, B., Galyametdinov, Y.G. *Dyes and Pigments*, 2021, 187, 109050.

[3] Lapaev, D.V., Nikiforov, V.G., Lobkov, V.S., ...Galyametdinov, Y.G., Galyametdinov, Y.G. *Journal of Materials Chemistry C*, 2020, 8(18), стр. 6273–6280.

Acknowledgements: Work carried out with financial support of RSF, grants 18-13-00112-P and 20-73-10091

e-mail: knjazev2001@mail.ru

Control of photophysical properties in lanthanide carboxylate complexes

M.A. Shmelev [a], S.A. Nikolaevskii[a], E.A. Varaksina[b], V.M. Korshunov[b], I.V. Taidakov[b],
N.V. Gogoleva[a], M.A. Kiskin[a], I.L. Eremenko[a]

[a]*Kurnakov Institute of General and Inorganic Chemistry RAN, Moscow, RUSSIA*
[b]*Lebedev Physical Institute, Moscow, RUSSIA*

Coordination compounds of lanthanides due to the unique optical characteristics of Ln^{3+} ions have been proposed as functional materials for luminescent light sources (for OLEDs, lasers and others), bioimaging, molecular luminescent thermometers and sensors. The antenna effect is used to solve the main problem of luminescent lanthanide materials by making an aromatic ligand with high extinction coefficients instead of the weakly absorbing Ln^{3+} ion as the centre of light absorption.

Lanthanides and carboxylate anions usually form oligomers and polymers. The addition of N-donor aromatic chelate ligand allows to control the nuclearity and structure of molecular complexes. One more way to modify the structure and photophysical properties is use of the insertion of d-block formed post-transition ions (Zn^{2+} and Cd^{2+}), N-donor aromatic and bridging ligands. This method also makes it possible to modify the luminescence characteristics due to local changes in the structure in the direction of increasing the rigidity of the system and the selection of a combination of ligands that are effectively involved in the transfer of energy to metal ions.

This report is a summary of the current results on the synthesis, structural features, and photophysical properties of heterometallic complexes with anions of aromatic carboxylic acids and co-ligands.

Acknowledgements – The work was supported by the Ministry of Science and Higher Education of the Russian Federation as a part of the state assignment of Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.

e-mail: mkiskin@igic.ras.ru

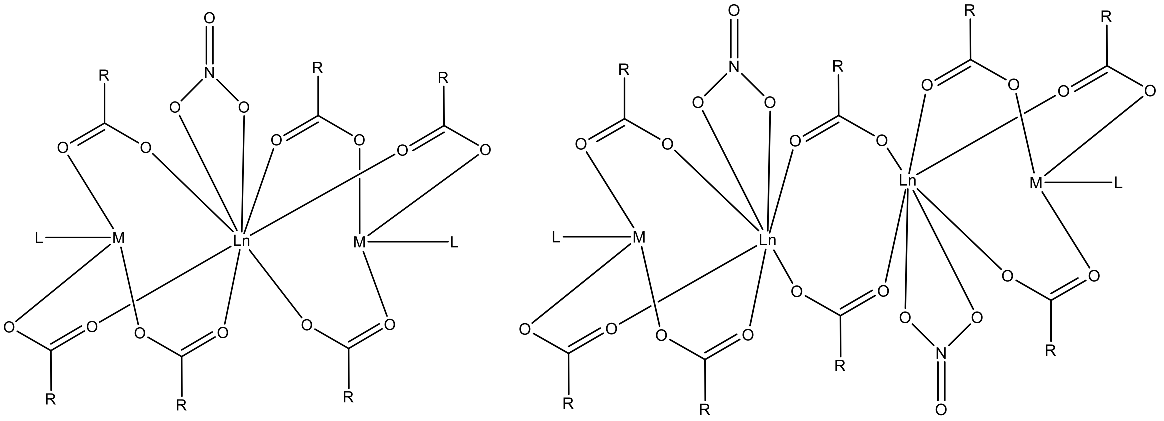
Zn-Ln and Co-Ln heterometallic complexes based on carboxylate ligands: tuneable luminescence and magnetic properties

S.A. Nikolaevskii[a], P.A. Petrov[b], D.S. Yambulatov[a], M.N. Sokolov[b], M.A. Kiskin[a],
I.L. Eremenko[a]

[a]*Kurnakov Institute of General and Inorganic Chemistry of the RAS, Moscow, RUSSIA*
[b]*Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA*

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

This report is focused on the synthesis, structure elucidation and study of luminescence as well as magnetic behaviour of M(II)-Ln(III) (M(II)= Zn, Co) complexes based on anions of pivalic, 1-nahpthoic, 1-naphthilacetic, 2-furoic and 4-biphenylcarboxylic acids. These compounds are mainly attributed to two structural types – tri- and tetranuclear (scheme 1). Variety of pyridine derivatives, P-donor ligands as well as N-heterocyclic carbenes were used as ancillary ligands L.



Scheme 1. Main structural types of M-Ln heterometallic complexes based on carboxylate ligands.

Quantum yields of several Zn-Ln (Ln(III) = Eu, Tb) compounds are exceed 60%. Co-Ln complexes possesses nontrivial magnetic properties including Single Molecule Magnet behaviour.

Acknowledgements – The investigation was partially supported by the Ministry of Science and Higher Education of the Russian Federation as part of the state assignment of Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences.

e-mail: sanikol@igic.ras.ru

Tuning physical-chemical properties of sandwich REE complexes via control of rotational state of phthalocyanine ligands

A.G. Martynov[a], G.A. Kirakosyan[a,b], K.B. Birin[a], A.A. Sinelschikova[a], Yu.G. Gorbunova[a,b], A.Yu. Tsivadze[a,b]

[a]*Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, RUSSIA*
[b]*Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, RUSSIA*

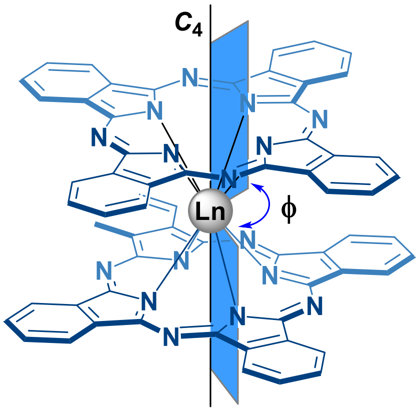


Fig. 1. Skew angle ϕ in sandwich phthalocyaninates which dictates the symmetry of coordination surrounding of REE ion.

Among various REE complexes sandwich double- and triple-decker phthalocyaninates attract special attention for elaboration of novel electronic and magnetic devices and materials. Varying the nature of macrocyclic ligands is known to adjust all possible physicochemical properties of complexes including magnetism; however, the influence of subtler physical and chemical factors, especially supramolecular interactions, has recently become of particular interest [1]. The reversibility of supramolecular assembling can be used as a tool for dynamic control of the properties of sandwich complexes, which makes it possible to create smart materials.

As one of goals of such control we chose the conformational state of phthalocyanine ligands which is described by the skew angle ϕ (Fig. 1).

Our studies demonstrate two major ways to achieve the control over conformational state of sandwich complexes. We differentiate variation of the tetrapyrrolic ligands in sandwich complexes at the synthetic step as a *static* control over ϕ, while *dynamic* control over this structural parameter at the post-synthetic step can be achieved by host−guest interactions if the appropriate receptor groups are introduced to the molecule.

For example, heteroleptic crown-substituted trisphthalocyaninates act as dynamic supramolecular scaffolds with switchable rotational states and tunable magnetic properties – we showed, that potassium cations reversibly intercalate between the crown-substituted phthalocyanine ligands, resulting in switching of the coordination polyhedron of the metal centre M* from square-antiprismatic ($\phi=45°$) to square-prismatic ($\phi=0°$) [2]. In turn, it results in significant increase in the axial component of the magnetic susceptibility tensor.

Other dynamic approaches include change of solvation and redox-processes which can be used to switch between different states of sandwich complexes. Spectral signatures of such switching will be summarized and discussed.

[1] A. G. Martynov, M. A. Polovkova, G. S. Berezhnoy, A. A. Sinelshchikova, F. M. Dolgushin, K. P. Birin, G. A. Kirakosyan, Y. G. Gorbunova and A. Y. Tsivadze, *Inorganic Chemistry*, 2020, **59**, 9424–9433.
[2] A. G. Martynov, M. A. Polovkova, G. S. Berezhnoy, A. A. Sinelshchikova, V. N. Khrustalev, K. P. Birin, G. A. Kirakosyan, Y. G. Gorbunova and A. Y. Tsivadze, *Inorganic Chemistry*, 2021, **60**, 9110–9121.

Acknowledgements – Authors thank Russian Science Foundation (project 18-73-10174_P) for financial support.

e-mail: martynov.alexandre@gmail.com

Recent advances in the synthesis of complexes of the rare-earth metals in the +2 oxidation state

William J. Evans

Department of Chemistry, University of California, Irvine, California 92697, United States

The +2 oxidation state chemistry of molecular rare-earth metal complexes has expanded from the initially identified three ions, Eu(II), Yb(II) and Sm(II), to the current state in which Ln(II) complexes are known for all the metals except the radioactive Pm. The discovery by Bochkarev and co-workers of the first molecular complexes of Tm(II), Dy(II), and Nd(II) was a critical part of that expansion. Those results stimulated new directions in research on dinitrogen reduction in our lab and led to a broad range of side-on bound $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ compounds across the lanthanide series. The dinitrogen reduction studies led us to more new Ln(II) ions and the current challenges to identify the optimal ligands for stabilizing these highly reducing species. Exploring the ligand space of Ln(II) complexes has led us to some new dinitrogen reduction chemistry that allows us to make connections back to the $Ln_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ compounds identified earlier. These connections will be described as well as current challenges in these areas.

e-mail: wevans@uci.edu

Do monovalent lanthanide compounds exist?

M.N. Bochkarev, A.A. Fagin, S.K. Bukhvalova

G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences,
Nyzhny Novgorod, RUSSIA

The problem of the existence of compounds of monovalent lanthanides and their expected properties are discussed. Arguments are given in favor of the fundamental possibility of the existence of such compounds and arguments against their existence. Attempts to synthesize monovalent thulium and samarium iodides are described. Methods for confirming the presence of monovalent metals in the obtained products and their reactivity are considered.

e-mail: mboch@iomc.ras.ru

Recent developments in redox transmetallation chemistry involving rare earth metals

Peter C. Junk,[a] Glen B. Deacon,[b] and Zhifang Guo[b]

[a] *College of Science & Engineering, James Cook University, Townsville, Qld, 4811, AUSTRALIA*
[b] *School of Chemistry, Monash University, Clayton, Vic. 3800, AUSTRALIA*

Redox transmetallation has been a very versatile synthetic approach to organolanthanoid complexes. We have developed a very high yielding and simple approach using lanthanoid metals as starting materials and treating them with organomercury reagents such as $Hg(C_6F_5)_2$. These reactions generate $Ln(C_6F_5)_x$ ($x = 2, 3$ depending on the lanthanoid metal) and can be used to produce many other metal organic complexes of the lanthanoids by treatment with protic reagents such as acidic organics, amines and alcohols. Alternatively, the chemistry can be performed in a one-pot synthesis as a redox transmetallation/protolysis reaction where lanthanoid metal, $Hg(C_6F_5)_2$ and LH (protic reagent) can be added to produce the LnL_x ($x = 2, 3$);

e.g. $Ln + Hg(C_6F_5)_2 + 2LH \rightarrow LnL_2 + Hg + 2C_6F_5H$ (for lanthanoid divalent metals)

While this chemistry works beautifully, as may be expected, it has attracted criticism for its involvement with the toxic mercury reagents, so more recently we have developed greener approaches in this synthetic endeavour. We have replaced the mercury reagents with organobismuth(III) and Ag(I) reagents in similar chemical pathways to synthesise the lanthanoid organometallics. The chemistry has required new approaches to organosilver reagents and has uncovered some unusual Bi chemistry. The overall story will be covered in this seminar.

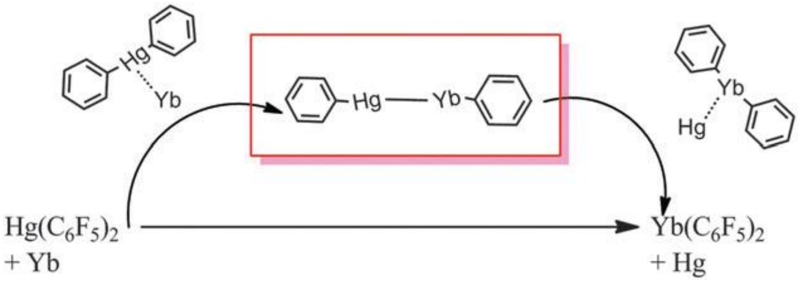


Fig. 1. Reaction mechanism of redox transmetallation of Yb by $Hg(C_6F_5)_2$

Acknowledgements – The authors thank the Australian Research Council (DP 190100798) for support of this work.

e-mail: peter.junk@jcu.edu.au

Sandwich complexes

Peter W. Roesky

Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Karlsruhe, GERMANY

First, a new class of pure sandwich complexes ([(η^9-C_9H_9)Ln(η^8-C_8H_8)]), which exclusively contain fully π-coordinated coplanar eight and nine-membered CH rings is presented.[1] The single molecular magnet character of the erbium(III) compound by magnetometric studies was proven. Aside from this, a detailed Raman spectroscopic analysis allowed us to add some insight into the vibrational behavior of the η^9-C_9H_9 moiety, that nicely corresponds to the properties of well-established aromatic C_nH_n systems.

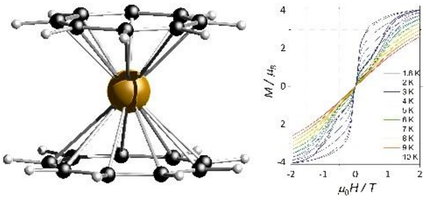


Fig. 1. A new class of sandwich complexes: [(η^9-C_9H_9)Ln(η^8-C_8H_8)] (left) and its magnetic hysteresis (right).[1]

In the second part of the lecture, the first example of a homoleptic lanthanide quadruple-decker is presented. The synthesis of this archetypal compound as well as mechanistic studies for its formation are shown.[2]

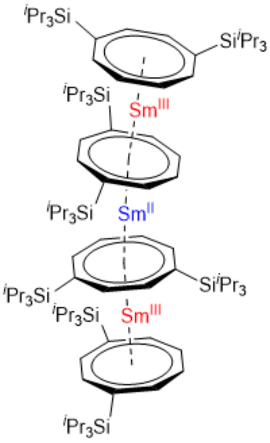


Fig. 2. The first well-defined neutral and homoleptic (same metal, same ligand) all-carbon based quadruple-decker complex.[2]

[1] L. Münzfeld, C. Schoo, S. Bestgen, E. Moreno-Pineda, R. Köppe, M. Ruben, P. W. Roesky, *Nat. Comm.* **2019**, *10*, 3135.

[2] L. Münzfeld, A. Hauser, P. Hädinger, F. Weigend, P. W. Roesky, *Angew. Chem. Int. Ed.* **2021**, *60*, 24493.

e-mail: roesky@kit.edu

Synthesis and study of polynuclear heterometallic complexes of nickel and REE with amino acids

A.A. Khusyainova[a,b], M.A. Lavrova[a], S.I. Bezzubov[b], Y.V. Logvinenko[a], D.D. Semeshkina[a], E.O. Yastrebova[a], A.R. Sawaretz[a,c], V.E. Goncharenko[a], V.D. Dolzhenko[a,c]

[a]*Department of Chemistry, Lomonosov Moscow State University*
[b]*Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow*
[c]*N. D. Zelinsky Instituteof Organic Chemistry Russian Academy of Sciences, Moscow*

Polynuclear heterometallic 3d-4f complexes may act as ion sensors, molecular magnets and precursors for creating 3d-4f mixed oxides. The synthetic technique for polynuclear cation complexes $[LnNi_6(AA)_{12}]^{3+}$ with various natural L-amino acids (AA = Gly, Ala, Val, Leu, Ile, Pro, Phe, Ser, Thr, Asn) was established. Due to $\{Ni_6(AA)_{12}\}$ framework formation with size-fixed cavity, such complexes can be selectively obtained for the first LREE, and a possibility of formation of complexes of different REE depends on synthesis conditions and type of the amino acid. Stability constant of complexes in solution estimated using UV-Vis spectroscopy. The effects of crystallization conditions on the composition of the gaining compounds were explored by the example of $[LnNi_6(Ala)_{12}][Ln_{1-x}Ln'(NO_3)_3(OH)(H_2O)]$. Certain facts, which contribute to cation Ln^{3+} enrichment of anion, have been established: cation complex sustainability decreasing, Ln^{3+} the ionic radius declaine and the supersaturation extent reduction. The kinetics of complex formation was studied by the case of $[LnNi_6(Ile)_{12}]^{3+}$, the generation of 2 intermediate products was fixed, the kinetic model for this process was proposed. The crystals containing large anions $[Ln''(dpa)_3]^{3-}$ (Ln'' = Eu,Tb; dpa = 2,6-pyridinedicarboxylate) were obtained for $[LnNi_6(Gly)_{12}]^{3+}$. The conditions of getting $[LnNi_6(AA)_{12}]^{3+}$ in crystalline form were optimized, structures were studied. It was also found that cations, which contain branched-chain amino acids, can be crystallized from solution with small anions (Cl^-, I^-, I_3^-, NO_3^-, ClO_4^-, BF_4^-, ClO_4^-), that provides opportunities for applying these complexes for separating of REE. The distribution coefficients of REE ions from the beginning and middle of the lanthanide series between the solid phase and the solution were estimated for some amino acids (Asn, Val, Ile, Ser).

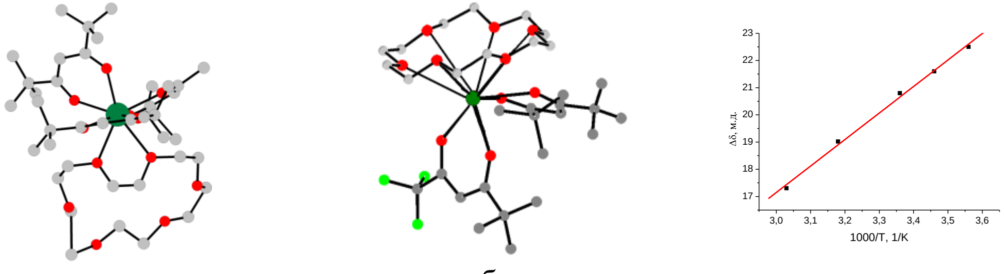
e-mail: Doljenko_VD@mail.ru

^{1}Н ЯМР исследование бета-дикетонатных комплексов празеодима с 18-краун-6

С. П. Бабайлов, П.А. Стабников

Институт неорганической химии им. А.В. Николаева СО РАН, Новосибирск

Методом ^{1}Н ЯМР охарактеризованы комплексы [Pr(ДПМ)$_3$(18-краун-6)] (**I,** Рис. а), [(Pr(ДПМ)$_3$)$_2$] (**II**), [(Pr(ДПМ)$_3$)$_2$(18-краун-6)], (**III**), [Pr(ДПМ)(ПТА)(18-краун-6)]$^+$ (**IV,** Рис б), и температурная чувствительность парамагнитных лантанид-индуцированных сдвигов этих комплексов в растворе CDCl$_3$ (Рис.б). Методами ЯМР оценена возможность формирования в растворе CDCl$_3$ инклюзивных комплексов при взаимодействии *трис*-β-дикетонатов лантанидов (Ln) с 18-краун-6 в случае более разветвленного, чем ПТА, лиганда (например, такого, как ДПМ). При взаимодействии [(Pr(ДПМ)$_3$)$_2$] и 18-краун-6 доминирующими формами комплексов в растворе являются **I**. Исследованные координационные соединения **I-IV** могут рассматриваться как ^{1}Н ЯМР парамагнитные лантанидные зонды для контроля локальной температуры в органических растворах с помощью анализа парамагнитных лантанид-индуцированных сдвигов (причем инклюзивным является только комплекс **IV**).



а б в

Рис. а - строение комплекса [Pr(ДПМ)$_3$(18-краун-6)] в растворе, б - строение комплексного катиона [Pr(ДПМ)(ПТА)(18-краун-6)]$^+$ в растворе, с - зависимость парамагнитных лантанид-индуцированных сдвигов (ЛИС) от обратной температуры на протонах групп CH комплекса [Pr(ДПМ)$_3$(18-краун-6)] в растворе CDCl$_3$.

Температурная зависимость ЛИС для протонов групп CH комплекса **I** достаточно хорошо аппроксимируется линейной зависимостью $\delta = A + B/T$ (найденные значения параметров равны: A= -12.1± 1.1 м.д., B= 9.8± 0.3 м.д.×К (Рис. в). В докладе парамагнитные свойства комплексов **I-IV** сопоставлены со свойствами других парамагнитных комплексов Ln и d-элементов и обсуждены перспективы для МРТ.

Работа выполнялась при поддержке Российского Научного Фонда (грант № 20-63-46026).

e-mail: babajlov@niic.nsc.ru

Cu^{2+} / Cd^{2+}-Ln^{3+} heterometallic malonates: ways of synthesis and magnetic properties

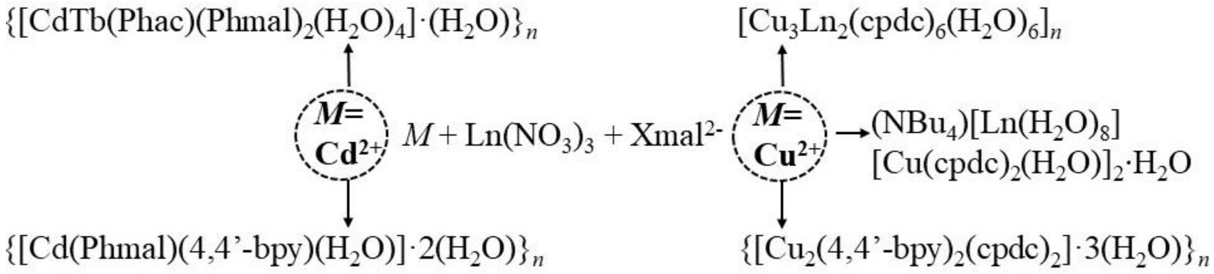
N.V. Gogoleva, P.Yu. Khapaeva, M.A. Shmelev, K.A. Babeshkin, N.N. Efimov, A.A. Sidorov, M.A. Kiskin, and I.L. Eremenko

N.S. Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, RUSSIA

Malonic acid allows one to synthesise complexes with a wide range of structures, metal combinations and dimensionality of polymer structure [1, 2]. It is possible to influence complexes structure features by directed variation of the malonic acid substituent. One can affect physicochemical properties of synthesised compounds as a result. Most of the lanthanide malonate complexes known by now are homometallic [3] and demonstrate perspective physicochemical properties. In this report we present the strategy of the first Cu-Ln and Cd-Ln malonates synthesis.

It was shown that possibility of lanthanide-containing malonate complexes synthesis depends either on d-metal nature or on malonate substituent ($Xmal^{2-}$). In the case of Cu^{2+}-Ln^{3+} (Dy, Eu, Gd, Tb, Yb) system only cyclopropane-1,1-dicarboxylic acid anions ($cpdc^{2-}$) made it possible to yield heterometallic complexes: 3D-polymer and ionic complex with NBu_4^+ cations (Scheme 1). For Cd^{2+} phenylmalonate anions allowed us to synthesize Cd-Ln compound. Phenylmalonic acid was partially decarboxylated in the reaction mixture. Addition of 4,4’-bipyridine (4,4’-bpy) leads to heterometal fragment degradation in the both cases. Cu^{2+} or Cd^{2+} layered polymers were synthesised as a result.

All the complexes were characterized by X-Ray diffraction analysis, IR-spectroscopy, PXRD and CHN-analysis. Magnetic properties of Cu-Ln complexes are discussed in the report. NBu_4-containing complexes demonstrated single molecular magnet behaviour.



Scheme 1. Synthesis of Cu-Ln and Cd-Ln substituted malonates.

[1] N.V. Gogoleva, E.N. Zorina-Tikhonova, A.S. Bogomyakov, N.N. Efimov, E.V. Alexandrov, E.A. Ugolkova, M.A. Kiskin, V.V. Minin, A.A. Sidorov and I.L. Eremenko, *Eur. J. Inorg. Chem.*, **2017**, 547–562.
[2] Z.V. Dobrokhotova, N.V. Gogoleva, E.N. Zorina-Tikhonova, M.A. Kiskin, V.V. Chernyshev, A.L. Emelina, M.A. Bukov, A.S. Goloveshkin, I.S. Bushmarinov, A.A. Sidorov, A.S. Bogomyakov, M.L. Kovba, V.M. Novotortsev and I.L. Eremenko, *Eur. J. Inorg. Chem.*, **2015**, 3116–3127.
[3] Z. Chen, X. Yu, X. Li, Q. Ye, K. Zhou, Y. Cai, L. Huang, L. Wang, Y. Li and C. Zeng, *Inorg. Chem. Comm.*, **2020**, *112*, 107744.

Acknowledgements – Authors thank the Russian Science Foundation (project no. 19-73-10181).

e-mail: gogolevanv@inbox.ru

Mixed-ligand homo- and heterometallic carboxylate complexes with Eu^{3+}, Gd^{3+} and Sm^{3+} ions: synthetic approaches, structure and physicochemical properties

I.A. Lutsenko,[a] A.A. Mishenina,[b] M.A. Uvarova,[a] M.E. Nikiforova,[a]
M.A. Kiskin,[a] I.L Eremenko[a]

a) N.S. Kurnakov Institute of General and Inorganic Chemistry of the RAS, Moscow
b) National Research University Higher School of Economics, Moscow

Lanthanide carboxylates attract the attention of scientists due to their unique coordination capabilities to form structures of various dimensions and nuclearities. In addition to the excellent magnetic and optical characteristics that complexes with lanthanide cations acquire, in recent years, interest has increased in terms of their manifestation of the properties of probes (temperature sensors in the early diagnosis of inflammatory processes, including oncological ones). Contrast agents are able to detail the foci of inflammation and make it possible to measure temperature at almost any depth of a biological object. Gadolinium chelate complexes (omniscan, prohans) have proven themselves well as contrast agents in magnetic resonance imaging, and samarium complexes (lexidronam, oxabiform) are used in osteology (they have an analgesic effect, therefore they are used for bone cancer).

In this work, using various approaches, carboxylate homometallic complexes were synthesized – molecular $[Eu_2(pfbenz)_6(MeOH)_4]$ (**1**, fig. 1a) and polymeric $\{[Gd(pfbenz)_2(OAc)(MeOH)]\}_n\cdot n MeOH$ (**2**), $\{[Gd(fur)_2(OAc)(H_2O)]\}_n\cdot CH_3CN$ (**3**), $\{[Gd(fur)_3(H_2O)_2]\}_n\cdot CH_3CN$ (**4**, fig. 1б), $\{[Sm(fur)_3(H_2O)_3]\}_n\cdot CH_3CN$ (**5**), as well as heteronuclear $[Fe_3Eu_2(O)(OH)_2(Piv)_{11}(HPiv)(1,10\text{-}phen)]\cdot 2C_6H_5CH_3$ (**6**) and $\{[Fe_6Eu_2K_2(O)_4(OH)_3(Piv)_{15}]\}n$ (**7**, fig. 1c), in which anions act as organic ligands pentafluorobenzoic (pfbenz), 2-furoic (fur), acetic (OAc) and pivalic (Piv^-) acids.

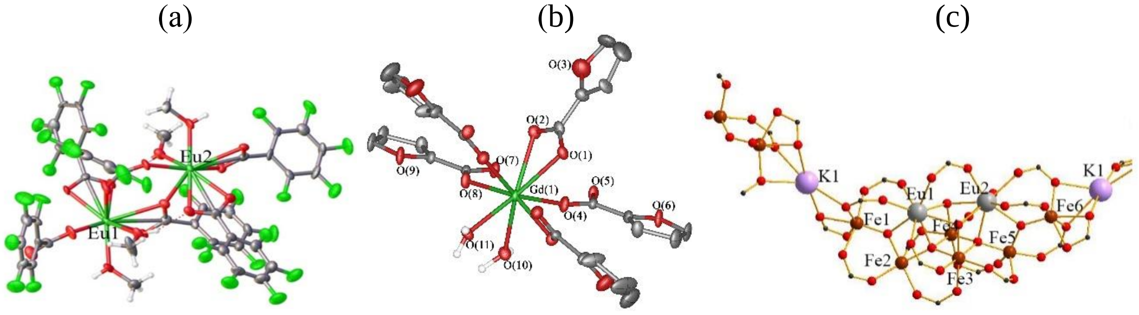


Fig. 1. Molecular complex **1** (a) and fragments of polymer compounds **4** (b), **7** (c)

The structure of all the obtained compounds was established by X-ray diffraction analysis, photoluminescence spectra were studied (**1**, **2**), and thermal behavior was determined by the method of simultaneous thermal analysis (STA) in an argon atmosphere (**1**, **4**).

The luminescence spectrum of 1 clearly shows the spectral bands characteristic of the f-f* transitions of the Eu^{3+} ion: $^5D_0$-$^7F_0$ (580 nm), $^5D_0$-$^7F_1$ (588 nm), $^5D_0$-$^7F_2$ (616 nm), $^5D_0$-$^7F_3$

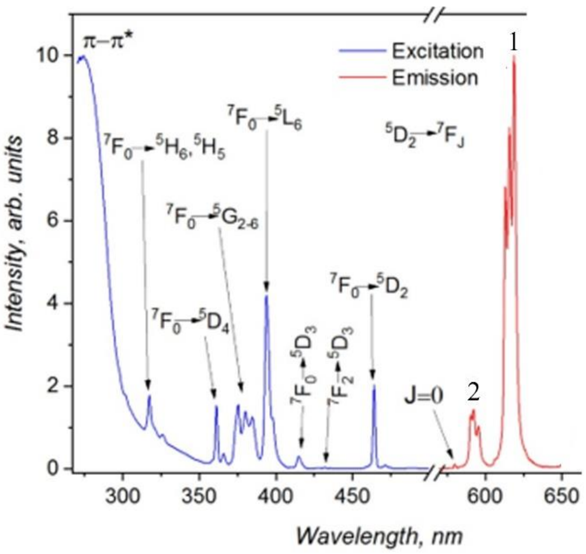


Fig. 2. - Photoluminescence excitation spectrum **1**, obtained at a recording wavelength of 616 nm and luminescence spectra **1** и **2**.

(655 nm), $^5D_0$-$^7F_4$ (680 nm). The spectral band corresponding to the hypersensitive transition $^5D_0$-$^7F_2$ is strongly split, which indicates a low symmetry of the coordination polyhedron. From a comparison of the relative intensities of the ligand excitation bands with the maxima at 270 and 395 nm, it can be concluded that the efficiency of excitation through the ligand environment is low in comparison with many known europium compounds. The total quantum yield (luminescence efficiency) was measured with optical excitation at a wavelength of 300 nm and corresponds to the π-π * excitation band of the electronic transition in the ligand environment. Quantum yield 1.8%.

The STA method was used to study the thermal behavior, stability and nature of destruction processes for **1** and **4**. According to the data in Table 1, complex **1** is thermally more stable, while destruction processes for **4** begin already from 69 °C.

Table 1. STA data for complexes **1** и **4** (Ar)

Complex	Stage / ΔT, °C	Δm (TG), %	$T_{endo/exo}$, °C	m_{fin}, %
1	1 / 93–290	43.8	104±0.7	
			181±0.7	
	2 / 290–380	24.1	357±0.7	
	3 / 380–500	3.5	386±0.7	27.6
4	1 / 69–126	6.4	96±0.7	
	2 / 126–461	31.3	443±0.7	60.8

Both complexes have minimal effects on weight loss (TG) curves and correspond to partial or complete escape of outer-sphere MeOH (**1**) or MeCN (**4**) molecules; on the DSC curves, these processes correspond to endothermic effects with extrema at 104 °C and 96 °C, respectively. In general, the destruction of organic parts for **1** and **4** ends already at 450 °C; the final mass of both complexes corresponds to the formation of oxides.

Acknowledgments: This work was financially supported by the Russian Science Foundation (project 20-13-00061); Korshunov V.A. and Taydakov I.V. (P.N. Lebedev Physical Institute RAS, Moscow) for determining the photoluminescent properties of the complexes.

e-mail: irinalu05@rambler.ru

Europium complexes with 3,5-dinitropyrazole: unusual luminescence thermal behavior

V.V. Utochnikova[a], I.A. Vatsadze [b], D.M. Tsymbarenko[a], A.S. Goloveshkin[c],
S. Z. Vatsadze[b]

[a]*Lomonosov Moscow State University, Moscow, RUSSIA*
[b]*Zelinsky Institute of Organic Chemistry RAS, Moscow, RUSSIA*
[c]*Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, RUSSIA*

Europium 3,5-dinitropyrazole complexes demonstrate an unusual luminescence behavior upon heating, i.e. there is a noticeable increase of the luminescence intensity beyond a temperature of 200 degrees [1].

The common knowledge on the luminescent behavior of nitro-group containing compounds teaches us that such substituents (which is also proved for azido-group) generally quench the emission. This indeed is true for the 3,5-dinitropyrazole ligand and it's metal complexes.

The main idea behind this research is that nitro-group appropriately placed in the ligand molecule would participate in the coordination to metal atom thus diminishing such quenching effects.

This report is focused on the synthetic and analytical issues concerned with the above-mentioned complexes (Fig. 1). The low luminescence quantum yield of Eu compound is compensated by very high absorption, resulting in intense luminescence even before heating. During heating, the europium luminescence intensity decreased until 200 degrees, whereas the elimination of the quenching NO_2-groups resulted in a significant increase of the luminescence intensity.

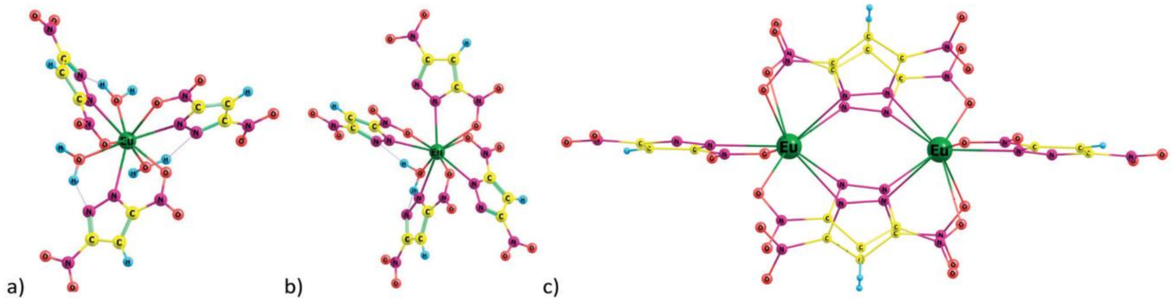


Fig. 1. The calculated ground state geometries of (a) the neutral complex EuL_3, (b) the anion $[EuL_4]^-$, and (c) the dimer $[Eu_2L_6]$ (L = 3,5-dinitropyrozolate anion).

We proposed to use such Eu complexes for determination of accidental overheating above 200 degrees. An on/ off ratio of 37 was reached, making target compound suitable for practical applications.

[1] V.V. Utochnikova, I.A. Vatsadze, D.M. Tsymbarenko, A.S. Goloveshkin and S.Z. Vatsadze, *PCCP*, **2021**, , *23*, 25480.

Acknowledgements – Authors thank RSF (20-73-10053) for financial support.

e-mail: vatsadze@ioc.ac.ru

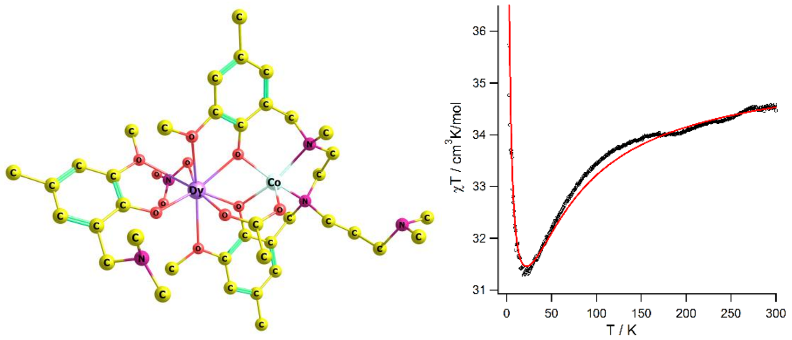
Computational study of single-molecule magnets based on lanthanides

A.A. Dmitriev[a,b], E.M. Kadilenko[a,b], M.A. Kiskin[c], A. Zabala-Lekuona[d], N.P. Gritsan[a,b]

[a]*Novosibirsk State University, Novosibirsk, RUSSIA*
[b]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, RUSSIA*
[c]*Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, RUSSIA*
[d]*University of the Basque Country, Donostia, SPAIN*

The design and synthesis of new coordination compounds with physical properties that are promising for practical application is an urgent task of modern coordination and physical chemistry and materials science. Application of Ln^{III} ions in such compounds is justified by the unique properties of such ions, i.e. their ability to exhibit prominent magnetic properties: high magnetic moments, significant magnetic anisotropy and slow magnetic relaxation (Single Molecule Magnetism, SMM, or Single Ion Magnetism, SIM). To understand in detail magnetic properties of the lanthanide complexes, it is necessary to use a large set of experimental and theoretical methods and techniques. In recent years, the contribution of quantum chemistry and computer simulation to the solution of this problem has increased significantly.

This report is focused on the computational study of the electronic structure and magnetic properties of a series of lanthanide (Dy, Yb) complexes showing properties of SMMs. To determine the electronic structure and magnetic properties of compounds under study, the high-level ab initio SA-CASSCF/CASPT2/SO-RASSI calculations with direct account of spin-orbit coupling were performed. DKH2-Hamiltonian was used to take into account the scalar relativistic effects. The calculated temperature dependence of magnetic susceptibility correlates well with the experiment. The magnetization blocking barriers and temperature dependences of magnetic susceptibility have been predicted and the contribution of different mechanisms on the magnetization relaxation was analyzed for all studied compounds. For the dinuclear complexes with two paramagnetic ions (Dy^{3+} and Co^{2+}), the dipole-dipole and exchange (within the Lines model) interactions were accounted using the POLY-ANISO module for the correct prediction of the electronic and magnetic properties. The computational results were compared with the experiment. The representative example of the studied complexes and their properties is shown in Scheme 1.



Scheme 1. The structure of the DyCo complex used in the calculations (left) and the experimental and calculated temperature dependence of magnetic susceptibility of this complex (right).

Acknowledgements – Authors thank the Ministry of Science and Higher Education of the Russian Federation (project FWGF-2021-0002) for financial support.

e-mail: dmitralexey@gmail.com

The incorporation of upper *vs* lower rim substituted thia- and calix[4]arene ligands into polydiacethylene polymeric bilayers for rational design of sensors to heavy metal ions

B.S. Akhmadeev, S. N. Podyachev, S.A. Katsyuba, S. N. Sudakova, G. Sh. Gimazetdinova,
V.V. Syakaev, O. G. Sinyashin, A.R. Mustafina

*Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS,
Kazan, RUSSIA*

1,3-Diketone calix[4]arene (CA) and thiacalix[4]arene (TCA), with the hydrophobic substituents introduced onto lower or upper rims respectively, form mixed aggregates with 10,12-pentacosadiynoic acid (PCDA) through the thin film hydration technique. Computer simulations, showing the arrangement of TCA and CA molecules in supramolecular clusters with PCDA molecules, suggest that PCDA assemblies with both cyclophanes are a convinient basis for the coordination of metal ions. However, photopolymerization of mixed aggregates reveals more disruption of the vesicular nanostructure of polydiacetylene (PDA) when CA molecules are included compared to TCA. The incorporation of the TCA and CA ligands influences the ability of the mixed PDA-bilayers to conformational and spectral changes and provides tight coordination of Tb^{3+} ions and efficient sensitizing of the Tb^{3+}-centered luminescence. The PDA-bilayers incorporated by terbium TCA complex provide more sensitive response on the series of heavy metal ions *vs* their CA-based analogues. The surface exposed TCA rims and carboxylate moieties of PDA provide two different binding sites for Tb^{3+} and heavy metal ions. Both distribution of Tb^{3+} and heavy metal ions between these sites and heterometallic complex formation are revealed as the factors affecting the luminescence response of PDA-TCA terbium complex in the solutions of heavy metal ions. The interplay between these factors is the reason for the different luminescence response of PDA-TCA terbium complex on Cd^{2+}, Hg^{2+} and Pb^{2+} ions. The PDA-vesicles incorporated by terbium TCA complex exhibit easier phase separation *vs* the PDA vesicles themselves, which favors the extraction of Pb^{2+} ions.

e-mail: bulat_ahmadeev@mail.ru

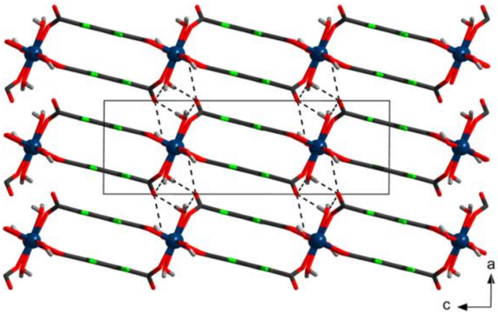
Synthesis, crystal structure, photoluminescence, and gas adsorption of scandium complexes with tetrafluoroterephthalate and tetrafluoroisophthalate ligands

A.M. Cheplakova, V.P. Fedin

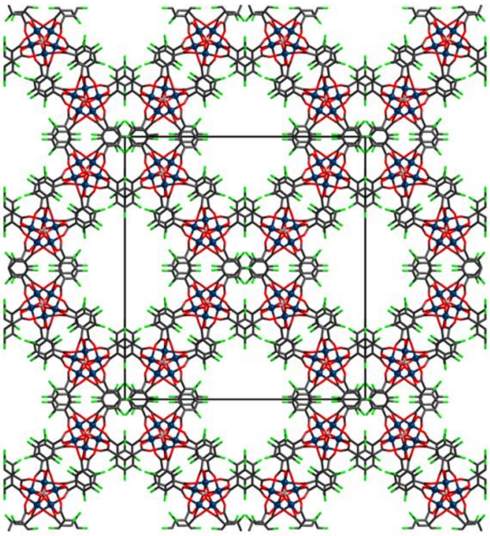
Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA.

Metal-organic frameworks (MOFs) are compounds that consist of metal ions or clusters linked by organic moieties to form a coordination framework, containing cages or cavities. Scandium is the lightest first-row d-element with a small size of the cation and high positive charge. This makes Sc(III) MOFs with O-donor ligands hydrolytically and thermally stable. On the other hand, an application of perfluorinated dicarboxylates is a promising approach to get novel MOFs with unique surface properties and selectivity of adsorption.

This report is focused on the ongoing study of Sc(III) complexes with tetrafluoroterephthalate (1,4-$tFBDC^{2-}$) and tetrafluoroisophthalate (1,3-$tFBDC^{2-}$) ligands and their properties. The use of linear bridging ligand mainly results in non-porous materials. Among these complexes, 3D coordination polymers $[Sc(H_2O)(tFBDC)_{1.5}]\cdot H_2O$ (**1**), $[Sc_2(H_2O)_2(tFBDC)_3]\cdot 2H_2O$ (**2**), and $[Sc(H_2O)(tFBDC)_{1.5}]\cdot 4H_2O$ (**3**) are supramolecular isomers. Complex 1 is obtained as a phase pure material, while 2 and 3 are found as admixtures. The reaction of $Sc(CF_3SO_3)_3$ with H_2(1,4-tFBDC) in the presence of NH_3 as a base produces layered coordination polymer $[Sc(H_2O)(OH)(tFBDC)]$ (**4**). Solid complexes 1 and 4 show ligand-centred purple/blue photoluminescence at room temperature with high quantum yields. The angular arrangement of carboxylic groups in tetrafluoroisophthalate 1,3-$tFBDC^{2-}$ leads to a highly porous perfluorinated framework [Sc(OH)(1,3-tFBDC)] (**5**), showing selective adsorption of C_2H_2 over C_2H_4 and C_2H_6, and C_6H_6 over C_6H_{12}.



$[Sc(H_2O)(OH)(1,4\text{-}tFBDC)]$



[Sc(OH)(1,3-tFBDC)]

Acknowledgements – Authors thank RSF (project 19-73-20087) and Ministry of Education and Science of Russian Federation for financial support.

e-mail: cheplakova@niic.nsc.ru

Synthesis and characterization of lanthanide chalcogenide nanoparticles

T.A. Pomelova

Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA.

The lanthanide chalcogenides are well-known objects of investigation as they demonstrate the high-temperature thermoelectric and solar energy conversion properties, and found application as pigments, phosphor host media and infrared window materials. One of the most efficient way to improve and modify the properties of materials is decreasing of the particles’ size and in case of such compounds it remains a challenging task. The high oxophility of lanthanides prevents using conventional for other oxygen-containing lanthanide compounds methods such as hydrothermal synthesis or sol-gel.

To solve this, we have applied top-down approach, especially, liquid exfoliation. This process requires layered compounds, and we found that even ones with charged layers could be exfoliated in appropriate conditions. We found that the stable dispersions of the binary, ternary and quaternary lanthanide chalcogenide compounds could be prepared in isopropanol, ethanol and acetonitrile during ultrasonic treatment. The colloids contain thin nanoplates with high aspect ratio (50-400 nm lateral size and 2-15 nm thickness). The colloids were successfully used for preparation of highly oriented films. We found that luminescent properties of nanostructured $KLnS_2$:Ln’ (Ln = La, Gd; Ln’ = Tb, Sm, Eu) are enhanced comparing to bulk samples.

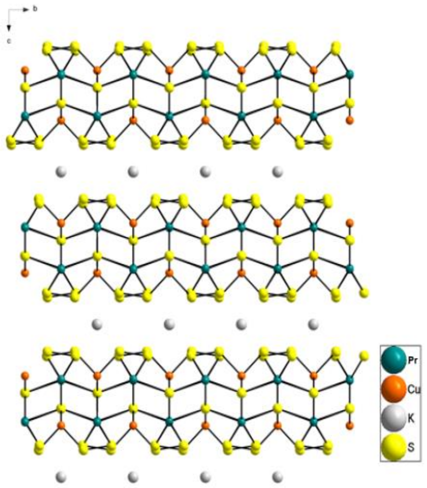


Fig. 1. Crystal structure of new layered compound $CsPr_2CuS_6$

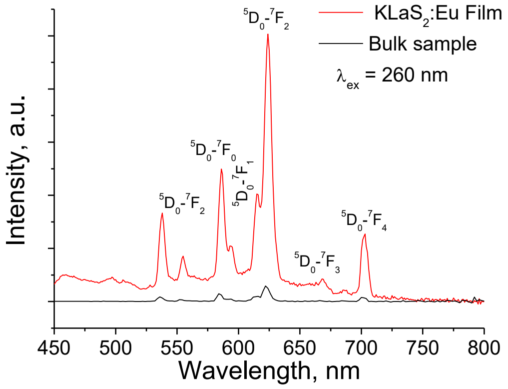


Fig. 2. Luminescence of $KLaS_2$: Eu nanostructed film in comparison with bulk sample

Acknowledgements – Authors thank RFS (projects 21-73-00240) and Ministry of Education and Science of Russian Federation for financial support.

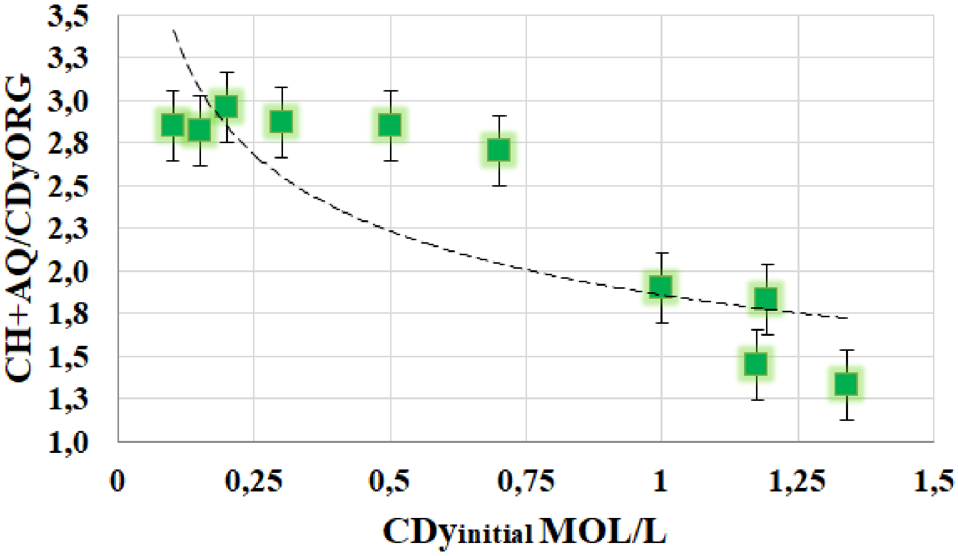
e-mail: pomelova@niic.nsc.ru

Study of the composition of extractable complexes of dysprosium by mono-2-ehtylhexyl ester 2-ethylhexylphosphonic acid (p507)

I.A.Erokhin, V.A.Dorozhko

St. Petersburg State Institute of Technology, department of rare elements technology and nanomaterials based on them, Saint-Petersburg, RUSSIA

The composition of extractable complexes of dysprosium by extraction dysprosium chloride ($DyCl_3$) solution by 0,75 mol/l mono-2-ethylhexyl ester 2-ethylhexylphosphonic acid (P507) in inert diluent was studied. The experiment carried out by contacting of extractant in acidic form at room temperature with solutions of $DyCl_3$ in a concentrate range from 0,05 to 1,6 mol/l with O/A=1 ratio. The metal concertation in aqueous phase of equilibrium extraction system measured by complexonometric titrimetry with the indicator «xylenol orange», protons concentration in aqueous phase measured by potentiometric titrimetry. The results are presented at Fig. 1.



Picture – The ratio of molar amount of the protons transferred to the aqueous phase from the organic phase to the molar amount of Dy^{3+} transferred from aqueous phase to the organic phase at the equilibrium state of the extraction process of $DyCl_3$ by extractant based on P507

Analysis of the data presented at the Fig. indicates, that with the increasing of initial dysprosium concentration, amount of protons transferred to the aqueous phase with the extraction of one mol of metal, is changing. With extraction from initial solution, containing from 0,05 to 0,8 mol/l dysprosium, there are 3 protons transferred. When the concentration of dysprosium is in the range from 1 to 1,6 mol/l the amount of protons is equal 2 or less. Therefore, the composition of the extractable complex in the first case could be $\overline{Dy(\mathrm{HA}_2)_3}$, that match with the data, described in work [1], using the similar extractant. With the increasing content of dysprosium over 0,8 mol/l the dysprosium can be extracted in form of $\overline{[Dy(HA_2)_2]Cl}$, $\overline{[DyHA_2]Cl_2}$, or polynuclear complexes like $\overline{Dy_n(HA_2)_m}$.

1. El-Hefny N. E. Comparative studies on Y (III) and Dy (III) extraction from hydrochloric and nitric acids by Cyanex 572 as a novel extractant / N.E. El-Hefny, M.S. Gasser, S.S. Emam, W.H. Mahmoud, H.F. Aly // Journal of Rare Earths. – 2018. – V. 36. – №. 12. – P. 1342-1350.

e-mail: iliaerokhin@yandex.ru

Extraction thermodynmics of the Nd and mono-2-ethylhrxyl ester 2-ethylhexylphosphonic acid

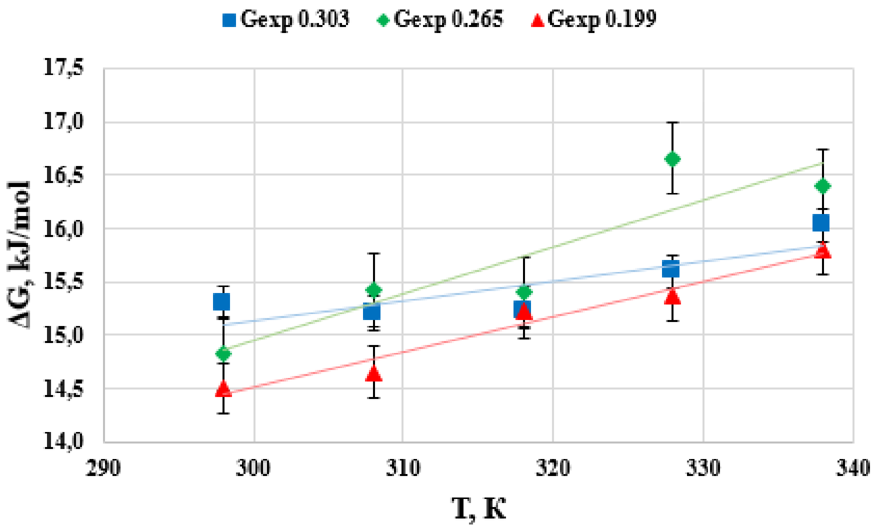
A.S. Orehova, V.A. Dorozhko

St. Petersburg State Institute of Technology, department of rare elements technology and nanomaterials based on them, Saint-Petersburg, RUSSIA

The thermodynamics of neodymium extraction by an extractant based on mono-2-ethylhexyl ether of 2-ethylhexylphosphonic acid (P507) investigated. Extraction was carried out by contact of the extractant P507 with aqueous solution of $NdCl_3$. Concentration of P507 was equal to 0.8 mol/l. Concentration of $NdCl_3$ were equal to 0.199 , 0.265 and 0.303 mol/l. The ratio O / A = 1. The temperature range was 25-65 °C. It is established that extraction proceeds according to the equation described in [1]:

$$Nd^{3+} + 3\overline{H_2A_2} \rightleftharpoons \overline{Nd(HA_2)_3} + 3H^+$$

The calculation of values of enthalpy (ΔH) and entropy (ΔS) carried out from the Gibbs free energy changes (ΔG). The system of Gibbs-Helmholtz's equations that written down at a temperature of each experimental point is for this purpose solved. The values of (ΔGexp) and (ΔGcalc) of Gibbs free energy changes in temperature range 25-65 °C are presented at figure.



Picture – The temperature dependence of the Gibbs free energy change during the extraction of neodymium of various concentrations from the chloride medium by P507 in the range of 25 – 65 °C

Based on the dependence, for three experiments conducted with an initial concentration of Nd chloride equal to 0.199 , 0.265 and 0.303 mol/l, respectively, there is an increase in the change in Gibbs free energy with an increase in temperature in the range of 25-65 °C, which indicates the possibility of extraction of neodymium above the equilibrium state at 25 °C with an increase in the extraction temperature.

1. Agarwal, V. Solvent extraction and separation of cerium (III) and samarium (III) from mixed rare earth solutions using PC88A / V. Agarwal, M.S. Safarzadeh // Minerals & Metallurgical Processing. – 2017. – Vol. 34. – №. 3. – P. 125-131.

e-mail: visssasha@yandex.ru

Генерация и люминесценция возбуждённых ионов лантанидов $^*Ln^{(n-1)+}$ при сонохимическом восстановлении Ln^{n+} сольватированным электроном

К.С. Василюк, Д.И. Галимов, С. М. Якупова, Б. Л. Гареев, А. М. Абдрахманов, Г.Л. Шарипов

Институт нефтехимии и катализа УФИЦ РАН, г. Уфа

Согласно известным литературным данным сольватированный электрон e_s является эффективным восстановителем ($E^0 = -2.9$ В) и, как правило, восстановление с помощью e_s органических и неорганических молекул, ионов и радикалов с положительными и незначительными отрицательными потенциалами проходит экзотермично (отрицательное значение изменения свободной энергии ($\Delta G \sim E_{ок} - E_{вос}$). Данное свойство сольватированного электрона может приводить к образованию восстановленных форм реагентов в электронно-возбужденном состоянии, поэтому эти реакции потенциально хемилюминесцентны. В настоящей работе показана способность ионов лантанидов к люминесценции вследствие химической генерации их электронно-возбужденных состояний в облучаемых ультразвуком растворах.

На основании известных потенциалов редокс-пар $Ln^{n+}/Ln^{(n-1)+}$ (n = 3 для Eu, Sm, Yb, Tm; n = 4 для Ce) и e_s проведена теоретическая оценка изменения свободной энергии процесса переноса электрона ΔG. Рассчитанные значения ΔG позволяют постулировать генерацию хемилюминесценции (ХЛ) в реакциях ионов лантанидов с сольватированным электроном $Ln^{n+} + e_s \rightarrow {}^*Ln^{(n-1)+}$ для Ln = Ce, Eu и Sm. Для иттербия и тулия процесс переноса электрона с заселением $5d^1$-уровней Yb^{2+} и Tm^{2+} – эндотермический.

Далее были изучены спектры однопузырьковой сонолюминесценции (ОПСЛ), фотолюминесценции, поглощения растворов $LnCl_3{\cdot}yH_2O$ (Ln = Eu, Sm, Yb, Tm, Ce; y = 6, 7), $(NH_4)_2Ce(NO_3)_6$, $EuCl_2$, $SmCl_2{\cdot}(THF)_2$ в воде и этиленгликоле, а также действия на ОПСЛ акцепторов радикалов. В случае церия(IV), европия(III) и самария(III) в спектрах ОПСЛ на фоне континуума растворителя обнаружены широкие бесструктурные максимумы люминесценции при 365, 465 и 754 нм, соответственно. Установлено, что эмиттерами данной ОПСЛ являются ионы $^*Ce^{3+}$, $^*Eu^{2+}$ и $^*Sm^{2+}$, а ключевой элементарной стадией обнаруженной сонохемилюминесценции (СХЛ) – реакция восстановления Ce^{4+}, Eu^{3+} и Sm^{3+} сольватированным в воде или этиленгликоле электроном. Последний образуется при сонолизе растворителя. Генерация СХЛ с участием иттербия и тулия при этих же условиях сонолиза не обнаружена.

Таким образом, на примере ионов европия, церия и самария обнаружено новое фундаментальное свойство лантанидов – способность к хемилюминесценции вследствие генерации электронно-возбужденных ионов $^*Ln^{(n-1)+}$ в элементарных актах восстановления Ln^{n+} (n = 3, 4) сольватированным электроном, при условии достаточности энергии реакции восстановления для электронного возбуждения $Ln^{(n-1)+}$.

e-mail: kristina.vasiluk@inbox.ru

Синтез, строение и фотолюминесцентные свойства комплексных соединений редкоземельных металлов с производными триазола

Е.А. Иванова[а,б], К.С. Смирнова[а], И.П. Поздняков[б,в], Е.В. Лидер[а,б]

[а]*Институт неорганической химии им. А.В. Николаева СО РАН, Новосибирск*
[б]*Новосибирский государственный университет, Новосибирск*
[в]*Институт химической кинетики и горения им В.В. Воеводского СО РАН, Новосибирск*

Процесс передачи поглощенной энергии с лиганда на ион лантанида с последующей люминесценцией во многом зависит от природы органического лиганда. Азотсодержащие гетероциклы, такие как имидазол, триазол, пиридин, пиразол и другие, широко используются в качестве лигандов для создания комплексов редкоземельных металлов с ярковыраженной люминесценцией. Данное направление остается одной из актуальных задач химии.

В данной работе получены комплексные соединения с 1-(1H-бензимидазол-1ил-метил)-1H-бензотриазолом (L^1) $[Ln(L^1)_2(H_2O)(NO_3)_3]_n$ и бис(1,2,4-триазол-1-ил)метаном (L^2) $[Ln(L^2)_2(NO_3)_3]_n$. Состав и строение соединений изучены с помощью элементного, рентгеноструктурного и рентгенофазового анализа, а также ИК-спектроскопии. Методом рентгеноструктурного анализа установлены два способа координации лиганда L^1: монодентатная координация атомом азота имидазольного цикла и бидентатно-мостиковая координация атомами азота имидадазольного и триазольного циклов, что приводит к образованию полимерных цепочек. Лиганд L^2 проявляет бидентатно-мостиковую координацию атомами азота триазольных циклов, связывая ионы лантанидов в металл-органический полимерный каркас.

Детально исследованы фотолюминесцентные свойства для лигандов и комплексных соединений: получены данные по спектрам возбуждения люминесценции и эмиссии, а также по квантовым выходам и временам жизни возбужденных состояний. В спектрах фотолюминесценции лиганда L^1 наблюдается флюоресценция, зависящая от длины волны возбуждения: при λ_{ex} = 325 нм наблюдается двухполосная эмиссия, максимумы которой расположены на 395 нм и 510 нм; при λ_{ex} = 405 нм – однополосная с максимумом на 510 нм. В спектрах фотолюминесценции лиганда L^2 наблюдается только однополосная эмиссия при λ_{ex} = 250 нм с максимумом на 325 нм. При комплексообразовании времена жизни возбужденных состояний увеличивается до микросекунд. Квантовый выход в комплексах европия(III) и тербия(III) увеличивается в 4,5 раза по сравнению с L^1. По данным спектров люминесценции комплексных соединений наблюдается полный или частичный перенос энергии с триплетного уровня лигандов на излучательный уровень ионов лантанидов.

Благодарности: Работа выполнена при поддержке Российского научного фонда (грант № 20-73-10207).

e-mail: ivanovaea@niic.nsc.ru

Способы снижения времени жизни возбужденного состояния комплексов лантанидов для увеличения эффективности OLED

М.И. Козлов, В.В. Уточникова

Московский государственный университет им. М.В. Ломоносова, Москва, РОССИЯ

Координационные соединения (КС) лантанидов являются перспективными материалами для эмиссионных слоёв органических светоизлучающих диодов (OLED), поскольку они обладают узкими эмиссионными полосами (~ 10 нм), что позволит достичь высокой чистоты света. Однако КС лантанидов редко демонстрируют яркость электролюминесценции (ЭЛ) выше ~100 кд/м^2 в отличие от других классов соединений, яркость ЭЛ которых достигает ~10000 кд/м^2. Таким образом, получение высокоэффективных OLED на основе КС лантанидов по-прежнему является как актуальной, так и нерешённой задачей в развитии технологии OLED.

В одной из предыдущих работ нашей группы было установлено, что одним из ключевых факторов, ограничивающих максимальные характеристики КС лантанидов в OLED, является время жизни возбуждённого состояния; для КС лантанидов оно обычно составляет ~1 миллисекунду, что повышает вероятность побочных процессов и снижает частоту излучательной рекомбинации электрон-дырочных пар. Для устранения этого ограничения мы предложили несколько способов понижения времени жизни: 1) дизайн КС лантанидов с легко поляризуемыми лигандами и лигандами-гасителями люминесценции, 2) получение смешаннолигандных комплексов, 3) введение иона иттербия в состав комплекса и 4) использование плазмонного резонанса.

В качестве легко поляризуемых лигандов были выбраны β-дикетонаты, а лиганда-гасителя люминесценции – дипиридо[a,c]феназин (DPPZ). Получение смешаннолигандных подразумевает введение в состав одного КС двух различных анионных лигандов, что приводит к снижению симметрии координационного окружения центрального иона, от которого зависит излучательное время жизни. Также было изучено влияние дополнительно иона иттербия в составе комплексов европия: введение иона иттербия снижает как квантовый выход, так и время жизни возбуждённого состояния европия, что может привести как к увеличению эффективности электролюминесценции европия, так и получению уникальных органических светодиодов с двойной эмиссией. Использование плазмонного резонанса заключается во введение наночастиц золота в непосредственной близости от эмиссионного слоя, что по литературным данным также способствует снижению времени жизни.

В работе рассмотрены перспективы предложенных способов повышения эффективности OLED на основе разнолигандных β-дикетонатов и ароматических карбоксилатов европия, тербия и иттербия.

e-mail: makariy.kozlov@gmail.com

Highly NIR-emitting ytterbium complexes containing 2-tosylaminobenzaldehyde-4-azidomethylbenzoylhydrazone anions as perspective luminescent biomarkers

D.S. Koshelev[a,b], R.E. Mustakimov[b,c], V.V. Utochnikova[a,b]

[a]*Faculty of the Material Science Lomonosov MSU*
[b]*Chemistry Department Lomonosov MSU*
[c]*Zelinsky Institute of Organic Chemistry RAS*

Lanthanide coordination compounds (CC) combine both the high absorption of organic ligands and the lanthanide luminescent properties that make them perspective in different areas such as sensing, OLEDs, or bioimaging. For the latter, lanthanide long excited state lifetimes, as well as the narrow emission bands and their constant positions in the spectra facilitate detection in living tissues.

Earlier[1] ytterbium complexes with the Schiff bases, i.e. 2-tosylaminobenzaldehyde-benzoylhydrazone, demonstrated high quantum yield (QY) of NIR luminescence up to 1.4%, and a molar extinction coefficient (ε) up to 40 000 $(M \cdot cm)^{-1}$, which makes these compounds prospective as bioimaging markers. However, the low solubility and lack of targeting groups require further ligand design. To increase solubility, in the present work, benzylidene fragment of the ligand was brominated, and to increase absorption, azido substituent was introduced into the benzoyl fragment of the ligand. Thus, modified 2-tosylamino(5-bromo)benzylidene-(4-azidomethyl)benzoyl hydrazone (H_2L2) and its non-halogenated analogue (H_2L1) were obtained by the condensation reaction of the corresponding aldehyde and (4-azidomethyl)benzohydrazide (**Fig. 1a**).

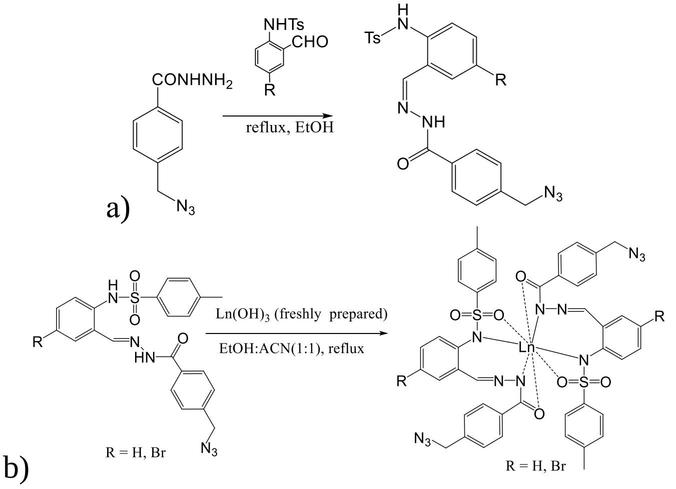


Fig. 1. Synthesis of a) organic ligands $H_2\mathbf{L}$, b) lanthanide CC - $Yb(\mathbf{L})(H\mathbf{L})$ (L =L1, L2).

Ytterbium complexes $Yb(\mathbf{L})(H\mathbf{L})$ ($\mathbf{L}$=L1, L2) were obtained with the corresponding Schiff bases by the reaction shown in Fig. 1b. Complexes $K[Yb(\mathbf{L})_2]$ were obtained by the reaction:

$$Ln(\mathbf{L})(H\mathbf{L})+KOH \rightarrow K[Ln(\mathbf{L})_2](H_2O)_n \text{ (n=2 for L1; 1 for L2)}$$

The compositions of the obtained compounds were confirmed by a combination of TG with MS of evolved gases, IR and NMR spectroscopy. Single-crystal XRD allowed solving structures of the 6 different complexes and 2 structures of organic ligand H_2L1. It turned out that the complex structures consist of mononuclear fragments $Yb(\mathbf{L})(H\mathbf{L})$ (Fig. 2a) or $[Yb(\mathbf{L})_2]$, which in the latter case are connected either to a polymer chain via a K^+ ion (Fig. 2b) or to binuclear fragments via two K^+ ions (Fig. 2c).

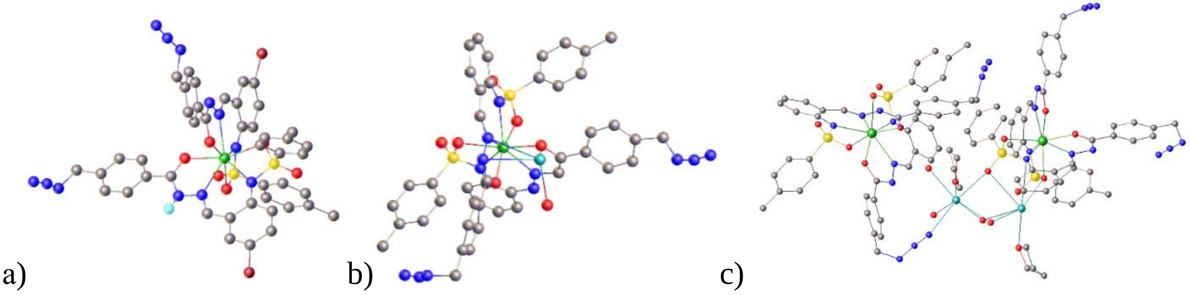


Fig. 2. Mononuclear fragments of a) $Yb(L1)(HL1)$ and b) $K[Yb(L2)_2]$. c) Dinuclear fragment of $K_2[Yb(L1)_2]_2$ structure.

The solubility of complexes increased upoh halogenation and upon the formation of $K[Yb(\mathbf{L})_2]$. The maximum solubility reached 40 g/L in THF, and for $K[Yb(\mathbf{L})_2]$ even water solubility was detected (~0.1 g/L).

The molar absorption coefficient reached 45300 $(M\cdot cm)^{-1}$ for $K[Yb(L1)_2]$ and the quantum yield of NIR luminescence reached 1.64% for $K[Yb(L2)_2]$. Quantum efficiency (QE) = $QY\cdot\varepsilon$ of the obtained compounds reached 680 $(M\cdot cm)^{-1}$ that exceeds the QE values of the commonly used biomarkers. The cytotoxicity of the $K[Yb(\mathbf{L})_2]$ is very low: cell viability decreases below 80% at concentrations over 80 mmol/L.

Thus, non-toxicity, high QE and high solubility make obtained compounds promising candidates to the emissive part of the targeted biomarkers.

[1] A. D. Kovalenko, P. O. Rublev, L. O. Tcelykh, A. S. Goloveshkin, L. S. Lepnev, A. S. Burlov, A. A. Vashchenko, Ł. Marciniak, A. M. Magerramov, N. G. Shikhaliyev, S. Z. Vatsadze and V. V Utochnikova, *Chem. Mater.*, **2019**, *31*, 759–773

Acknowledgements – The authors acknowledge Russian Scvience Foundation (20-73-10053) for financial support.

e-mail: daniil.s.koshelev@gmail.com

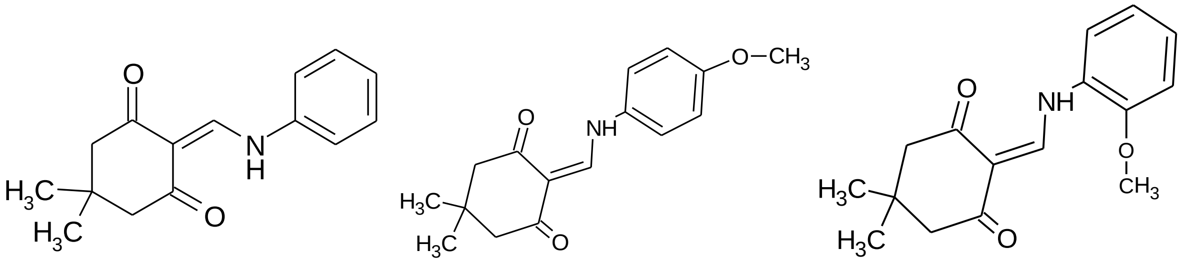
Lanthanide(III) complexes with β-enamindione derivatives: structure and photoluminescent properties

K.S. Smirnova[a], E.A. Ivanova[a,b], I.P. Pozdnyakov[b,c], V.V. Dotsenko[d], E.V. Lider[a,b]

[a]*Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, RUSSIA*
[b]*Novosibirsk State University, Novosibirsk, RUSSIA*
[c]*Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, RUSSIA*
[d]*Kuban State University, Krasnodar, RUSSIA*

The preparation of new lanthanide coordination compounds is one of current interest direction of chemistry, since they exhibit luminescent and magnetic properties, as well as a wide spectrum of biological activity. The ligand choice is one of the key points, as excitation of the system occurs indirectly, namely due to an "antenna" mechanism. With this effect, the organic ligand first absorbs light, goes into an excited state and transfers energy to the metal ion with subsequent emission. However, exactly lanthanide(III) ion is responsible for the definite emission colour.

In this work, β-enamindione derivatives were used as antenna ligands (Fig. 1). Coordination compounds were obtained by mixing solutions of the corresponding lanthanide(III) nitrate and ligand. A series of synthesized complexes with the general formula $[LnL_2(NO_3)_3]$ was characterized by various physicochemical methods: IR-spectroscopy, elemental, single-crystal X-ray diffraction and powder X-ray diffraction analyses.



L^1 L^2 L^3

Fig. 1. Structural formulas of ligands.

According to single-crystal XRD analysis, ligands are coordinated by a bidentate-bridging mode *via* oxygen atoms with the formation of polymer structures (Fig. 2.). The lanthanide(III) coordination sphere is supplemented by three nitrate groups, bidentate-coordinated, so the coordination number of the central atom is ten.

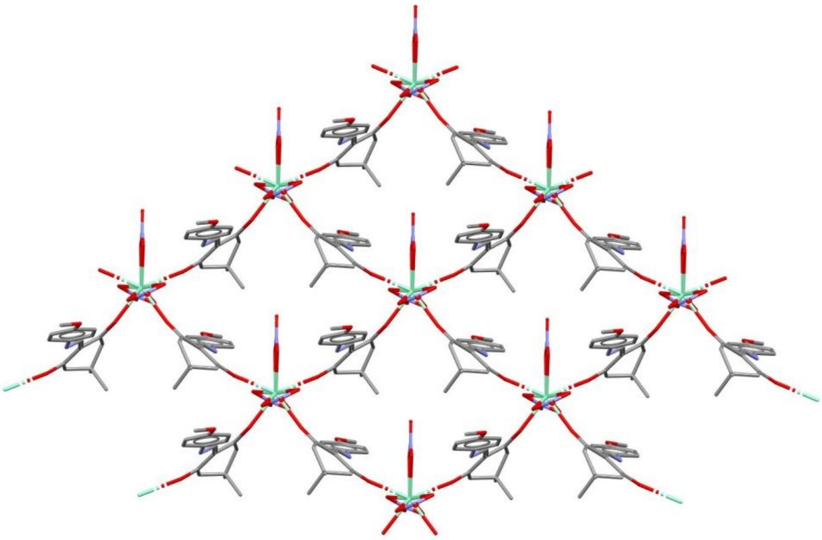


Fig. 2. Layered structure of the complex $[Tb(L^2)_2(NO_3)_3]_n$.

The photoluminescent properties were investigated for the ligands and the lanthanide(III) complexes. L^1 was shown to exhibit blue emission with picosecond lifetime of excited states, while L^2 and L^3 demonstrate green and blue emission, respectively, with nanosecond lifetimes (Fig. 3). The L^2 ligand has the most quantum yield – 40.6%. Luminescence sensitization is occurred for europium(III), terbium(III), and samarium(III) complexes. The emission spectra of these compounds exhibit bands characteristic for each lanthanide(III) ion.

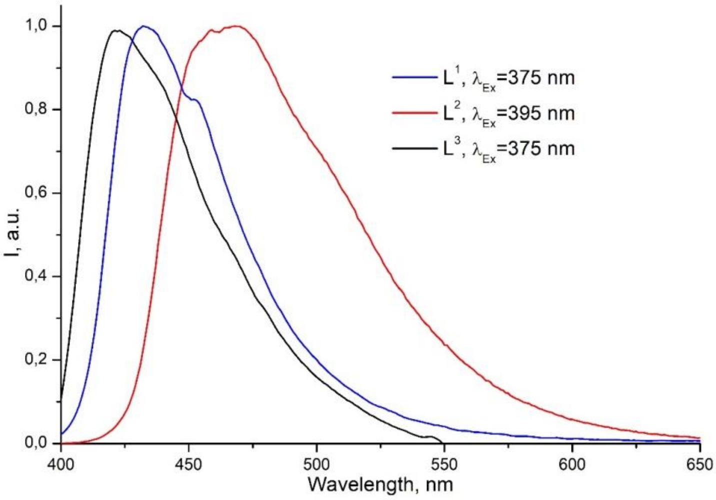


Fig. 3. Emission spectra of ligands L^1– L^3.

Acknowledgements – This work was supported by the Russian Science Foundation (Project №20-73-10207).

e-mail: smirnova_ksenya96@mail.ru

A novel approach to increase Tb-Eu-based luminescent thermometer sensitivity

L.O. Tcelykh, V.Yu. Kozhevnikova, V.V. Utochnikova

Lomonosov Moscow State University, Moscow, RUSSIA

Luminescence thermometry is potentially superior in many fields, where temperature measurements are required. Its obvious advantages include the possibility of the contactless temperature measurement of fast moving objects or objects of very small size, temperature measurement with a large surface coverage, etc. Luminescence thermometry is a success when many other thermometry methods fail, i.e. in nanotechnology and bioapplications, and even (nano)theranostics, as luminescence probes are inherently polyvalent materials. The simultaneous combination of properties such as thermometry and bioimaging provides advantages for magnetic resonance imaging and X-ray computed tomography. Luminescent thermometers are potentially suitable for both high temperature and cryogenic applications, and can be used in harsh environments. Flow temperature measurements, motor surface temperature measurements, and other engineering applications have already benefited from this method. Luminescent thermometers allow simultaneous surface temperature mapping with high resolution.

As the basis of such a thermometer, lanthanide compounds are promising, the luminescence bands of which have a small width and a constant position. Among them, coordination compounds are especially important due to the high intensity of luminescence sensitized by the ligand. The use of two emitting metals compounds makes it possible to use the ratio of the intensities of the luminescence bands of different metals as a signal and eliminate the need for additional calibration of the thermometer.

The temperature dependence of the luminescence of Tb-Eu complexes is usually caused by a change in the rate of reverse energy transfer from europium to terbium with temperature. If the rate of non-radiative processes is larger than of radiative, it can be described using the classical Mott-Seitz model, which considers the competition between the radiative transition and nonradiative reverse energy transfer. In our group, it was previously shown that for a three-level system, to which terbium-europium compounds belong, the temperature sensitivity is limited by the value of E_a/kT^2, where k is the Boltzmann constant, T is the temperature, and E_a is the activation energy, which corresponds to the energy gap between the excited states of terbium and europium ($3200\ cm^{-1} = 4604\ K$). Thus, the sensitivity of such a system, if described by the Mott-Seitz model, decreases with the temperature increase; e.g. at 100 ^oC, its limit is 3.3%/^oC [1].

We proposed that it is possible to increase the sensitivity, in particular that at the elevated temperature, if the operation of a thermometers is based not only on the reverse energy transfer. We propose to introduce another process that will proceed with different efficiency for terbium and europium ions, i.e. a quenching by the OH-vibrations of the ligand. As the objects of investigation, we selected bimetallic Tb-Eu complexes with 2-, 3- and 4-hydroxybenzoic anions (H(hbz) = H(2-hbz), H(3-hbz), H(4-hbz)) and different metal ratios due to high luminescence intensity and thermal stability of lanthanide aromatic carboxylates.

Despite europium complexes with the selected ligands do no emit light, bimetallic Tb-Eu complexes with 3- and 4-hydroxybenzoates demonstrate europium luminescence with the quantum yield up to 77%. Selected 3- and 4-hydroxybenzoates demonstrated temperature-dependent luminescence in the range of 25-100 °C. For 3-hydroxybenzoate of Tb-Eu, thermometer sensitivity reached 4%/°C at 100 °C, which exceeds the expected limit of 3.3%/°C at this temperature and is the highest reported value at this temperature. Temperature resolution is about 3 °C.

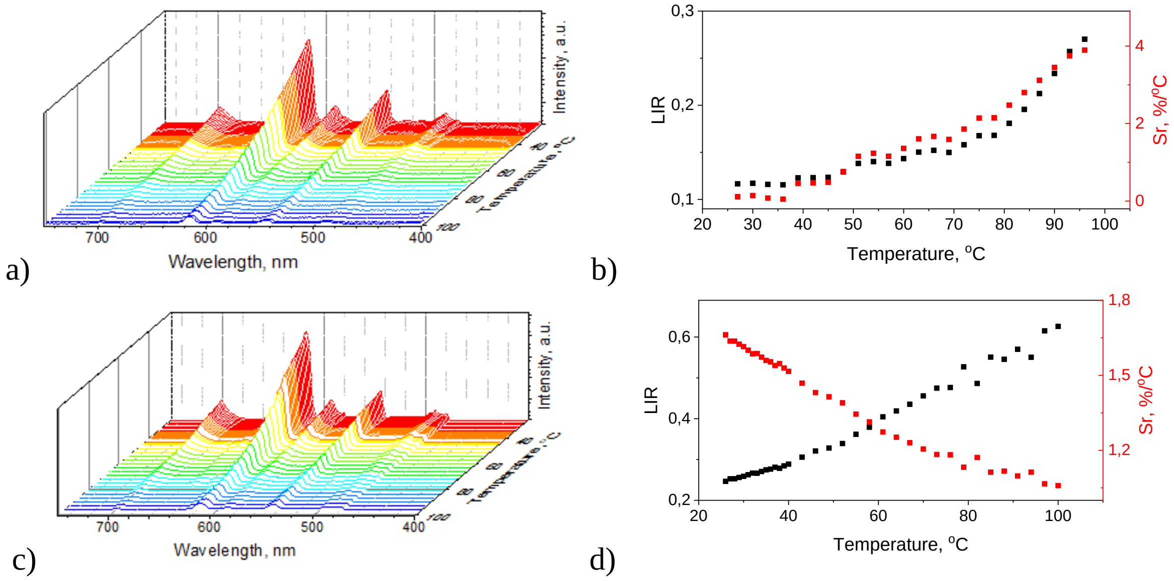


Fig. 1. a,c) Luminescence spectra at various temperatures and b,d) ratio of europium (612 nm) and terbium (545 nm) luminescence bands intensities (LIR = I(Eu)/I(Tb)) and sensitivity Sr of a,b) $Eu_{0.2}Tb_{0.8}(3\text{-}hbz)_3(H_2O)_n(C_2H_5OH)_m$ and c,d) $Eu_{0.2}Tb_{0.8}(4\text{-}hbz)_3(H_2O)_n(C_2H_5OH)_m$.

[1] Popelensky T.Y., Utochnikova V. V., *Dalt. Trans. Royal Society of Chemistry*, **2020**, 49, 12156–12160.

Acknowledgements – Authors thank Russian Science Foundation (grant 20-73-10053).

e-mail: lyuba.tselih@mail.ru

Using modern machine learning methods to study lanthanide coordination patterns

A.O. Dmitrienko

Plekhanov Russian University of Economics, Moscow, RUSSIA
M. V. Lomonosov Moscow State University, Moscow, RUSSIA

Rare-earth elements have high coordination numbers and a complex shape of coordination polyhedra. Another common feature is the shallowness of the potential energy surface: different coordination environments are close in energy, and corresponding barriers are low. That leads to many distorted and intermediate structures that a hard to classify. It remains unclear even whether directed covalent bonds play a significant role in the coordination environment of lanthanides or electrostatic arguments can explain all their diversity.

Over the decades since the beginning of the century, two significant changes have revolutionized structural chemistry. The first is the rapid accumulation of records in experimental structure databases. The second is the availability of modern statistical and data science analysis methods.

The first revolution is easy to express in numbers. The Cambridge Structural Data Bank, created in the eighties, reached one million records in 2019; in January 2022, it contained 49,458 lanthanide complexes. Even specialized search queries like “polymer structures with europium atoms connected by a carboxylate bridge” now give out more than a thousand matches. It is irrational to process such a large amount of data manually. We always need automated methods.

The second revolution is subtler than the first one. Machine learning methods allow us not to define the relevant features and categories in advance. They “learn” them statistically from many examples. Previously available only to computer science experts, those methods are now available to many researchers in different fields.

The most successful approach to the study of coordination polyhedra with a large coordination number is the method of Continuous Shape Measurements (CShM). The method uses a priori mathematical representations — Johnson polyhedra and their spherical analogs — heavily. On the one hand, this gives the analysis a clear interpretation: which of the idealized polyhedra is my object more like?. On the other hand, the choice of ideal polyhedra is quite arbitrary and affects the results strongly.

As an alternative and complement to CShM, it is interesting to conduct an utterly empirical analysis: measure the all-to-all “distances” (measure of difference, root-mean-square Cartesian difference for the best overlap, RMSD) between the coordination polyhedra and find the structure in the resulting matrix using modern unsupervised machine learning techniques. The clusters found in this way will correspond to stable coordination preferences and will not use any a priori knowledge about ideal polyhedra.

We carried out studies of lanthanide complexes with different coordination numbers within this framework. We calculated the RMSD distance matrix with a simple branches-and-bounds algorithm and visualized it using the t-SNE and UMAP dimensionality reduction methods. In most cases, the clusters corresponding to stable coordination preferences appear. We investigated the relationship between the results and the CShM scores and discussed how the cluster population changes with lanthanide atomic number.

Acknowledgements – Author thank Plekhanov Russian University of Economics for financial support.

e-mail: kate@sci.chem.msu.ru

Стендовые доклады

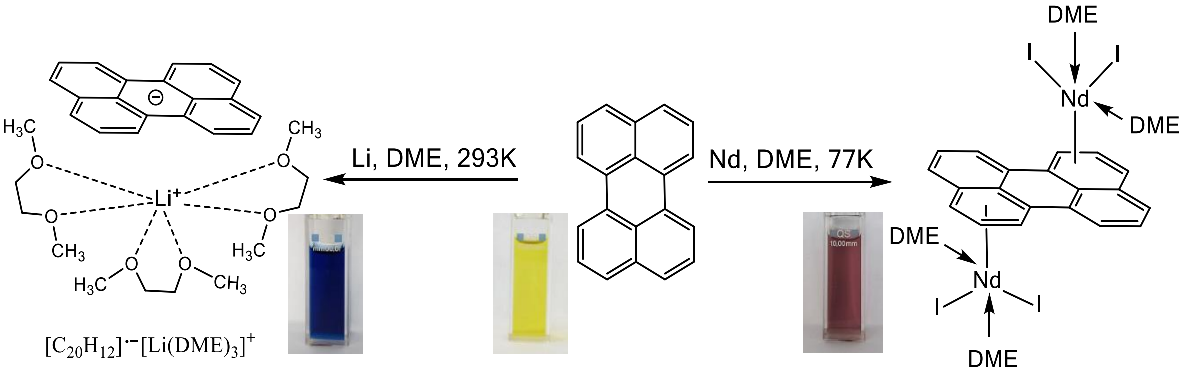
Synthesis and properties of new lanthanides complexes with perylene

T. V. Balashova, S.K. Polyakova, M. N. Bochkarev

G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences,
Nizhny Novgorod, RUSSIA

Interest in the development of new materials based on perylene derivatives is associated with their exceptional chemical and photochemical stability, high quantum yields of fluorescence, and a wide range of luminescence colours achieved by change of substitutions in the perylene core [1]. It is known only small number of perylene complexes containing the metal-ligand σ-bond with alkali and transition metals [1, 2]. Similar complexes with lanthanides in the literature are absent.

In this work, the possibilities of the reduction of perylene with lanthanide diiodides are considered. It was found that $TmI_2(DME)_3$ does not react with free perylene, as well as with free naphthalene, as was shown earlier [3]. In contrast, NdI_2 reacts very vigorously at 77K to give a blue solution characteristic of the perylene radical anion, which is confirmed by ESR spectroscopy data. After a few seconds, the color of the solution became burgundy, and the ESR signal disappeared. An extremely unstable compound of trivalent neodymium $[NdI_2(DME)_2]_2(C_{20}H_{12})$, containing two $NdI_2(DME)_2$ fragments bonded by bridging perylene dianion was isolated from the reaction mixture as extremely air unstable dark green precipitate. The composition of the product was confirmed by fragmental analysis, IR, ESR spectroscopy, and magnetic measurements.



Li and K react with perylene to give complexes $(C_{20}H_{12})M(DME)_3$ (M = Li, K), existing in the form of ion pairs, in which perylene is a radical anion. This was evidenced by the ESR spectra of solutions with a characteristic blue color. Both compounds were synthesized for further reactions with lanthanide iodides aiming to get new perylene-lanthanide derivatives.

[1] S. Lentijo, J. A. Miguel, P, Espinet. *Inorg. Chem*., **2010**, *49*, 9169–9177.
[2] C. Näther, H. Bock, Z. Havlas, T. Hauck. *Organomet.*,**1998,** *17*, 4707-4715.
[3] M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, H. Schumann, J. Demtschuk. *Chem. Commun*., **1997,** 1783-1784.

Acknowledgements – This work was supported by the RSF (Grant No. 22-23-00547)

e-mail:petrovsk@iomc.ras.ru

Lanthanide complexes with polychlorinated 2-mercaptobenzothiazolate ligands exhibiting intensive luminescence in near infrared range

A.V.Belyakova[a,b], V.A. Ilichev[a], A.F. Rogozhin[a], A.V. Rozhkov[c], M.N. Bochkarev[a]

[a]Razuvaev Institute of Organometallic Chemistry of RAS, Nizhniy Novgorod, RUSSIA
[b]Lobachevskiy State University of Nizhniy Novgorod, Nizhniy Novgorod, RUSSIA
[c]Saint Petersburg State University,Saint Petersburg, RUSSIA

Near infrared (NIR) luminescent materials based on trivalent lanthanides such as Nd, Er and Yb have attracted great attention in recent years due to their potential use in lasers, bioimaging and telecommunication systems.

NIR luminescent organic complexes of these lanthanides should be free of multiphonone quenchers which are C-H and C=O bonds. Therefore, polyhalogenated “antenna” ligands are used in the design of such complexes. We have recently shown that perfluorinated 2-mercaptobenzothiazole effectively sensitizes the NIR emission of Nd, Er and Yb compounds. [1, 2] In current work we have synthesized lanthanide ate complexes with novel fully and partially chlorinated 2-mercaptobenzothiazoles (mbt^{Cl}) (Fig. 1). The triplet levels of the ligands were determined using low-temperature phosphorescence spectra of the Gd derivatives. Surprisingly, it was found that the triplet level of the perchlorinated mbt^{Cl} ligand (19400 cm^{-1}) was significantly lowered as compared with perfluorinated mbt (21500 cm^{-1}) and even protonated mbt ligands (20400 cm^{-1}). As expected, due to an absence of quenching bonds in lanthanide environment the ate complexes with perchlorinated mbt^{Cl} ligands show intensive and long-lived luminescence in the NIR range.

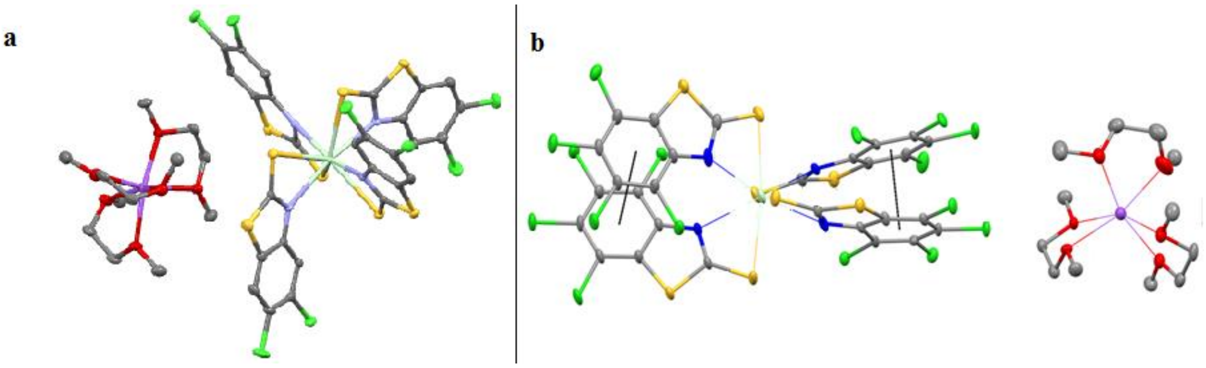


Fig. 1. Molecular structure of [(Nd(mbt^{Cl})$_4$)$^-$(Na(DME)$_3$)$^+$]ate complexes with partially (a) and fully chlorinated (b) mbt^{Cl} ligands.

[1] V.A. Ilichev, L.I. Silantyeva, A.N. Yablonskiy, B.A. Andreev, R.V. Rumyantcev, G.K. Fukin and M.N. Bochkarev, *Dalton Trans.*, **2019**, *48*, 1060-1066.
[2] A.F. Rogozhin, L.I. Silantyeva, A.N. Yablonskiy, B.A. Andreev, I.D. Grishin and V.A. Ilichev, *Opt. Mater.*, **2021**, *118*, 111241.

Acknowledgements – This work was supported by RSF (project 20-73-10115).

e-mail: alyona.belyakova.2000@yandex.ru

Effect of Lu^{3+} and Gd^{3+} additives on the structure and luminescent properties of $NaYF_4$: Sm^{3+}, Gd^{3+}/Lu^{3+} nanoparticles

A.A. Betina, A.S. Mereshchenko

Saint-Petersburg State University, Saint-Petersburg, RUSSIA

In recent years, the design of the multifunctional nanomaterials is one of the rapidly developing field of technology. Among this type of materials, one of the most widely studied are hybrid inorganic functionalized nanocomposites containing rare earth elements, which is due to their potential use for non-invasive diagnostics of living tissues: luminescent imaging, magnetic resonance and positron emission tomography, as well as the possibility of creating targeted radiopharmaceuticals and preparations for photothermal therapy for the treatment of tumors. It is important to study the dependence of luminescence intensity and particle size on the composition of the materials. In work, we studied the dependence of these parameters in the $NaYF_4$ nanoparticles doped with Sm^{3+}, where yttrium was also partially replaced by Gd^{3+} and Lu^{3+}.

Nanoparticles with a mixed crystal matrix were synthesized by hydrothermal method. Upon excitation at 401 nm, samples with Sm^{3+} demonstrated luminescence bands with maxima at 561, 595, 646 nm. The molar fraction of Sm^{3+} corresponding to the maximum luminescence efficiency was found to be 0.02. Then, the particles $NaY_{0,98}Sm_{0,02}F_4$ were doped with Gd^{3+} and Lu^{3+}. The luminescence maximum corresponds to 0.005 for Gd^{3+} and Lu^{3+}. The particle size varies between 58-800 nm, for $NaY_{1-x}Sm_xF_4$, and 44-800 for $NaY_{0,98-x}Sm_{0,02}Gd_xF_4$ and 800-1266 nm for $NaY_{0,98-x}Sm_{0,02}Lu_xF_4$ strongly depending on Gd/Lu concentration. The cell volume increases linearly when doped with Gd^{3+}, and decreases when doped with Lu^{3+}.

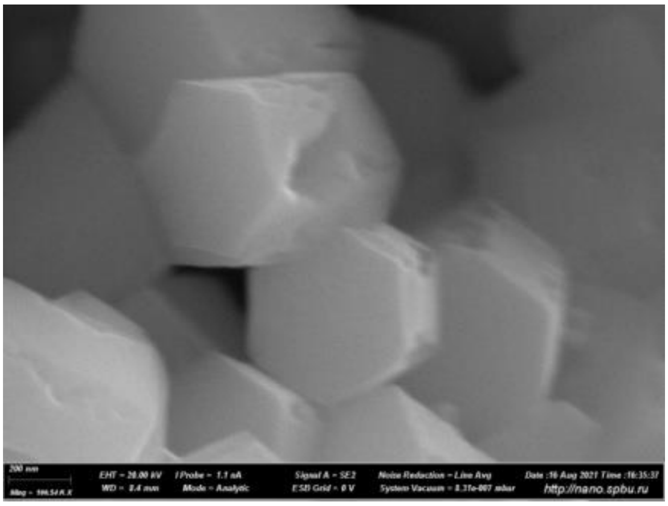


Fig. 1. SEM image of the sample $NaY_{0,98}Sm_{0,02}F_4$.

Acknowledgements – The measurements were performed at the Research Park of Saint-Petersburg State University (‘‘Magnetic Resonance Research Centre’’, ‘‘SPbU Computing Centre’’, ‘‘Cryogenic Department’’, ‘‘Interdisciplinary Resource Centre for Nanotechnology’’, ‘‘Centre for X-ray Diffraction Studies’’, ‘‘Chemical Analysis and Materials Research Centre’’, and ‘‘Centre for Optical and Laser Materials Research’’). This research was funded by Fellowship of President of Russia MD-1191.2022.1.3.

e-mail: betina.ann@yandex.ru

Rare-earth nitrate complexes of different dimensions: synthesis, crystal structure and properties

A.A. Vorobyova,[a] G.D. Chistyakov,[a] V.E. Goncharenko,[a] K.A. Lyssenko,[a] S.I. Troyanov,[a]
K.V. Zakharov,[a] A.N. Vasiliev,[a,b] A.I. Boltalin,[a] I.V. Morozov[a,b]

[a]Lomonosov Moscow State University 119991, Moscow, RUSSIA
[b]National University of Science and Technology "MISiS"119049, Moscow, RUSSIA

Nitrate complexes of rare-earth elements demonstrate a variety of composition and structure, but their properties remain insufficiently studied. Using both known and new synthetic approaches, previously unknown nitrate complexes of lanthanides were obtained in our work. The crystal structure of the obtained compounds was established by X-ray diffraction analysis. In the course of the work, a systematic study of nitrate complexes of rare-earth elements with various counterions was carried out. In this case, several families were synthesized, which made it possible to trace the crystallographic regularities in the series of lanthanides and to reveal the stability limits for compounds of the same type:

1. $\mathbf{(NO)_3[\mathit{Ln}_2(NO_3)_9]}$, Ln = La – Gd; $\mathbf{(NO)_2[\mathit{Ln}(NO_3)_5]}$, Ln = Tb – Lu
2. $\mathbf{(\mathit{A},\mathit{B})_2[\mathit{Ln}(NO_3)_5]}$, Ln = Dy, Ho, Er, Tm, Yb, A,B = PyH, N-NO$_2$Py, NO$_2$
3. $\mathbf{(PhenH_2)[\mathit{Ln}(NO_3)_5]}$, Ln = Eu, Dy

In addition, new synthetic approaches were tested, which made it possible for the first time to obtain nitrate complexes of a previously unknown composition and structure: framework $\mathbf{(BMIM)_6[La_4(NO_3)_{18}](C_2H_4Cl_2)}$ (Fig. 1a) (BMIM – butylmethylimidazolium cation), chain $\mathbf{NO[Ho(NO_3)_4]}$, layered $\mathbf{(H_3O)_2[La_3(NO_3)_{11}(H_2O)_2](H_2O)_5}$ (Fig. 1b).

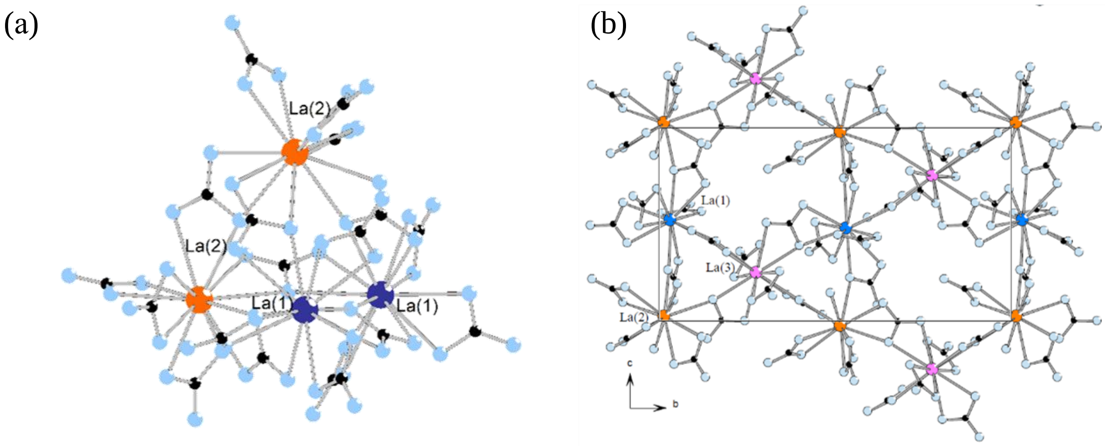


Fig. 1. Structure of $[La_4(NO_3)_{18}]^{6-}$ anion (a); $[La_3(NO_3)_{11}(H_2O)_2]_n^{2n-}$ layer (b)

Anhydrous nitrate complexes of lanthanides can exhibit the properties of Lewis acids and find applications in organic catalysis. The presence of series of compounds of the same type makes it possible to trace the change in such functional properties as luminescence and molecular magnetism, as well as to reveal patterns between the composition, nature of the metal, and the manifested properties.

Acknowledgements – This work was supported by NUST "MISiS" grant No. K2-2020-039.

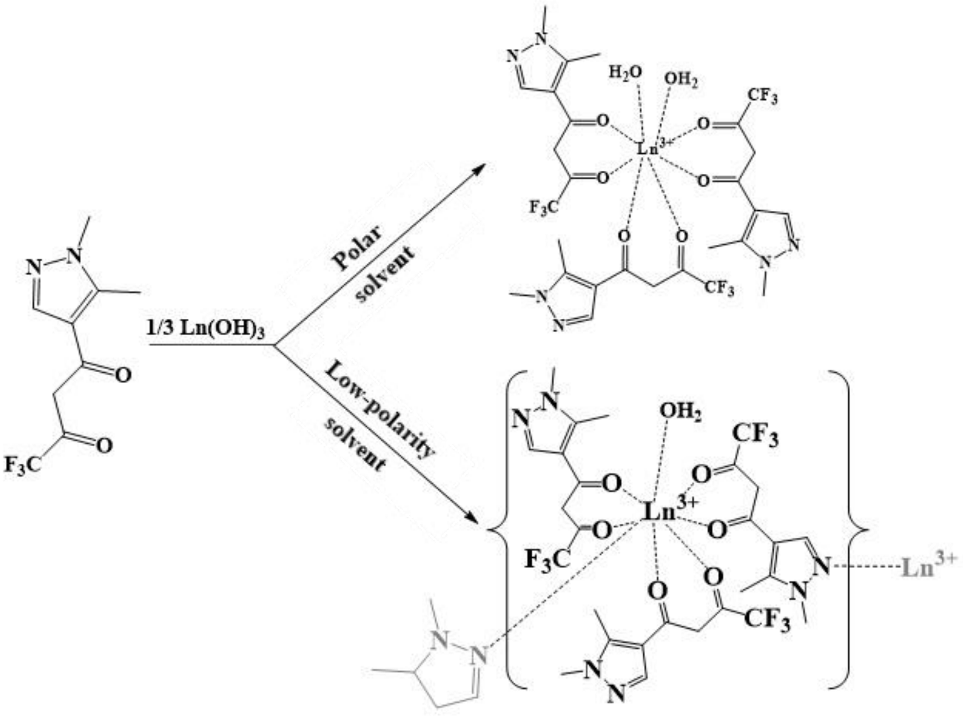
e-mail: vorobyova.anna9@gmail.com

Dimensionality control of lanthanide β-diketonates by changing the polarity of the reaction medium

V.E. Gontcharenko[a], I.V. Taydakov[b], Y.A. Belousov[a,b]

[a]*Lomonosov Moscow State University, Moscow, RUSSIA*
[b]*Lebedev Physics Insitute, Moscow, RUSSIA*

Six new complexes of rare earth elements (mainly europium) were synthesized and analyzed with the use of single crystal X-ray diffraction. The compounds were obtained by boiling a suspension of lanthanide hydroxide in the solution of β-diketone ligand L of different polarity (Scheme 1.).



Scheme 1. Scheme of the synthesis of the complexes obtained in the work.

When using ligand solutions in aqueous ethanol, ethyl acetate, and acetonitrile, complexes with a polymeric structure are formed, and in the case of acetonitrile solution the structure of the complex is a crystallosolvate [1].

The use of more polar reaction media (dioxane, acetone) leads to the formation of non-polymeric complexes - crystallosolvates. It should be noted that the use of aqueous methanol as a solvent also leads to a non-polymeric complex in which the coordination sphere of the terbium atom is saturated with two methanol molecules instead of two water molecules, which is possible due to the small size of the solvent molecules [2]. It is worth adding that the resulting acetone and dioxane crystallosolvates also differ in the mutual arrangement of water molecules coordinated to the europium atom, which is associated with the influence of the solvent.

Thus, a change in the polarity of the reaction medium makes it possible to adjust the dimensionality of the resulting complex (0D, 1D). The resulting coordination compounds exhibit characteristic luminescence of lanthanide ions (except for the gadolinium complex) upon excitation with 350 nm wavelength light.

Table 1. Dependence of the lanthanide complex structure on the polarity of the reaction medium.

Solvent	Polarity index	Chemical formula
EtOAc	4.4	$[Eu(L)_3(H_2O)]_n$ $P2_12_12_1$
EtOH:H_2O 4:1	5.48	$[Ln(L)_3(H_2O)]_n$ $P2_1/n$ (Ln=Eu, Gd,Tb)
MeCN [1]	5.8	$[Eu(L)_3(H_2O)]_n$*1,2(MeCN)
Dioxane:H_2O 1:1	7.5	$[Eu(L)_3(H_2O)_2]$*1,5($C_4H_8O_2$)
Acetone:H_2O 1:1	7.65	$[Eu(L)_3(H_2O)_2]$*1(H_2O)*1(C_3H_8O)
MeOH:H_2O 1:1 [2]	7.65	$[Tb(L)_3(MeOH)_2]$

[1] I. V. Taidakov, A. N. Lobanov, A. G. Vitukhnovskii, and Z. A. Starikova. *Russ. J. Coord. Chem., 39(6), 2013, 437–441.*
[2] I. V. Taydakov, R. I. Avetisov, and N. P. Datskevich. *Russ. J. Coord. Chem., 45(12), 2019, 883–888.*

Acknowledgements – Authors thank RFBR (project 20-33-70208) for financial support and Lomonosov Moscow State University Program of Development for providing access to single X-ray diffraction equipment.

e-mail: victo.goncharenko@gmail.com

Scandium halide and alkyl complexes bearing anionic-tethered pincer NHC ligands

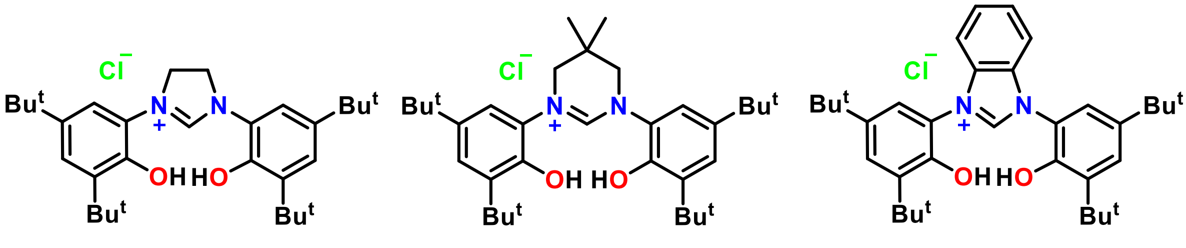
G.A. Gurina[a,b], A.V. Markin[b], A.A. Trifonov[b,c]

[a]*National Research Lobachevsky State University (UNN), Nizhny Novgorod, RUSSIA*
[b]*G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, RUSSIA*
[c]*A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Nizhny Novgorod, RUSSIA*

Due to their outstanding σ-donating abilities, N-heterocyclic carbenes (NHCs) have recently emerged as powerful supporting ligands for transition metal catalysts.[1] In contrast, the use of NHC ligands for coordination to oxophilic high-oxidation-state metals has been far less investigated. Although monodentate NHCs are excellent supporting ligands for rare-earth metal complexes, the metal–carbene bond is still significantly weaker and more reactive in these electropositive metal systems than it is in late transition metal systems.

Pincer-type ligand systems have gained wide recognition in coordination chemistry as they form stable metal complexes with strong metal-ligand bonds.[2] From HSAB theory (hard soft acid base), it follows that anionic-functionalized NHC ligands readily coordinate with electropositive metals which are Lewis acidic in character, with the anionic functions acting as anchors counterbalancing the tendency of the undesired NHC dissociation from the electron-deficient metal center. So, pincer ligands combining a soft NHC with two harder anionic groups must be particularly effective in the stabilization of rare-earth-NHC complexes, generating systems with strong metal–carbene bonds.

We expect that, following the success of monodentate NHCs, chelating NHCs with anionic functions will become perspective objects in the field of organo-rare-earth chemistry. In order to reduce the tendency for ligand dissociation, symmetrical (OCO)-type NHC-donor systems $\mathbf{L^{1-3}H_3}$, where a neutral carbene donor is surrounded by two identical anionic functions, were chosen (Chart 1). In this report, synthesis, isolation, and characterization of a large series of scandium complexes bearing pincer-type bis-(N-phenoxide)-NHC ligands are described.



L^1H_3 L^2H_3 L^3H_3

Chart 1. Phenolic-tethered NHC precursors employed in this study.

[1] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature*, **2014**, *510*, 485–496.
[2] D. Pugh, A. A. Danopoulos, *Coord. Chem. Rev.*, **2007**, *251*, 610–641.

Acknowledgements – Authors thank RFBR (project 20-33-90191) for financial support.

e-mail: live_love_peace@mail.ru

Hybrid systems based on carbon quantum dots and terbium complexes with thiacalix[4]arene ligands as luminescent ratiometric nanothermometers

A.P. Dovzhenko[a], R.R. Zairov[a], A.R. Mustafina[b]

[a]*Kazan (Volga region) Federal University, Kazan, RUSSIA*
[b]*Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, Kazan, RUSSIA*

Intracellular temperature attracts special attention in last decades. This essential physiological property is accountable for the rates of biological reactions and the biomolecule diffusion course, such as exocytosis, oxidation phosphorylation, and the transmembrane transport of ions. That makes cell temperature measurements crucial in a big number of practical applications. Luminescence-based temperature sensing is outstanding in this sphere due to its merits of being noninvasive and precise [1-3].

In this work, was developed a facile strategy for synthesis of novel hybrid polystyrenesulfonate(PSS)-coated nanoparticles consisted of carbon dots (CD) and Tb^{3+} complex as a single excited dual band luminescent nanothermometer (Fig. 1).

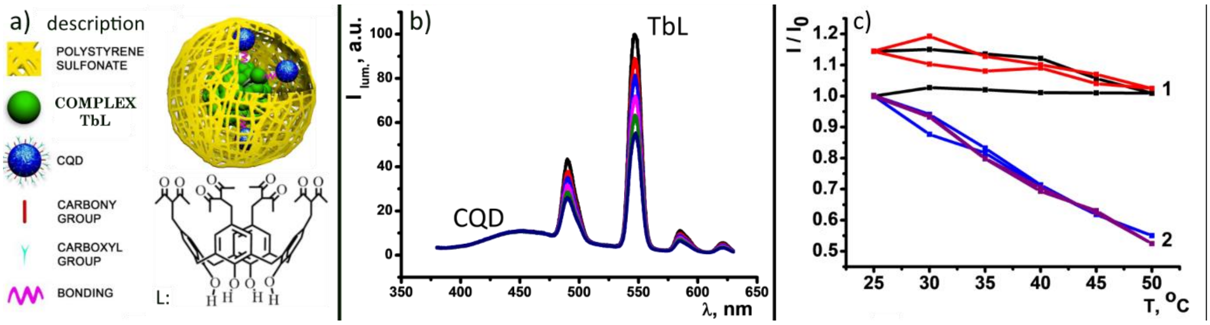


Fig. 1. Schematic description of hybrid nanoparticle and structure of ligand of complex [TbL] (a), emission spectra of this nanoparticles (lex =360 nm) as a function of temperature (b), temperature dependence of 450nm (1) and 547 nm (2) bands of PSS-{CDs-[TbL]} upon two heating-cooling cycles(c)

Ligand environment of the Tb3+ complex had to satisfy the specific requirements, such as: (1) high complex stability, (2) incomplete coordination sphere of Tb^{3+} ions, (3) efficient and temperature responsive Tb^{3+}-centered luminescence. The $[TbL]^{+}$ complex with 1,3-diketonate derivatives of calix[4]arene (L) fits well to the aforesaid requirements. The capacity of the hybrid nanoparticles to simultaneously emit in the blue and green regions of spectrum originates from two different emissive components CDs and $[TbL]^{+}$ complex, correspondingly. Green and blue emitting blocks were incorporated into the polysodium polystyrolesulfonate (PSS) aggregates through the solvent-exchange synthetic technique. Due to their unique optical properties, temperature sensing over the range of 35–45 °C can be accomplished via changes in fluorescence intensity with high sensitivity values (S_j=3.55 % $°C^{-1}$).

[1] Gong D. et al. Sens. Actuators B Chem. 2017, 252, 577–583.
[2] Zairov R.R., Dovzhenko A.P. et al. scientific reports 2020, 10, № 1, 20541.
[3] Shi X. Li Z. et al. Small 2019, Vol, 15, № 48, 1901507.

e-mail: aleksej_dovghenko@mail.ru

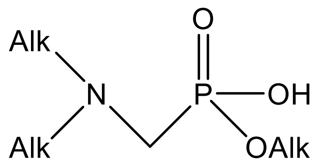
Мембранная экстракция редкоземельных элементов О-2-этигексил-N,N-ди-2-этилгексиламинометилфосфоновой кислотой

Е.В. Зайцева, Л.И. Ахбарова, Р.А. Марданшина, А.Р. Латыпова, Я.В. Курашов,
О.Е. Чибирев, А.Р. Гарифзянов

Химический институт им. А.М. Бутлерова, КФУ, Казань, РОССИЯ

В связи с высоким спросом на редкоземельные элементы (РЗЭ) актуальной задачей является разработка эффективных гидрометаллургических процессов их концентрирования и разделения. Значительный интерес в этом отношении представляет метод мембранной экстракции с импрегнированными жидкими мембранами (ИЖМ).

Целью настоящей работы является изучение мембранной экстракции трехзарядных катионов редкоземельных элементов с использованием нового мембранного переносчика – ***О-2-этилгексил-N,N-ди-2-этилгексиламинометил-фосфоновой кислоты*** (HR):



Alk = $-CH_2CH(C_2H_5)C_4H_9$

В качестве матрицы ИЖМ использовались гидрофобные фторопластовые фильтры с диаметром пор 0,45 мкм, жидкая фаза – раствор HR в керосине. Концентрацию катионов РЗЭ в водных фазах определяли фотометрическим методом с Арсеназо(III).

Было выяснено, что с ростом концентрации переносчика в мембранной фазе проницаемость мембраны увеличивается, но лишь до определенного значения, затем зависимость выходит на предел вследствие увеличения вязкости мембранной фазы.

Скорость переноса неодима(III) возрастает с увеличением концентрации нитрата натрия в отдающем растворе, но перестает расти при концентрациях нитрат-иона, превышающих 0.2 М, с переходом мембраны в «режим насыщения», и скорость массообмена начинает лимитироваться диффузионными процессами.

Была исследована зависимость эффективности переноса ионов РЗЭ от концентрации азотной кислоты в отдающем растворе. Проницаемость мембраны для всех катионов уменьшается при повышении концентрации HNO_3 до 0.02 М и далее плавно увеличивается до определенного значения (табл.1).

Табл. 1. Проницаемость ИЖМ ($J\cdot10^6$ м/с) по отношению к катионам РЗЭ при различных концентрациях HNO_3 в отдающем растворе

Катион РЗЭ	***Концентрация HNO_3, моль/л***							
	0.0002	0.01	0.02	0.05	0.1	0.2	0.3	0.4
La^{3+}	***5.09***	***0.271***	***0.276***	***0.918***	***1.37***	***1.99***	***2.03***	***1.23***
Nd^{3+}	***4.27***	***2.39***	***1.91***	***2.24***	***2.85***	***3.49***	***3.88***	***3.56***
Sm^{3+}	***3.01***	***1.13***	***1.77***	***2.82***	***4.91***	***5.73***	***6.96***	***5.63***
Er^{3+}	***6.73***	***2.55***	***3.32***	***6.12***	***9.54***	***10.9***	***11.6***	***11***

При высоких концентрациях азотной кислоты (0.1 – 0.3 М) эффективность экстракции в ряду РЗЭ существенно растет с увеличением атомной массы элементов, что представляет несомненный практический интерес.

Полученные экспериментальные результаты свидетельствуют о том, что при изменении pH отдающего раствора происходит изменение механизма мембранной экстракции катионов РЗЭ в исследованной системе. При pH > 2 в мембранную фазу переходит хелат LnR3, а в случае кислых нитратных исчерпываемых растворов транспорт осуществляется через образование ионного ассоциата $\{[Ln(HR)_3]^{3+}\cdot 3NO_3^-\}$.

Для оценки возможности использования исследуемых ИЖМ в гидрометаллургических процессах исследована мембранная экстракция ионов гадолиния(III) из раствора, содержащего 10-кратные избытки катионов Ca (II), Mg (II) и Al (III). Полученный принимающий раствор был проанализирован на атомно-эмиссионном спектрометре с микроволновой азотной плазмой. Установлено, что катионы кальция, магния и алюминия не мешают мембранному транспорту гадолиния и не переходят в принимающий раствор, при этом катион Gd (III) извлекается количественно.

Исследованные ИЖМ сохраняли транспортные свойства при контакте с рабочими водными растворами в течение 260 часов.

Полученные результаты свидетельствуют о возможности практического использования данных ИЖМ для разделения и концентрирования ионов РЗЭ.

e-mail: zaev@mail.ru

Magnetic and optical properties of liquid-crystal lanthanide derivatives

M.E. Karyakin,[a] A.S. Krupin,[a] A.A. Knyazev,[a] Yu.G. Galyametdinov[a,b]

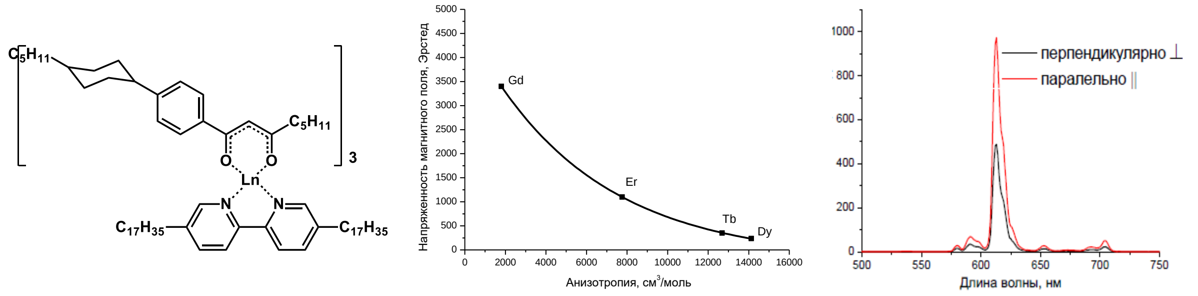
[a]*Physical and Colloid Chemistry Department, Kazan National Research Technological University, Kazan 420015, RUSSIA*
[b]*Kazan Physical-Technical Institute, RAS, Kazan 420029, RUSSIA*

Liquid crystals have found wide application as an anisotropic medium in various devices for displaying and processing information. Orientation of LC in devices is carried out, as a rule, by an electric field. This control method has certain disadvantages associated with electrochemical reactions at the interface between the electrode and LC molecules under the influence of an electric field. The use of magnetic fields to control an LC medium does not have this disadvantage; in addition, the orientation of molecules in the mesophase can be changed at any angle. However, for easy and fast control of the magnetic field, LCs must have a large anisotropy of magnetic susceptibility, which is unattainable for organic liquid crystals. From this standpoint, lanthanide ions are very attractive, exhibiting a paramagnetic anisotropy that is one or two orders of magnitude higher than that for organic LCs. Tb(III), Dy(III), Ho(III), Er(III), and Tm(III) ions have the highest absolute values of the magnetic susceptibility anisotropy. The introduction of a lanthanide ion into a liquid crystal molecule makes it possible to obtain a mesophase capable of being oriented by relatively weak magnetic fields. In this case, the presence of a lanthanide ion in the structure of a liquid crystal makes it possible to impart unique optical and luminescent properties to the latter. However, in this case, problems arise in obtaining low-viscosity LC phases associated with high coordination numbers of lanthanides. That is why, until recently, it was not possible to obtain low-viscosity mesophases with high magnetic anisotropy.

Liquid-crystalline adducts of lanthanide tris(β-diketonates) with 5,5'-diheptadecyl-2,2'-bipyridine were obtained in this work (Fig. 1, a). It was found that the resulting complexes exhibit smectic A and nematic polymorphism upon heating. Upon cooling from the isotropic state, the complexes vitrify with the preservation of the texture of the smectic A mesophase. It is shown that the phase transition temperatures of the complexes do not have a definite dependence on the lanthanide(III) ion.

The magnetic properties of lanthanide-mesogens were studied when they were oriented by weak magnetic fields by the method of dielectric spectrometry. It was found that the dielectric properties of lanthanide-mesogens are largely affected by the ligand environment, while the type of lanthanide ion does not make a significant contribution. The value of the dielectric anisotropy $\Delta\varepsilon$ of the complexes in the temperature range of existence of the nematic phase is in the range of 0.5 – 3.0, which makes it possible to effectively control the orientation of the LC director using an electric field.

Using the method of magnetic birefringence, it was found that, depending on the choice of rare-earth ion, the complexes can be oriented with their long molecular axis, parallel or perpendicular to the magnetic field. The possibility of controlling the orientation of nematic lanthanide-mesogens containing Tb(III) and Dy(III) ions using weak magnetic fields of 200 Oersted was shown for the first time (Fig. 1, b). While organic liquid crystals require fields of 1500 Oersted or more for orientation, the known non-nematic derivatives of lanthanides are oriented by magnetic fields of 10000-12000 Oersted.



a **b** **c**

Fig. 1 - Structural formula of the Ln(CPDK$_{3-5}$)$_3$Bpy$_{17-17}$ complex, where Ln is the lanthanide ion (a); Dependence of the critical field H on the anisotropy of the magnetic susceptibility of some nematic lanthanide-mesogens (b); Polarized luminescence spectra of the oriented Eu(III) complex (c)

The combination of unique luminescent, liquid-crystal properties and the possibility of lanthanide-mesogens orientation by weak magnetic fields made it possible to obtain luminescent media with controlled luminescence polarization. A twofold change in the luminescence intensity of lanthanide-mesogens was found upon a change in the direction of orientation of molecules relative to the plane of polarization of the exciting beam (Fig. 1, c).

Thus, the introduction of a lanthanide ion into the structure of a liquid crystal molecule makes it possible to use the orientational behavior of lanthanide-containing mesophases with a high anisotropy of magnetic susceptibility to control their luminescent properties.

Acknowledgements – The authors would like to thank the Russian Foundation for Basic Research (projects 20-03-00620)

e-mail: belgesto@list.ru

Acid-base approach to the synthesis of heterometallic chalcogenide complexes of lanthanides and transition metals (Ni, Ti, Zr)

A.Yu. Konokhova, A.G. Demkin, M.Yu. Afonin, T.S. Sukhih and S.N. Konchenko

Nikolaev Institute of Inorganic Chemistry SB RAN, Novosibirsk, RUSSIA

Heterometallic complexes of lanthanides with transition metals are promising objects for research. Such compounds may have exceptional catalytic, unusual magnetic and luminescent properties. Few heterometallic *d*/4*f* chalcogenide complexes are known; therefore, the development of methods for the synthesis of such compounds is an urgent task. In this work, we proposed a new synthetic approach based on the acid-base interaction. Transition metal hydrosulfide complexes ($[Cp_2Ti(SH)_2]$, $[^{tBu}Cp_2Zr(SH)_2]$ и $[(dppe)Ni(SH)_2]$) were chosen, in which the SH group was capable of splitting a proton; act as a Brønsted acid. The lanthanide complexes with the allyl ligand $[Cp^*{}_2LnAllyl]$ were chosen as the base substrates.

The reactions of $[^{tBu}Cp_2Zr(SH)_2]$ with lanthanide allyl complexes $[Cp^*{}_2LnAllyl]$ (Ln = Ho, Dy) were studied. As a result, four-nuclear products have been obtained (Fig. 1, I), the core of which consists of two $\{ZrLnS_2\}$ fragments.

Reactions of $[Cp^*{}_2LnAllyl]$ with the titanium complex $[Cp_2Ti(SH)_2]$ in toluene result in substantially different products: five-nuclear clusters $[(CpTi)_3(\mu_3\text{-}S)_6(Cp^*Ln)_2]$ (Ln = Dy, Nd, Tb, Gd) (Fig. 1, II). The core $\{Ti_3Ln_2\}$ is a triangular bipyramid of metal atoms, on each face of which there is a μ_3-sulfide bridging ligand. When carrying out similar reactions in tetrahydrofuran, binuclear products $[Cp^*{}_2Ln(\mu\text{-}S)_2TiCp(thf)]$ (Ln = Dy, Tb, Gd, Nd, Tm) are formed.

The reaction of the nickel hydrosulfide complex $[(dppe)Ni(SH)_2]$ with $[Cp^*{}_2DyAllyl]$ leads to the formation of a tetranuclear compound. Its core can be described as an octahedron $\{Dy_2S_4\}$ along two edges of which the $\{(dppe)Ni\}$ fragments are attached (Fig. 1, III).

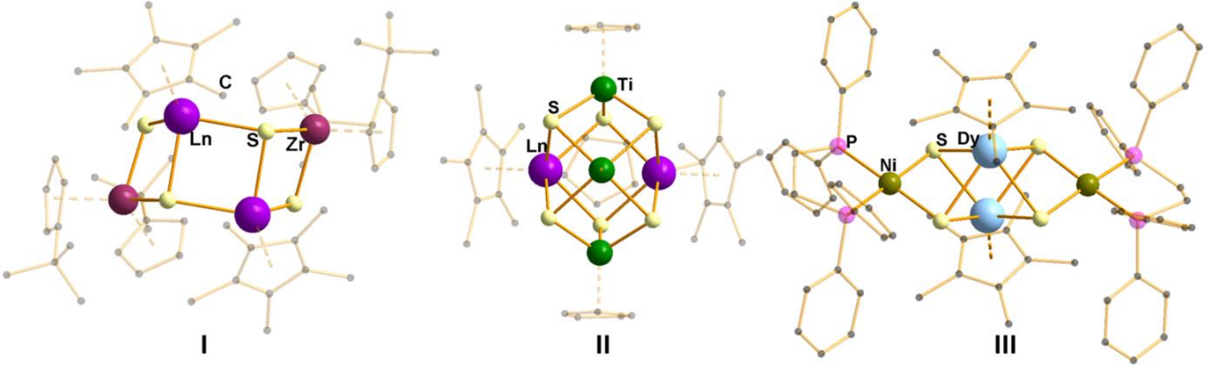


Fig. 1. Structures of complexes I - $[^{tBu}Cp_2Zr(\mu\text{-}S)(\mu_3\text{-}S)LnCp^*]_2$, II - $[(CpTi)_3(\mu_3\text{-}S)_6(Cp^*Ln)_2]$, III - $[((dppe)Ni)_2(\mu_3\text{-}S)_4(Cp^*Dy)_2]$.

As a result of the study, it has been shown that the use of the acid-base approach is promising for the preparation of heterometallic *d*/4*f*-sulfide complexes.

Acknowledgements – Authors thank Russian Science Foundation (project 16-13-10294) and Ministry of Education and Science of Russian Federation for financial support.

e-mail: kon-an-yu-97@yandex.ru

Luminescence of rare-earth ions in diopside glasses of $MgCaSi_2O_6$ composition

V.V.Sokolov[a], A.E. Kokh[b], N.G.Kononova[b] , M.I.Rakhmanova[a]

[a]*Institute of Inorganic Chemistry SB RAS*
[b]*Institute of Geology and Mineralogy SB RAS*

The study of magnesium-calcium silicate of $MgCaSi_2O_6$ composition with a variable content of magnesium and calcium, known as a mineral of diopside, attracts the attention of researchers with a number of interesting properties. The high solubility of many metal oxides in pure colorless diopside makes it possible to obtain and study materials as phosphors [1], decorative and ornamental materials [2], due to their high biocompatibility with bone tissue as implants [3]. It is possible to obtain these materials in a glassy state in the entire range of compositions of the $MgSiO_3$ – $CaSiO_3$ system [4], the properties of which, with the exception of the structure of glasses [4, 5], are little studied.

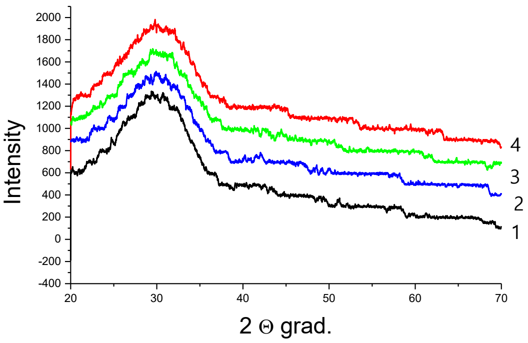
The luminescence of rare-earth ions has been well studied in crystalline magnesium-calcium silicate; there is information on the luminescence of europium and terbium ions in glass-crystalline ceramics. Therefore, it is of interest to study the luminescence of rare-earth ions and in glasses of $MgCaSi_2O_6$ composition.

The initial crystalline $MgCaSi_2O_6$ powder for obtaining diopside glasses was prepared by mixing the corresponding amounts of standard chemical reagents MgO, $CaCO_3$ and SiO_2. The reagent mixture was calcined in an alundum crucible up to 1400° C with two grinding during heating for homogenization.

For the preparation of diopside glasses doped with rare-earth elements, in 3 g of prepared $MgCaSi_2O_6$ powder was introduced 3-5 mass. % rare earth oxide (Nd, Sm, Eu, Dy or Tb). A thoroughly mixed mixture was loaded into a glasscarbon crucible and melted using induction heating. The glasses were obtained by quenching of the superheated to 1600° C melt. For better homogeneity, the glasses were additionally remelted.

For research, plates with a thickness of 1-2 mm were cut and polished from the prepared glasses.

The amorphous state of the prepared glasses is confirmed by the presented diffraction patterns obtained on a DRON-3 diffractometer (Fig. 1)



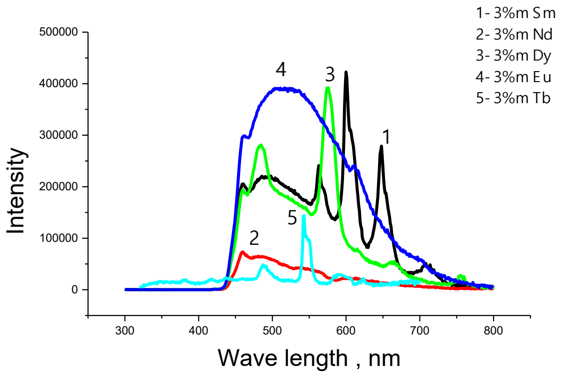


Fig. 1 Fig. 2

Fig. 1. Diffractograms of diopside glasses:1 – undoped glass; 2 – 3 % Pr; 3 – 3 % Eu; 4 - 3 % Tb.

Fig. 2. Luminescence spectra (Em) of diopside glass doped with 3 mass% rare earth oxide (λex 280 nm)

Excitation and luminescence spectra of diopside glasses doped with rare-earth ions were obtained using a Fluorolog-3 spectrofluorimeter.

The characteristic luminescence spectra of diopside glasses doped with rare-earth ions are shown in Fig. 2. Three types of luminescence spectra can be distinguished.

Broadband luminescence for glasses doped with neodymium and europium with a maximum emission in the range of 460 - 490 nm and 500 - 540 nm, respectively.

Broadband luminescence for glasses doped with samarium and dysprosium with emission bands characteristic for crystalline samples.

And in the case of terbium-doped glasses, the broadband luminescence is suppressed by the luminescence bands characteristic for crystalline samples.

Fig. 3 shows the luminescence spectra of diopside glass doped with terbium depending on excitation in the absorption bands (Fig. 4) in the range of 280-380 nm

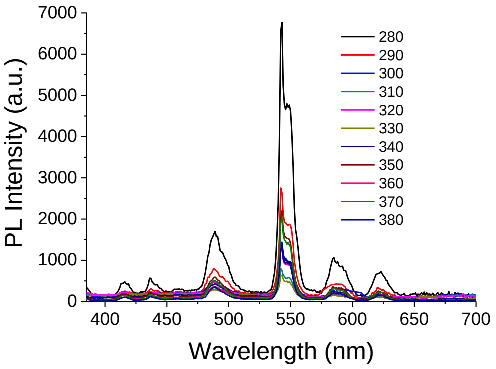


Fig. 3

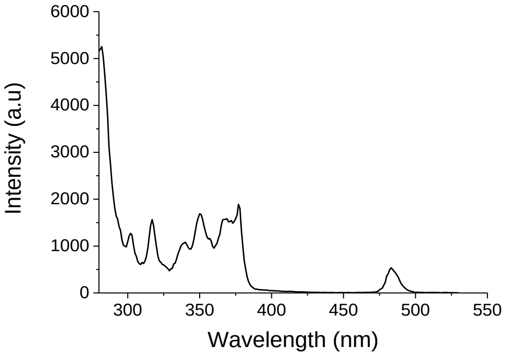


Fig. 4

Fig. 3. Luminescence spectrum of diopside glass doped with 3 mass.% terbium oxide upon excitation at different wave lengths

Fig. 4. Luminescence excitation spectrum of diopside glass doped with 3 mass.% terbium oxide

More detailed results, comparison with the research data of glass-ceramic and crystalline samples will be discussed and presented.

1. Sahu Ishwar Prasad // J Mater Sci: Mater Electron, 2016, V. 27, P. 10353–10363].
2. RF Patent n.2569942 (2014).
3. Kansal Ishu, Goel Ashutosh, Tulyaganov Dilshat U.// J. Mater. Chem., 2011, V. 21, P. 16247 .
4. Cormier L., Cuello G.J.// Geochimica et Cosmochimica Acta, 2013, V. 122, P. 498-510
5. Jabraoui H., Malki M., Hasnaoui A., Badawi M., Ouaskit S., Lebegue S. and Vaillsc Y. // Physical Chemistry Chemical Physics · July 2017

e-mail: v.v.sokolov@ngs.ru

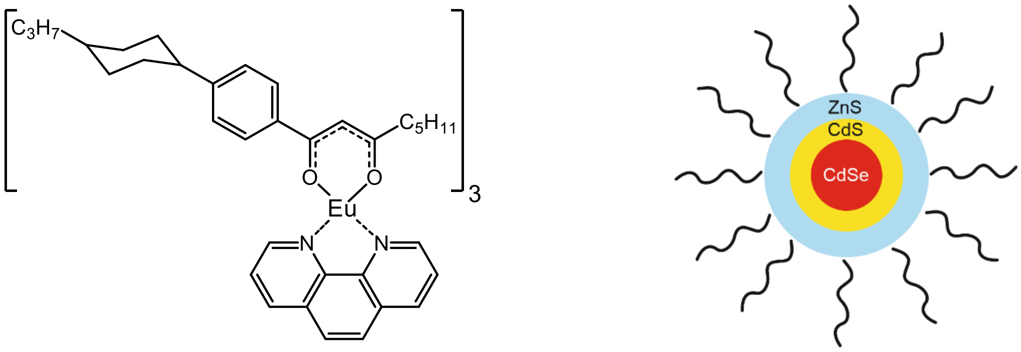
Fluorescent markers based on composites of lanthanide(III) complexes and hybrid quantum dots

A.S. Krupin,[a] D.O. Sagdeev,[a] M.E. Karyakin,[a] R.R. Shamilov,[a] A.A. Knyazev,[a] Yu.G. Galyametdinov[a,b]

[a]*Kazan National Research Technological University*
[b]*Zavoisky Physical-Technical Institute*

Lanthanide compounds have been widely used as markers and tags to protect various types of goods, securities and banknotes. Clearly defined monochromatic radiation bands of luminescence of lantanide compounds make it possible to create «fingerprints» (or bar codes). It is possible to create unique «fingerprints» with a high degree of protection by mixing several luminophores in the marker. Semiconductor quantum dots (QD), due to their widely managed dimension-optical properties, are very promising materials in the labelling of important documents and products. In this connection, compositions of lanthanides(III) and quantum dots are interesting due to the noticeable difference in luminescence lifetime (by several orders of magnitude). This enable time-allowed luminescence to distinguish spawns belonging to different luminophores.

In this work luminescent mixtures based on the anizometric complex of europium(III) and hybrid quantum dots CdSe/CdS/ZnS of two types with intense radiation in blue (λ_{em} = 480 nm) and green (λ_{em} = 530 nm) are obtained and investigated (fig. 1).



a b

Fig. 1. Structures of the Europium(III) complex (a) and colloidal quantum dot «core-shell» CdSe/CdS/ZnS (b).

The luminescent lifetime of Eu(III) complex in film had of 470 μs. In turn, the lifetime of QD radiation was less than 2 orders of magnitude. The anisometric compounds of lanthanides, due to their structure (anisotropic form, long hydrocarbon substitutes at the ends of molecules) were soluble in organic solvents, lack of crystallization when sprayed with solution and mixed well with quantum dots.

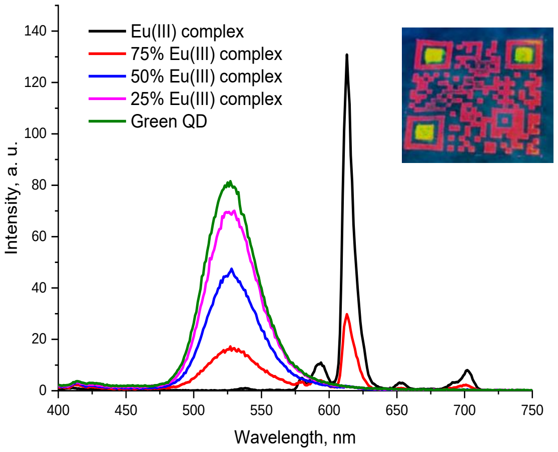


Fig. 2. Composite solution luminescence spectra based on Eu(III) complex with green quantum dots CdSe/CdS/ZnS

When the components are changed in the marker, their luminescence changes almost linearly (Fig. 2). This confirms that there is no chemical interaction between the luminophores. By varying the component ratios in materials, one can purposefully change the radiation color. The work produced composite materials based on the Eu(III) complex and the quantum dots CdSe/CdS/ZnS with different component ratios. It was shown that due to the structural features of the Europium(III) complex, the quantum dots are evenly distributed in the matrix of coordination compounds of lanthanides. It had been established that when the content of the components in the composition is changed, the intensity of their luminescence changes almost linearly. This confirms the absence of Ferster resonance transfer of energy in the system of lanthanide complexes and quantum dots. The possibility of purposeful variation of the radiation color by changing the component ratio in the composition was demonstrated. In the obtained films, because of the marked difference in the lifetime of luminescence, it is possible to separate the peaks belonging to the quantum dots and coordinating compounds. Such composites have the potential to be used as time-allowable luminescence materials for optoelectronics, luminescent labelling and visualization in biomedicine and can be used to label important documents, products, fuels and semi-products.

Acknowledgments: This research was funded by the Russian Science Foundation, grant 20-73-10091.

e-mail: krupin_91@mail.ru

Synthesis, crystal structure and luminescent properties of lanthanide bis-acylpyrazolonates

I.V. Loginov, Y.A. Belousov, M.A. Kiskin, V.E. Gontcharenko

Lomonosov Moscow State University, Moscow, RUSSIA.

4-acyl-pyrazol-5-ones are heterocyclic analogues of diketones. These compounds have a number of advantages: great potential for ligand modification due to the addition of substituents to the heterocycle, good solubility in ligands and complexes in most solvents, which simplifies synthesis and growth of single crystals. 4-Acyl-5-pyrazalonates of REE are considered to be a well-studied group of complexes, which has attracted increasing interest due to the search for high-performance luminophores.

Bis-acylpyrazolones) are the ligands that have two 4-acylpyrazol-5-one moieties separated by a methylene chain $(CH_2)_n$. By changing the length of the methylene fragment, it is possible to change the metal-to-metal distance. That should affect the luminescent properties of the resulting substance. This report is devoted to the synthesis of bis-acylpyrazolonates with different lengths of the methylene fragment and comparison of the luminescence properties of the obtained complexes.

The synthesis was performed by reacting lanthanide hydroxide with H_2Q_nQ, where HQ is 3-methyl-1-phenyl-4-acylpyrazol-5-ones linked together by a $(CH_2)_n$ chain that allows varying the ligand length. The $[Ln_2(Q_nQ)_3]$ complexes (Ln = Sm, Eu, Gd, Tb, Dy; n = 3, 5) have been synthesized. The resulting substances were analyzed with the use of single crystal X-ray diffraction. Their photoluminescence spectra were studied.

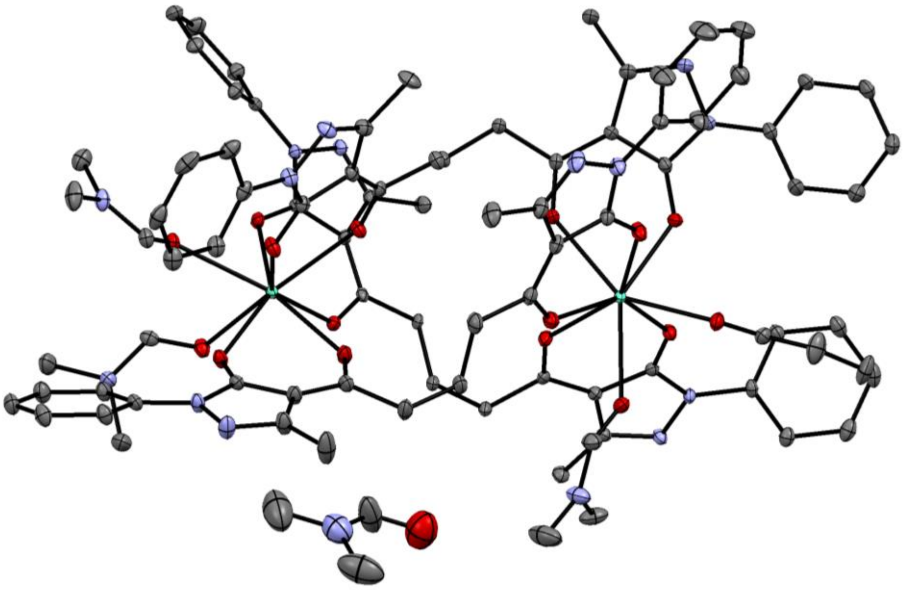


Fig. 1. The structure of $[Tb_2(Q_3Q)_3(DMF)_4]$

Acknowledgements – Authors thank RFBR (projects 19-03-00263).

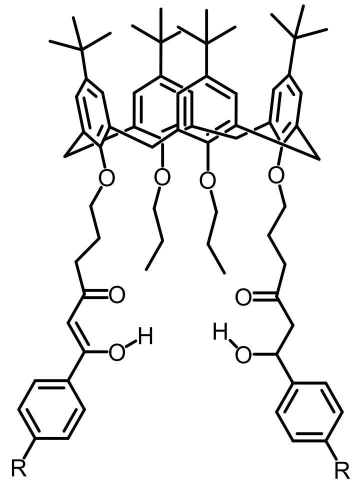
e-mail: loginov.ivan.victorovich@yandex.ru

Bis-1,3-diketo-derivatives of calix[4]arenes – new ligands for sensibilization of Eu^{3+} luminescence

G.Sh. Mambetova,[a] A.E. Shvedova,[a] S.N. Sudakova,[b] V.V. Syakaev,[b] I.M. Vatsouro,[c] V.V. Kovalev,[c] S.N. Podyachev[b]

[a]*Kazan National Research Technological University, K. Marks Str., 68, 420015, Kazan*
[b]*Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Arbuzov str., 8, 420088, Kazan, Russia*
[c]*Lomonosov Moscow State University, Lenin's Hills 1, 119991 Moscow, Russia*

Non-invasive or semi-invasive spectroscopic methods for determining temperature have gained a great attention in recent decades as an accurate technique for remote evaluation of temperature changes both in biological fluids or for tissues of living organisms.



L_1 R = H
L_2 R = OCH_3
L_3 R = F
L_4 R = CF3
L_5 R = CN
L_6 R = CH_3

Luminescent thermometers on a basis of lanthanide complexes are of a growing attention due to unique properties of the lanthanide-centered luminescence. The sensing in the physiological range is of particular importance due to a possible application of such luminescent thermometers in biomedicine. Calix[4]arenes are known as a convenient scaffold for embedding of both the binding sites for lanthanide ions and additional groups. The ligand's structure optimization can adjust the triplet excited states of ligands and such way impact on the luminescence efficacy. The present report introduces the lower-rim substituted calix[4]arenes (**L_{1-6}**) bearing two 1,3-diketone and two propyl groups as new ligands for sensitization Eu^{3+}-centered luminescence. Temperature sensitivity of lanthanide complexes is exemplified in particular for the ligand **3** coordinating the Eu $^{3+}$ ions via 1,3-diketonate groups (Fig.1).

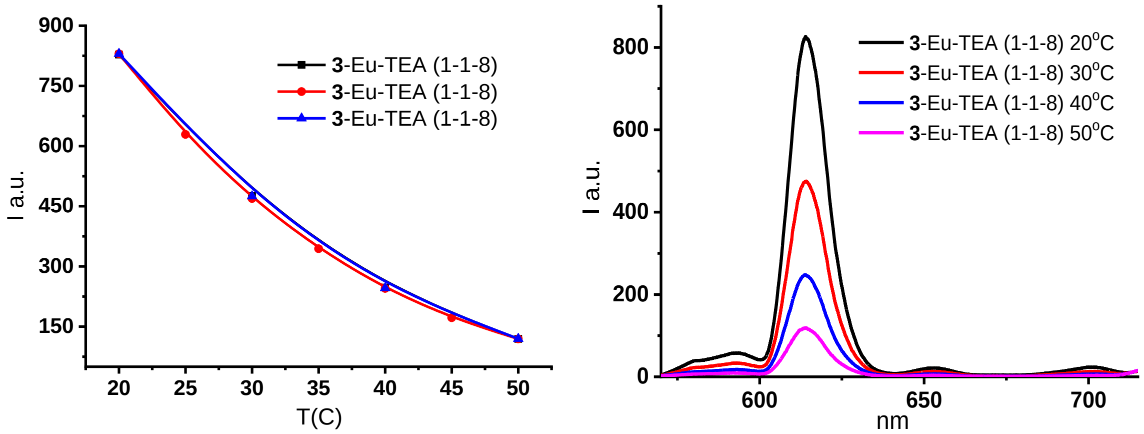


Fig. 1 - Temperature dependence of the Eu^{3+} luminescence intensity (I a.u.) of the main $^5D_0 \rightarrow ^7F_3$ transition (613 nm) obtained by the heating and cooling the DMF solutions of the europium complexes with L_3.

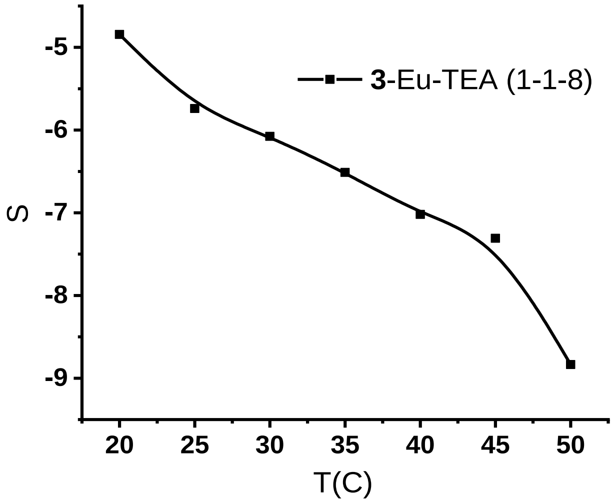


Fig. 2. Relative sensitivity of the Eu^{3+} luminescence intensity (*S*) to the temperature changes (20-50˚C) of the europium complexes with L_3.

Relative sensitivity of the luminescence intensity (*S*) to the temperature changes (20-50˚C) was calculated in accordance with formula $S_I = \Delta I/(I \cdot \Delta T) \cdot 100\%$ and represented for the europium complexes with L_3 in Fig. 2, where ΔI is the change in the luminescence intensity with the temperature variation ΔT and *I* is the luminescence intensity at a given temperature. It appeared that ligands $L_{1\text{-}6}$ can effectively sensitize the luminescence of Eu^{3+} ions, but do not impact on the luminescence of Tb^{3+} ions. Eu^{3+} complexes of these ligands have exhibited also a rather good temperature-dependent luminescence with high sensitivity in physiological range (20-50°C) and can be applied in the monitoring of temperature changes in biological fluids or living organisms. Different physico-chemical techniques and quantum-chemical calculations are applied for studying the complex formation of these calix[4]arenes with Eu^{3+} ions.

Acknowledgements:
The authors are grateful to the Assigned Spectral-Analytical Center of FRC Kazan Scientific Center of RAS and thank the Russian Science Foundation (grant 21-13-00115) for financial support

e-mail: goolnaz31@mail.ru

Поверхностная модификация наноструктурированного углерода с интеркалированным Eu^{3+} для флуоресцентного мечения

Масгутов И.И.[a], Исаев А.В.[b,c], Байрамуков В.Ю.[d], Еремин А.В.[c]

[a]*Санкт-Петербургский политехнический университет Петра Великого, 195251, Санкт-Петербург, Россия*
[b]*Санкт-Петербургский государственный технологический институт (технический университет), 190013, Санкт-Петербург, Россия*
[c]*Институт высокомолекулярных соединений РАН, 199004, Санкт-Петербург, Россия*
[d]*Петербургский институт ядерной физики им. Б.П. Константинова Национального исследовательского центра «Курчатовский институт» , 188300, Гатчина, Россия*

Химия и физика соединений и материалов на основе углерода взрывоподобно развивается с момента синтеза и открытия фуллереноподобных структур в 1985, позднее - нанотрубок, и, наконец – графеновых материалов [1]. В настоящее время отдельным направлением исследований каркасных углеродных соединений является изучение структур включающих атомы металлов, например эндоэндральные соединения фуллеренов [2], однако подобные соединения часто труднодоступны из-за высокой сложности синтеза.

В настоящей работе были исследованы достаточно простые с точки зрения методики получения графеноподобные материалы, полученные при пиролизе фталлоцианинов редкоземельных элементов [3] и некоторые пути их модификации.

Полученные металл-углеродные структуры обладают высокопористым ажурным строением с внутримолекулярными пустотами, в составе базовых доменов структур которых атомы металлов связаны прочными M-C связями. Подобное строение дает возможность химической модификации поверхности полученных материалов по аналогии с графеном. Модифицированные материалы, обладающие высокой флуоресценцией могут быть использованы, например, в биологии, - в виде квантовых точек для биовизуализации или определения патологических состояний.

В рамках данной работы получены европий(III)-содержащие графеноподобные материалы, которые были получены окислением поверхностных групп модифицированным методом Хаммерса [4]. Очищенные препараты металлсодержащие оксидов графена в водных растворах представлены в виде отрицательно заряженных коллоидных частиц с преобладающим размеров около 60 нм. Далее металлсодержащие оксиды графена, имеющие значительное количество свободных карбоксилатных групп переводились в высокореакционноспособный хлорангидрид, и, далее, модифицировались присоединением дисульфида (Na_2GSSG) биогенного биологически активного трипептида – γ-L-глутамил-L-цистеиноиглицина (GSH, глутатиона) (рис.1), содержащегося во всех клетках организмов млекопитающих в значительных концентрациях и участвующего в тиолдисульфидной редокс-системе организма и системах биологической регуляции [5]. GSH также активно востребован связанными с ним транспортными рецепторами клеток. Методами конфокальной микроскопии наблюдалось активное проникновение флюоресцирующих глутатион-модифицированных европийсодержащих углеродных частиц в клетки HeLa.

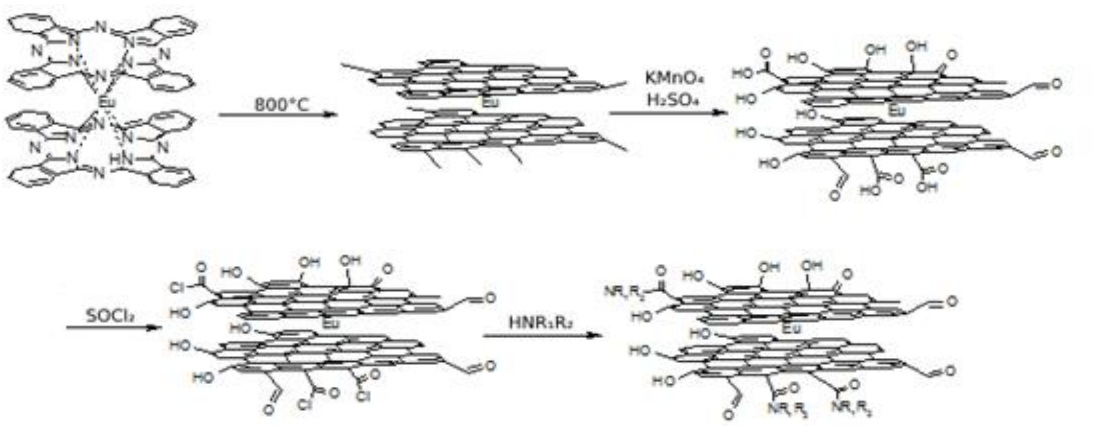


Рис. 1. Схема синтеза и модификации наноструктурированного углерода с интеркалированным Eu^{3+}.

Полученые материалы благодаря флуоресцентным свойствам иона европия могут быть использованы для флуоресцентного мечения в биомедицинских применениях.

[1] А.В. Елецкий. УФН 170, 2, 113-142 (2000).
[2] Kroto, H. W.; Heath, J. R.; OBrien, S. C.; Curl, R. F.; Smalley, R. E. Nature 1985, 318, 165.
[3] V. Yu. Bayramukov, A. I. Kuklin, D. N. Orlova, V. T. Lebedev Structure of Yttrium Bis-Phthalocyanine Pyrolyzed Derivatives Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques vol. 13 N. 5 pp. 10–19 (09 2019).
[4] Hummers WS, Offeman RE. Preparation of graphitic oxide. J Am Chem Soc 1958;80(6):1339.
[5] Oktyabrsky O.N., Smirnova G.V. Redox regulation of cellular functions Biochemistry (Moscow). 2007. T. 72. № 2. C. 132-145.

e-mail: yaiskandar21@mail.ru

Luminescent heterometallic europium(III)-lutetium(III) metal-organic frameworks

V.G. Nosov, A.A. Vidyakina, A.S. Mereshchenko

Saint-Petersburg State University, Saint-Petersburg, RUSSIA

The series of $(Eu_xLu_{1-x})_2bdc_3{\cdot}nH_2O$ heterometallic europium(III)-lutetium(III) terephthalates with x in the range from 0 to 1 was synthesized in the aqueous solution by the mixing of the $EuCl_3$ and $LuCl_3$ taken in stoichiometric ratios with the excess of Na_2bdc (bdc^{2-} = 1,4-benzene-1,4-dicarboxylic (terephthalate) ion). At the Eu concentration of 1-40 at. %, heterometallic europium(III)-lutetium(III) terephthalates are formed as a mixture of $(Eu_xLu_{1-x})_2bdc_3$ and $(Eu_xLu_{1-x})_2bdc_3{\cdot}4H_2O$ crystalline phases. At higher Eu concentrations, a single crystalline phase is formed, $(Eu_xLu_{1-x})_2bdc_3{\cdot}4H_2O$. All the synthesized samples containing Eu(III) demonstrate bright red emission corresponding to $^5D_0\rightarrow{}^7F_J$ (J = 0-4) transitions of Eu^{3+} ion upon the 280-nm excitation into $^1\pi\pi^*$ excited state of terephthalate ion. Analysis of the fine structure of $^5D_0\rightarrow{}^7F_0$ emission band allowed us to conclude that Eu^{3+} ion unevenly distributed between Ln_2bdc_3 and $Ln_2bdc_3{\cdot}4H_2O$ phases: $Ln_2bdc_3{\cdot}4H_2O$ crystalline phase is enriched by europium (III) ions. Also, the local symmetry of Eu^{3+} ion in heterometallic Eu-Lu terephthalates was proposed based on careful analysis of the emission spectra fine structure and the structural data. In $Eu_2bdc_3{\cdot}4H_2O$, the local symmetry of Eu^{3+} ion is pseudo-C_4. In $(Eu_xLu_{1-x})_2bdc_3{\cdot}4H_2O$, the addition of lutetium ions leads to the Eu^{3+} local symmetry distortion to C_2 or lower point group. The local symmetry of Eu^{3+} is proposed to be C_1 in anhydrous $(Eu_xLu_{1-x})_2bdc_3$. $^5D_0$ excited state lifetimes are significantly larger for Eu^{3+} in Ln_2bdc_3 crystalline phase than the corresponding values for Eu^{3+} in $Ln_2bdc_3{\cdot}4H_2O$ due to efficient luminescence quenching of Eu^{3+} by coordinated water molecules in $Ln_2bdc_3{\cdot}4H_2O$. The Eu^{3+} luminescence quantum yields of terephthalate ion decrease with the increase of europium concentration from 2 to 100 at. % Eu from 22 to 10% upon excitation into $^1\pi\pi^*$ singlet electronic excited state. The emission quantum yield of Eu^{3+} is significantly larger for Eu-Lu terephthalates containing a low concentration of Eu due to the absence of Eu-Eu energy migration and the presence of Ln_2bdc_3 crystalline phase with a significantly smaller non-radiative decay rate compared to the $Ln_2bdc_3{\cdot}4H_2O$.

Acknowledgements – The measurements were performed at the Research Park of Saint-Petersburg State University (''Magnetic Resonance Research Centre'', ''SPbU Computing Centre'', ''Cryogenic Department'', ''Interdisciplinary Resource Centre for Nanotechnology'', ''Centre for X-ray Diffraction Studies'', ''Chemical Analysis and Materials Research Centre'', and ''Centre for Optical and Laser Materials Research'').

e-mail: a.mereshchenko@spbu.ru

Complex formation of novel organophosphorus analogs of nitrilotriacetic acid toward rare-earth elements

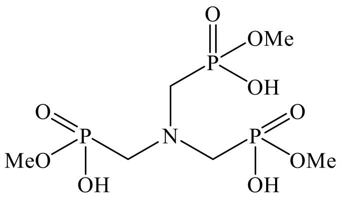
I.I. Mirzayanov, I.D. Shurygin, A.R. Garifzyanov

Kazan (Volga region) Federal University, Kazan, RUSSIA

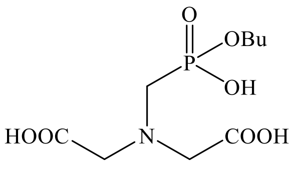
Titrilotriacetic acid (NTA) and their organophosphorus analogues are multidentate ligands which form complexes with all metals. Due to the high denticity of these compounds, they form chelate structures, including a nitrogen atom and a complexing metal ion, which leads to strong binding. These properties make it possible to use NTA-like ligands as scale inhibitors in closed systems, to create new hybrid materials for ion exchangers, and to develop anti-corrosion films. In addition, such compounds are potential chelates for contrast agents for MRI, as well as for the removal of heavy metals from the body. At the same time, an urgent problem is the control of organophosphorus ligands in the environment and their removal, because, unlike NTA, they are difficult to biodegrade. In this regard, the introduction of these compounds into various areas of human life requires certain fundamental knowledge, especially about their behaviour in an aqueous solution. Therefore, the study of the thermodynamic characteristics of the complexation reactions of the compounds under consideration is an important task.

Previously, we described the method of synthesis and obtained new NTA-like organophosphorus complexones containing (O-alkyl)methylenephosphonic fragments as acid groups, and studied their complexing properties toward cations of alkaline earth metals and d-elements [1]. In this paper, the complexing properties of compounds of this class toward rare-earth elements ions are discussed.

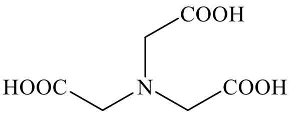
Nitrilotri(O-methyl)methylenephosphonic (**H_3L^1**) and N-[(O-butyl)phosphorylmethyl]imino-diacetic (**H_3L^2**) acids were obtained as medium potassium salts as the most convenient form for isolation and purification by recrystallization.



H_3L^1



H_3L^2



HTA

The complexing properties were studied by pH-metric titration followed by mathematical data processing using the CPESSP program [2]. The calculated stability constants of the complexes [ML] ($\lg K_{M+L}$) are presented in Table 1. 1. (Acidic forms of $[MHL]^+$ complexes were also found, not shown in the table).

It should also be noted that, for **H_3L^1**, the formation of solid forms at pH < 4.5 was noted for all elements except yttrium(III), lanthanum(III), and cerium(III), so only complexes of these rare-earth elements ions are discussed. In homologous **H_3L^1** (containing an ethyl, n-propyl, and n-butyl group instead of a methyl one) and a glycine derivative, bis[(O-butyl)phosphoryl-methyl]glycine, the formation of solid forms is observed over the entire pH range under study.

Table 1. Stability constants of [ML] complexes for $\mathbf{H_3L^1}$and $\mathbf{H_3L^2}$ (T 25.0°C, I 0.2 M (KNO_3))

M	L	lg$K_{\mathrm{M+L}}$
Sc^{3+}	$\mathbf{H_3L^2}$	12.83
Y^{3+}	$\mathbf{H_3L^1}$	6.18
	$\mathbf{H_3L^2}$	11.99
La^{3+}	$\mathbf{H_3L^1}$	6.33
	$\mathbf{H_3L^2}$	9.37
Ce^{3+}	$\mathbf{H_3L^1}$	6.39
	$\mathbf{H_3L^2}$	10.08
Nd^{3+}		10.89
Sm^{3+}		11.83
Gd^{3+}		11.94
Tb^{3+}		12.10
Er^{3+}		12.24
Yb^{3+}		12.44

We analyzed the patterns of changes in the stability constants of $\mathbf{H_3L^2}$complexes in comparison with NTA using the principle of free-energy relationship. The use of this principle showed that the correlation dependence lg$K_{\mathrm{M+L}}[ML^2]^0$ – lg$K_{\mathrm{M+L}}$[M**nta**]^0 (where **nta** is the NTA anion) exhibits two distinct linear areas: the initial with steep slope being formed by points corresponding to light lanthanides with large ionic radii (La, Ce, Nd, Sm, Gd), and the second, flatter one – Sc, Y and heavy lanthanides (Tb, Er, Yb), which have a smaller ionic radius.

[1] A.R. Garifzyanov, I.D. Shurygin, R.A. Cherkasov, *Russ. J. Gen. Chem. (Engl. Transl.)*, **2018**, *88*, 1860-1866; DOI: 10.1134/S1070363218090165.
[2] U.I. Salnikov, A.N. Glebov, F.V. Devyatov *Poliyadernye kompleksy v rastvorakh (Polynuclear Complexes in Solutions)*, Kazan: KGU, **1989**, 288 p.

Acknowledgements – This study was financially supported by the Russian Foundation for Basic Research (project no. 20-33-90235).

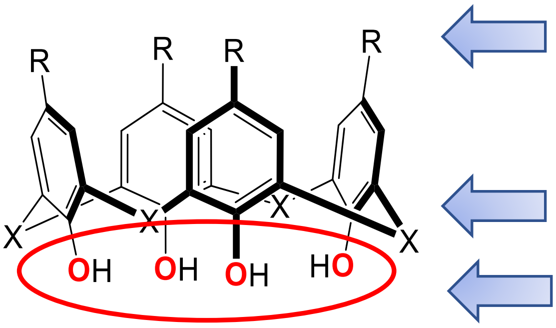
e-mail: ildar4016@mail.ru

Synthesis, structure and properties of novel f-complexes based on (thia)calix[4]arenes in the crystalline phase

M.V. Kniazeva[a], I.V. Strelnikova[b], A.S. Ovsyannikov[a], D.R. Islamov[a], P.V. Dorovatovskii[c], A.T. Gubaidullin[a], S.E. Solovieva[a,b], I.S. Antipin[a,b]

[a]*A.E. Arbuzov Institute of Organic and Physical Chemistry - FRC Kazan Scientific Center of RAS, Kazan, RUSSIA*
[b]*Kazan Federal University, Kazan, RUSSIA*
[c]*National Research Centre “Kurchatov Institute”, Moscow, RUSSIA*

(Thia)calix[4]arenes in *cone* conformation containing four hydroxyl groups of phenolic fragments are excellent polydentate ligands for the formation high-nuclearity of rare earth metal complexes and coordination structures in crystalline phase with potential functional properties (magnetism, luminescence) for different application and materials [1-2]. The convenience of this type of platform is due to the ability to tune the properties of clusters by varying the structure of the macrocycle, for example, by introduction the substituents of different nature and size on the of upper or lower rim [3]. Therefore, the development of new rational synthetic methods for the synthesis of functional multinuclear lanthanide complexes based on (thia)calix[4]arenes is still relevant.



the possibility of varying the substituent

the possibility of varying of nature of atoms bridge

preorganized polydentate cavity

Scheme 1. (Thia)calix[4]arenes - excellent polydentate ligands for f-metal clusters formation.

Here we report the synthesis, structure and magnetic properties of coordination compounds formed by the interaction of (thia)calix[4]arene derivatives in *cone* conformation with f-metal cations [M = Dy, Er, Tb, Eu, Lu].

1. S. Sanz, R.D. McIntosh, C. M. Beavers, S. J. Teat, M. Evangelisti, E. K. Brechin and S. J. Dalgarno *Chem. Commun.*, **2012**, 48, 1449-1451
2. T. Kajiwara, M. Hasegawa, A. Ishii, K. Katagiri, M. Baatar, S. Takaishi, N. Iki, M. Yamashita, *Eur. J. Inorg. Chem.*, **2008**, 5565–5568
3. P. Hahn, S. Ullmann, A. Kahnt, B. Abel, B. Kersting *Inorganica Chimica Acta,* **2021,** 514, 119983

Acknowledgements – Authors thank RSF (projects 19-73- 20035)

e-mail: knyazeva255@gmail.com

Synthesis, Crystal Structure and Optical Properties of $CsLnZnS_3$ (Ln=Pr- Ho)

S. J. Park[a], T. A. Pomelova[b]

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

Recently, quaternary chalcogenides containing combination of *d*- and *f*-elements and alkali (A) metal became highly investigated due to utility of reactive flux method. The low melting points of the A_xQ_y (Q= S, Se or Te) fluxes (433-723 K) and their ability to act as both reagent and reaction medium have led to the isolation of low-dimensional kinetic species that cannot be obtained by the use of traditional high-temperature solid-state reactions. Among them compounds $ALnMQ_3$ possess the $KZrCuS_3$ structure type are the one of the most numerous. These compounds that exhibit interesting variations of their magnetic and optical properties. Most of them are selenides and tellurides. Now we report our recent results of preparation, structure and properties of $CsLnZnS_3$ family.

The new compounds $CsLnZnS_3$ (Ln = Pr-Ho) have been synthesized from solid at 1073K. Theses white-colored isostructural compounds crystallize in the $KZrCuS_3$ structure type with four formula units in space group *Cmcm* of the orthorhombic system. The structure of these compounds is composed of LnS_6 octahedra and ZnS_4 tetrahedra that share edges of ${}^2{}_\infty[LnZnS_3]^-$ layers separated by Cs atoms. These layers separated by layers of face- and edge- sharing CsS_8 bicapped trigonal prisms. The optical band gaps for $CsLnZnS_3$ (Ln = Pr-Ho) varies from 1.7 to 3.8 eV for Ln = Eu and Ln = Dy, respectively. These values are the highest for known $ALnMQ_3$ compounds.

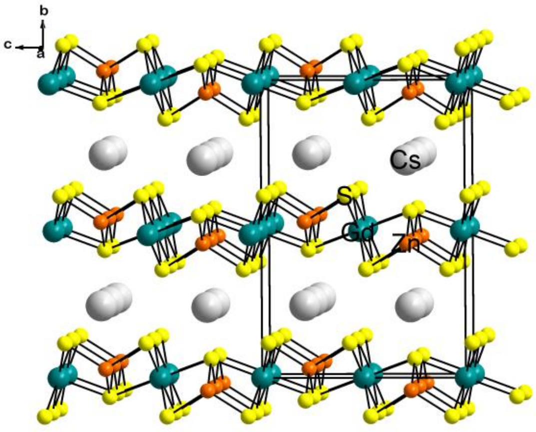


Fig. 1. Crystal structure of $CsGdZnS_3$

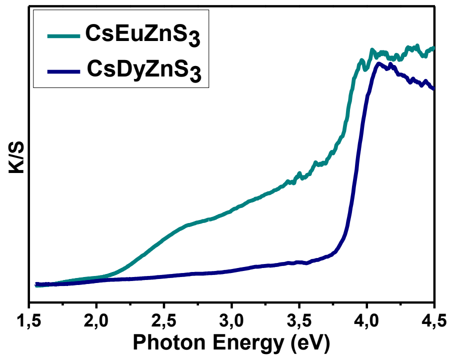


Fig. 2. Optical band gap

e-mail: sangjun7094@gmail.com

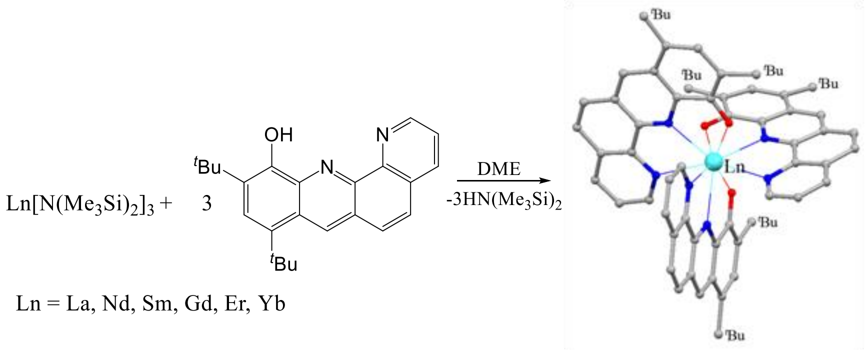
New Oxybenzophenanthroline Complexes of Lanthanides

S.K. Polyakova, T.V. Balashova, M.V. Arsenyev, R.V. Rumyantcev, M.N. Bochkarev

G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences,
Nizhny Novgorod, RUSSIA

Unique luminescent properties of lanthanides compounds have made them the subject of intense study for the past few decades. The most frequently used ligands for the construction of lanthanide complexes are N^O-donor ligands, for example, 8-hydroxyquinoline, 10-hydroxybenzoquinoline. It is known that complexes of rare-earth metals with oxyquinoline and oxybenzoquinolinates ligands have excellent photo- and electroluminescent properties. Modification of the ligand makes it possible to change its electronic and steric properties, and thus is an effective way to control luminescence properties of their complexes.

In the search of new effective fluorophores we have synthesized a new ligand 8,10-di-tert-butylbenzo[b][1,10]phenantrolin-11-ol and a set of lanthanide complexes based on this ligand. 8,10-di-tert-butylbenzo[b][1,10]phenantrolin-11-ol (HL) have been prepared by alkylation of 8-aminoquinoline with 3,5-di-tert-butyl-6-methoxymethylcatechol followed by oxidation of the reaction mixture. Complexes LnL_3 (Ln = La, Nd, Sm, Gd, Er, Yb) were synthesized by the reaction of respective lanthanide tris(trimethylsilylamide) with HL in DME solution.



Scheme 1. Synthetic route of complexes.

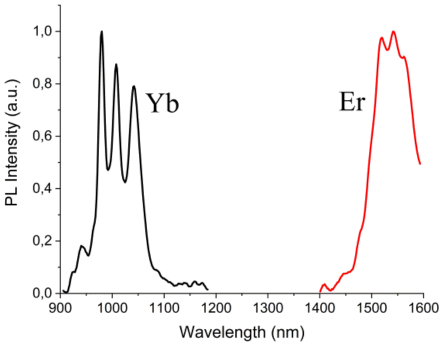


Fig. 1. PL spectra of Er and Yb complexes.

According to X-ray analysis, in the YbL_3 complex the metal atom is coordinated by three tridentate bonded ligands via oxygen and nitrogen atoms. Two ligands are nearly flat, the while the third ligand deviates significantly from the plane. The PL spectra of erbium and ytterbium complexes in the solid state and solution exhibit metal-centered emission, which is characteristic of the corresponding Ln^{3+} ion.

The study of electroluminescent, photovoltaic, and electrochemical properties of the obtained compounds will be the subject of further research.

Acknowledgements – This work was supported by the Russian Science Foundation (project No 22-23-00547)

e-mail: spqrzl6968@gmail.com

Novel ditopic 2-mercaptothiazoles as potentional ligands for lanthanide-containing luminescent coordination polymers

A.F. Rogozhin, V.A. Ilichev, M.N. Bochkarev

G.A. Razuvaev Institute of Organometallic Chemistry of RAS, Nizhny Novgorod, RUSSIA

Lanthanide luminescence is applicable in many modern technologies such as OLEDs, up-conversion materials, lasers, fiber amplifiers. Organosulphide thiazolate ligands, which act as efficiently absorbing antennas and effective sensitizers of lanthanide luminescence[1], and their perfluorinated analogs made it possible to synthesize a number of lanthanide complexes exhibiting long-lived and intense luminescence in the near-IR range[2].

Ditopic mercaptothiazoles were proposed as ligands for coordination luminescent lanthanide compounds and polymers. Among the compounds of this class, only one compound was known, the formation of **Dmbt** was assumed in 1927, and the synthesis was described in 1960[3]. In this work we have synthesized the set of novel ditopic mercaptothiazoles (Fig. 1).

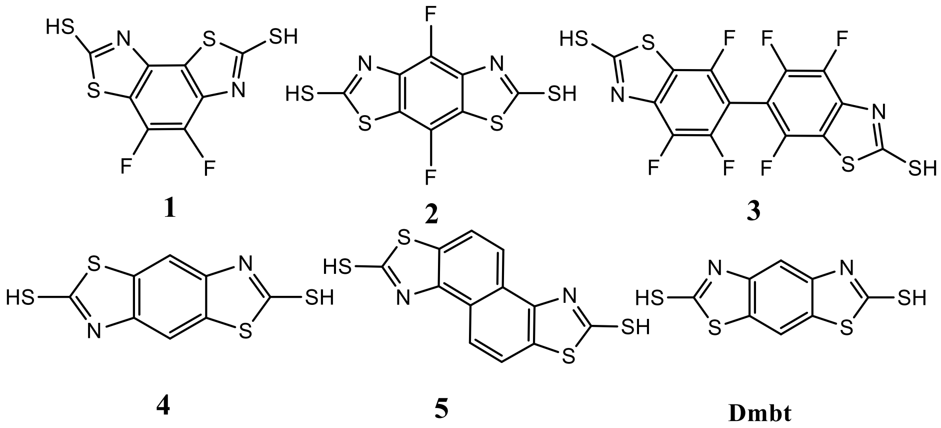


Fig. 1. The set of synthesized bisthiazoles.

Disodium complexes of bisthiazoles **1-5** and **Dmbt** were also synthesized, structurally characterized and the triplet levels of the ligands were determined from their low-temperature phosphorescence spectrum. For the bisthiazoles **1-4** and **Dmbt** the triplet level values range from 21200 cm^{-1} to 21600 cm^{-1} while for **5** the value of the triplet state is 18900 cm^{-1}. The triplet levels of the bistiazoles have rather high values relative to the position of the resonant *f* levels of many lanthanides, including Tb (20400 cm^{-1}), Sm (17800 cm^{-1}) and Eu (17500 cm^{-1}). Consequently, synthesized bistiazoles are capable of sensitizing the metal-centered PL of most lanthanides.

[1] V.A. Ilichev, A.P. Pushkarev, R.V. Rumyantcev, A.N. Yablonskiy, T.V. Balashova, G. K. Fukin, D.F. Grishin, B.A. Andreev and M.N. Bochkarev, Phys.Chem.Chem.Phys., 2015,17, 11000-11005

[2] A. F. Rogozhin, L. I. Silantyeva, A. N. Yablonskiy, B.A.Andreev, I. D.Grishin and V. A. Ilichev, Opt. Mat. 2021, 118, 111241

[3] G. Grandolini, Gazz. Chim. Ital. 1960, 90, 1221–1229

Acknowledgements – This work was supported by the Russian Science Foundation (project No 20-73-10115).

e-mail: atonrog@gmail.com

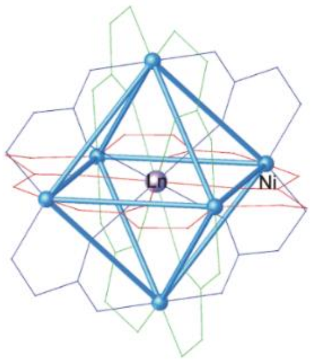
Синтез и исследование полиядерных комплексов РЗЭ и Ni с лейцином, изолейцином и валином

А.Р. Саварец[а,б], Ю.В. Логвиненко[а], Е.А. Васюта[а], Е.А. Новикова[а], Е.А. Коркунова[а],
В.Д. Долженко[а,б]

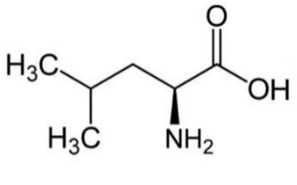
[а]*Московский государственный университет имени М.В.Ломоносова,*
химический факультет, Москва, РОССИЯ
[б]*Институт органической химии имени Н.Д.Зелинского, Москва, РОССИЯ*

Уникальные магнитные и люминесцентные свойства редкоземельных элементов (РЗЭ) определяют их широкую сферу применения, в связи с этим разработка способов их разделения является актуальной научной задачей. Химические свойства лантаноидов в одинаковой степени окисления крайне близки, что приводит к сложности их разделения простыми химическими методами. Применяемые сегодня методы разделения РЗЭ основаны на многократном повторении процессов экстракции или ионного обмена и предполагают использование дорогих, химически малоэффективных и неэкологичных соединений. Использование жесткого каркаса с полостью заданного размера для селективного извлечения ионов лантанидов может сделать задачу разделения РЗЭ более эффективной. Полиметаллические каркасы $\{M(A)_2\}_6$ (где M – лантаниды и лантан, A - аминокислота), стабилизированные крупными катионами отвечают заданным требованиям жесткости, однако в настоящий момент отсутствуют подходы для варьирования размеров полости.

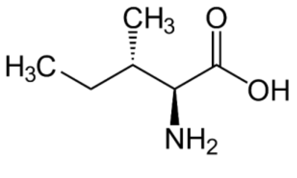
В работе синтезированы новые катионные комплексы состава $[M\{Ni(Ile)_2\}_6]^{3+}$, где Ile – L-изолейцин, M – ряд La-Eu, $[M\{Ni(Leu)_2\}_6]^{3+}$, где Leu – L-лейцин, M – ряд La-Sm, $[M\{Ni(Val)_2\}_6]^{3+}$, где Val – валин, M – ряд La-Eu. Методом ЭСП изомолярных растворов изучено изменение устойчивости катионного комплекса в растворе в ряду M. Полиядерные гетерометаллические катионы выделены из раствора в виде солей с небольшими неорганическими анионами NO_3^-, ClO_4^-, PF_6^-, BF_4, Cl^-, I^-. Полученные соединения охарактеризованы методами РФА, ИК, ДТА, ICP-MS. Изучено влияние природы растворителя на синтез комплексов $[M\{Ni(A)_2\}_6]^{3+}$. Показана возможность применения данных комплексов для разделения РЗЭ, получены коэффициенты разделения в растворе. Изучена кинетика комплексообразования $[M\{Ni(Ile)_2\}_6]^{3+}$.



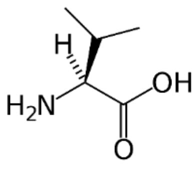
Структура $[M\{Ni(A)_2\}_6]^{3+}$



L-лейцин



L-Изолейцин



L-валин

e-mail: alekesander.savaretz@yandex.ru

Synthesis of "core-shell" CdS/ZnS quantum dots doped with europium(II) ions

D.O. Sagdeev,[a] R.R. Shamilov,[a] V.K. Voronkova,[b] A.A. Sukhanov,[b]
Yu.G. Galyametdinov[a,b]

[a]*Kazan National Research Technological University*
[b]*E.K. Zavoisky Kazan Physical-Technical Institute*

Quantum dots (QDs) and lanthanide compounds are currently among the most studied luminescent materials [1–2]. One of the current trends is the creation of materials that combine the properties of quantum dots and lanthanide compounds. One of the ways is the doping lanthanide ions into the crystal lattice of semiconductor nanoparticles, which makes it possible to change the electronic structure of quantum dots, and hence their optical and magnetic properties.

In this study, hydrophobic colloidal CdS/ZnS “core-shell” quantum dots doped with divalent europium ions were obtained and characterized for the first time.

The synthesis of $Cd_{0.96}Eu_{0.04}S$ "cores" was carried out in an aqueous medium at pH = 12 using L-cysteine as a stabilizing agent. Next, a passivating shell of zinc sulfide was grown on the resulting hydrophilic nanoparticles. At the same time, the stabilizer was replaced from L-cysteine to oleic acid. The resulting $Cd_{0.96}Eu_{0.04}S/ZnS$ nanoparticles were dispersed in toluene.

The obtained nanoparticles were characterized by a number of spectrometric research methods. The elemental composition was confirmed by X-ray fluorescence analysis, the crystal structure of wurtzite was confirmed by X-ray diffraction. Average hydrodynamic size of the nanoparticles with stabilizer and solvate shell studied by dynamic light scattering method was about 3.5 nm.

Using the electron paramagnetic resonance (EPR) method, signals corresponding to europium ions in the +2 oxidation state were detected in the samples (Fig. 1a), therefore, in the process of incorporation into the structure of nanoparticles, Eu^{3+} ions are reduced (they do not exhibit paramagnetic properties) to the Eu^{2+} state.

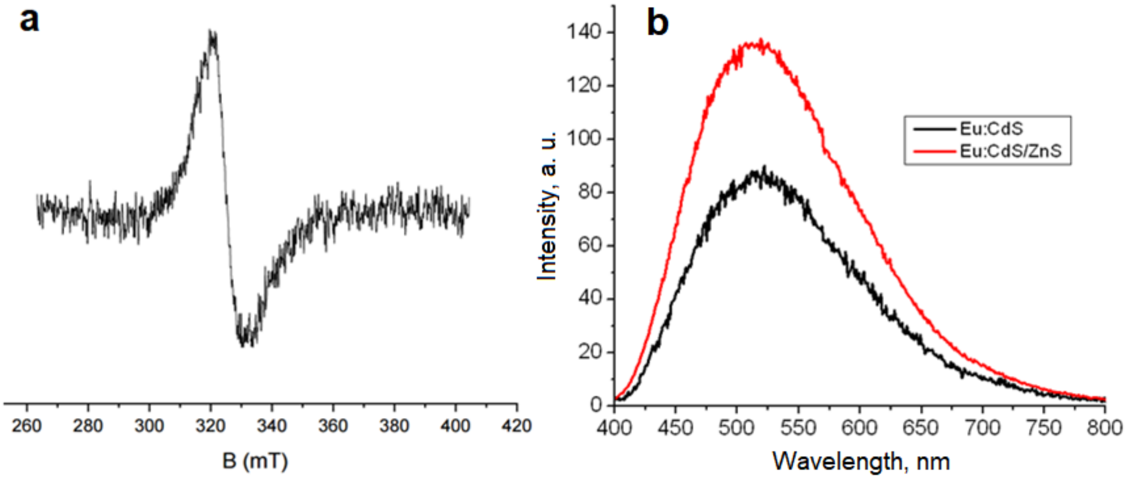


Fig. 1 – Spectrum a) EPR b) luminescence of $Cd_{0.96}Eu_{0.04}S/ZnS$ QDs

The luminescent properties of the obtained nanoparticles were also studied. QDs synthesized in the aqueous phase have a wide emission band caused by defects in the crystal structure of the semiconductor. The luminescence peak of doped quantum dots show blue shift from 560 to 520 nm relative to undoped CdS quantum dots obtained under similar conditions.

It was shown, that the growth of the ZnS shell and the transfer of nanoparticles from water to the organic phase do not affect the position and shape of the luminescence peak (Fig. 1b).

It is shown that a decrease in the pH value to 8 and 10 during the synthesis of $Cd_{0.96}Eu_{0.04}S/ZnS$ “cores” leads to the appearance of an additional peak at 433 nm in the QD luminescence spectra (Fig. 2), which is related to the radiative transition in Eu^{2+} ions. The absence of this peak in quantum dots synthesized at pH = 12 is probably due to the quantum confinement effect. In larger nanoparticles formed at high pH, the radiative level of Eu(II) appears to be above the conduction band boundary.

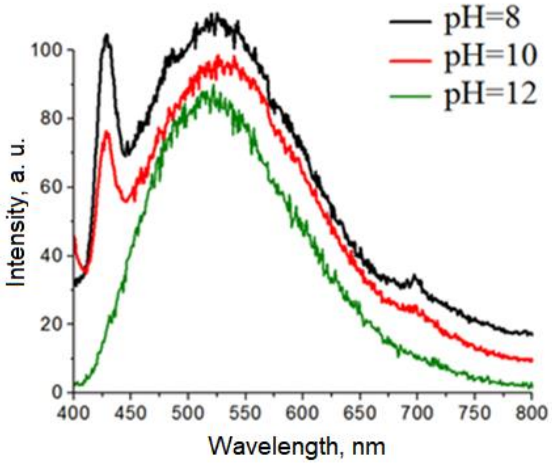


Fig. 2 – Dependence of the luminescence of Cd0.96Eu0.04S QDs on the pH of the reaction medium

Bibliography:
1. C. Pagis, M. Ferbinteanu, G. Rothenberg, S. Tanase, ACS Catalysis, 6, 9, 6063-6072 (2016).
2. A. A. Knyazev, A. S. Krupin, E. Yu. Molostova, K. A. Romanova, Yu. G. Galyametdinov, Inorg. Chem., 54, 18, 8987–8993 (2015).

Acknowledgements: The work was supported by the Russian Foundation for Basic Research, project 20-03-00620 A.

e-mail: demsagdi@yandex.ru

Synthesis, crystal structure and luminescent properties of new lanthanide complex compounds based on 1-(carboxymethyl)-1H-pyrazole-3,5-dicarboxylic acid

Anastasia V. Sidoruk[a], Alexey M. Lunev[a], Victoria E. Gontcharenko[a,b], Yury A. Belousov[a,b],
Mikhail A. Kiskin[c]

[a]*Lomonosov Moscow State Universsity, Moscow, RUSSIA*
[b]*P.N.Lebedev Physical Institute of RAS, Moscow, RUSSIA*
[c]*N.S. Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, RUSSIA*

Historically, lanthanides have been divided into two subgroups: "cerium" for light lanthanides and "yttrium" for heavy ones. When switching to heavier elements, the effect of lanthanide compression is manifested, which often leads to a decrease in the coordination numbers of the central atom, and in the case of complexes with polydentate ligands, it can also lead to a change in the dimension of the polymer. Nevertheless, isostructural complex compounds exist within the same subgroup. This phenomenon underlies the synthesis of mixed-metal phases, which are used as sources of white light, fluorescent thermometers and ratiometric sensor materials.

In present work, coordination compounds based on a new ligand – 1-(carboxymethyl)-*1H*-pyrazole-3,5-dicarboxylic acid (H_3L) and metals of the entire lanthanide series of composition $[LnL(H_2O)_x]$ are synthesized and investigated. The crystal structures of the samarium, europium, dysprosium and ytterbium complexes were determined using X-ray diffraction. According to the PXRD data, in one isostructural group there are derivatives of La^{3+}-Tb^{3+} - three-dimensional metal-organic frameworks (MOF) $[LnL(H_2O)_2]$, and in the other – Dy^{3+}-Lu^{3+} $[LnL(H_2O)]$ complexes, which are 2D polymers. The derivatives of Sm, Eu, Tb and Dy have intense luminescence sensitized by an antenna ligand.

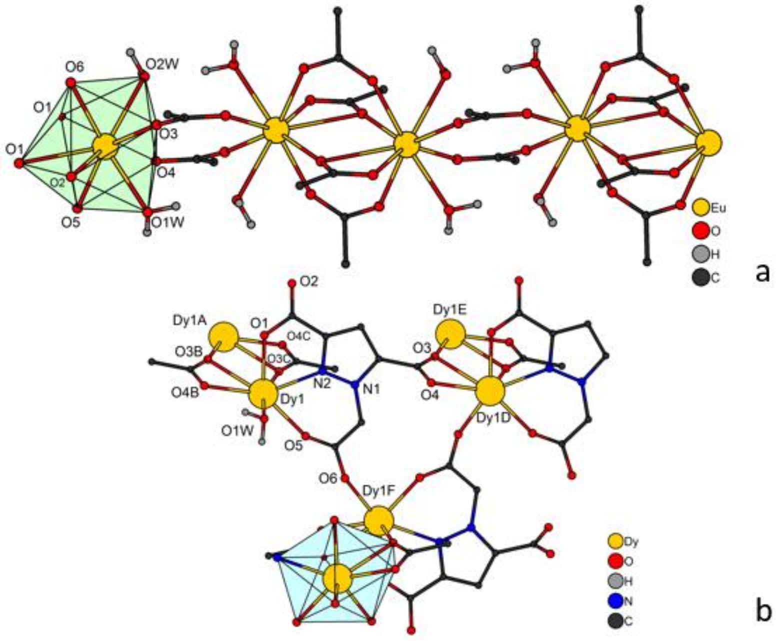


Fig. 1. Fragments of polymeric structure for (a) $[EuL(H_2O)_2]_n$, (b) $[DyL(H_2O)]_n$

Acknowledgements – Authors thank RFBR (projects 19-03-00263).

e-mail: avs_1999@mail.ru

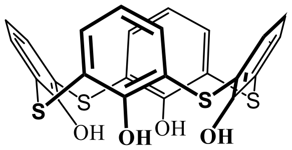
Structure and photophysical properties of the Yb^{3+} complexes with *p*-nitrothiacalix[4]arene

S.N. Sudakova,[a] S.N. Podyachev,[a] V.V. Syakaev,[a] G.Sh. Mambetova,[b] A.N. Masliy,[b]
A.E. Shvedova,[b] R.R, Zairov,[a] D.V. Lapaev,[c] A.R. Mustafina[a]

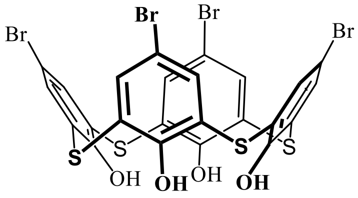
[a]Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Arbuzov str., 8, 420088, Kazan, RUSSIA
[b]Kazan National Research Technological University, K. Marks Str., 68, 420015, Kazan
[c]Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, Sibirsky tract, 10/7, 420029, Kazan

The near-infrared (NIR) luminescent ytterbium (Yb^{3+}) compounds are widely applied as building blocks of nanomaterials for bioimaging and photothermal therapy. This is due to unique photophysical characteristics of Yb^{3+}-centered luminescence. Literature data demonstrate fine examples of the convenient excitation of NIR luminescence of Yb^{3+} by means of the efficient intraligand charge transfer (ILCT). Visible light sensitized near-infrared luminescence of Yb^{3+} via ILCT states requires specific structure of the ligand based on combination of electron-withdrawing and electron-donating moieties. It is worth noting that the thiacalix[4]arene backbone allows to embed different groups at its upper rim, while the lower phenolic/phenolate rim is open for the complex formation with lanthanide ions. Moreover, the diversification of the upper rim substituents allows to modify the ligand-centered triplet level responsible for a feeding of the excited lanthanide-centered levels. Therefore, the series of thiacalix[4]arenes with diverse tetra-substitution of their upper rims is introduced as the ligands for Yb^{3+}.

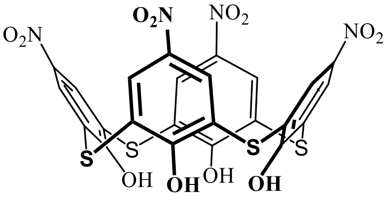
The structure variation of the thiacalix[4]arenes L(**1-3**) with upper-rim substituents (R=H, Br and NO_2) is represented with an aim to highlight the specificity of the substituents in their influence on the complex formation and Yb^{3+}-luminescence of the complexes. The steady state and time-resolved Yb^{3+}-centered luminescence data are correlated with both spectral properties and structural features of the ligands in order to recognize the impact of the different factors on the luminescence of the complexes.



1



2



3

The addition of Yb^{3+} to the basified solution of L(**3**) results in the increased absorbance at 400 nm with disappearance of the lower energy absorption bands at 450-500 nm (Fig. 1a). The analysis of the spectral changes resulted from the variation of both L(**3**) and $Yb(NO_3)_3$ through the Job-plotting (Fig. 1b) indicates that the complex formation of Yb^{3+} ions with L(**3**) in the basified DMF solutions predominantly occurs in 1:1 stoichiometry followed by deprotonation of three phenolic moieties (Fig. 1c).

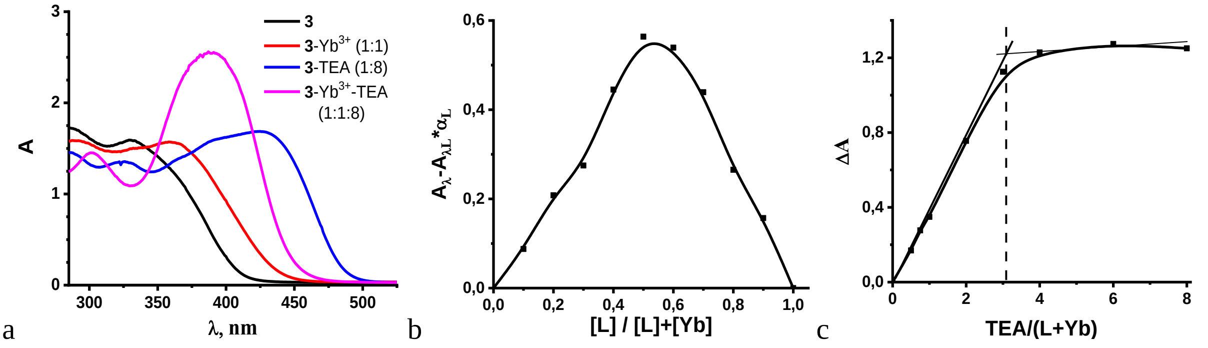


Fig. 1 - (a) UV-Vis absorption spectra of **3** (C_L=0.05 mM) in DMF; **3** with $Yb(NO_3)$ with NEt_3 (TEA) (b) The Job’s plot profiles of DMF solutions at the varied **3**:Yb^{3+} molar ratios and (c) ΔA of the DMF solutions of **3** with $Yb(NO_3)_3$ at the varied TEA:L molar ratio (λ =400 nm, $C_{Yb}3+ = C_L$ = 0.05 mM).

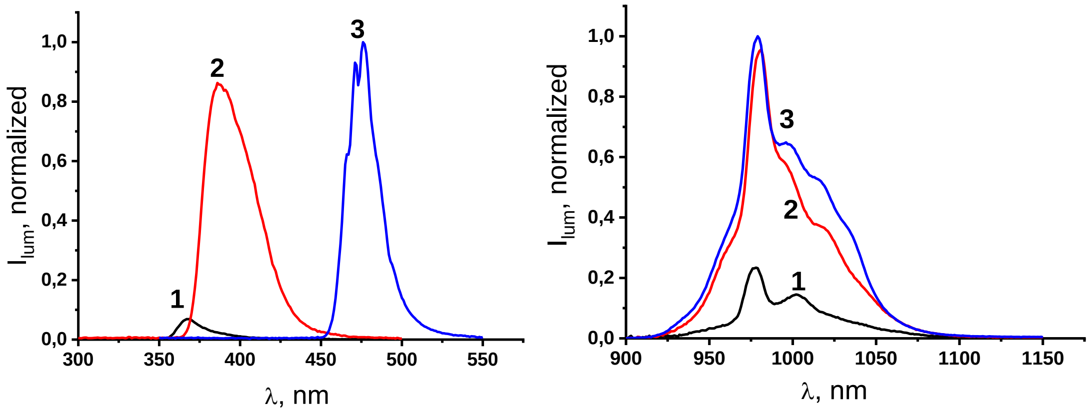


Fig. 2 - (a) Excitation and (b) emission spectra of the Yb^{3+}- complexes with ligands **1, 2** and **3** in DMF solution

Comparative analysis of the luminescent spectra reveals no significant impact of the lower laying triplet energy level of **3** (R=NO_2) *vs* that of **2** (R=Br) on the Yb^{3+}-luminescence. This argues for the effect of the upper-rim substituents R=NO_2, Br on the flexibility of the outer-sphere environment of Yb^{3+} ions *vs* ligand **1** (R=H) as the main reason for the bright NIR luminescence. However, the advantage of **3** (R=NO_2) *vs* **2** (R=Br) is the excitation of the bright NIR-luminescence by the lower energy irradiation (Fig. 2), which provides the lower absorption by the chromophores of biological background.

Acknowledgements: The authors are grateful to the Assigned Spectral-Analytical Center of FRC Kazan Scientific Center of RAS

e-mail: sudakova@iopc.ru

Sonotriboluminescence of suspensions of $Tb(acac)_3 \cdot H_2O$ crystals in water

A.A. Tukhbatullin, G.L. Sharipov

Institute of Petrochemistry and Catalysis UFRC RAS, Ufa, RUSSIA

The luminescence of suspension, which occurs under sonication, also called as sonotriboluminescence (STL), was found for the suspensions of known triboluminescent materials [1–3]. The STL of suspensions was considered mainly in organic solvents. In continuation of our studies, the sonotriboluminescence of terbium acetylacetonate suspensions in water was studied in this work to establish the patterns of light emission that occurs during ultrasonic treatment of aqueous suspensions.

Intense bands of the Tb^{3+} ion at 488, 544, and 585 nm that correspond to the $^5D_4 \rightarrow {}^7F_{6,5,4}$ transitions are recorded in the STL spectrum during sonication on an aqueous suspension of terbium acetylacetonate [4]. The STL spectrum of suspensions coincides with the photo- and triboluminescence spectrum of terbium acetylacetonate. [4]. The luminescence intensity during STL of $Tb(acac)_3 \cdot H_2O$ is much higher than that during sonoluminescence of aqueous solutions of terbium salts. This is due to the different mechanisms of luminescence excitation. The luminescence during STL of crystal suspensions occurs as a result of a specific tribological effect [5–8] caused by electrical discharges in the crystalline layer. The excitation of the STL suspension in water occurs as a result of the bombardment of emitters by charged particles generated during ultrasonic treatment of disperse systems, and not as a result of the collisional excitation of emitters inside cavitation bubbles, which is characteristic of sonoluminescence.

[1] G.L. Sharipov, A.M. Abdrakhmanov, A.A. Tukhbatullin, *Tech. Phys. Lett.* **2009**, *35*, 452–455.
[2] M. Virot, R. Pflieger, J. Ravaux, S.I. Nikitenko, *J. Phys. Chem. C*, **2011**, *115*, 10752–10756.
[3] A.A. Tukhbatullin, G.L. Sharipov, N.F. Burangulova, A.G. Mustafin, *Ultrason. Sonochem*. **2019**, *50*, 251–254.
[4] R.G. Bulgakov, S.P. Kuleshov, A.N. Zuzlov, R.R. Vafin, *Russ. Chem. Bull*. **2004**, *53*, 2712–2714.
[5] K. Nakayama, *Tribol. Lett*. **2010**, *37*, 215–228.
[6] A.L. Collins, C.G. Camara, E. Van Cleve, S.J. Putterman, *Rev. Sci. Instrum*. **2018**, *89*, 013901.
[7] J.C.G. Bünzli, K.L. Wong, *J. Rare Earths*. **2018**, *36*, 1–41.
[8]A.A. Tukhbatullin, G.L. Sharipov, *Opt. Mater.* **2020**, *109*, 110402.

Acknowledgements – This research was performed within the budget theme of Institute of Petrochemistry and Catalysis UFRC RAS. The spectrophotometric and microscopic studies of the crystals and suspensions were performed on a unique equipment of the "Agidel" Collective Usage Center at the Institute of Petrochemistry and Catalysis (Ufa Federal Research Center, Russian Academy of Sciences).

e-mail: adis0501@mail.ru

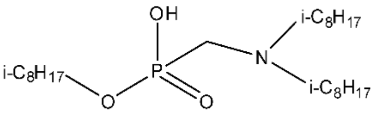
Экстракция редкоземельных элементов O-2-этилгексил-N,N-бис(2-этилгексил)аминометилфосфоновой кислотой

Е.К. Конькова, Е.О. Чибирев, А.Р. Гарифзянов

Казанский (Приволжский) федеральный университет, Химический институт им. А.М. Бутлерова, г. Казань

Метод жидкостной экстракции находит широкое применение в гидрометаллургии и аналитической химии редкоземельных элементов (РЗЭ).

В данной работе исследовалась экстракция ионов церия(III), самария(III) и эрбия(III) новым реагентом O-2-этилгексил-N,N-бис(2-этилгексил) аминометил-фосфоновой кислотой (HR).



Экстракция ионов РЗЭ проводилась из нитратных сред раствором HR в хлороформе. Время контакта фаз составляло 40 минут, при соотношении объемов водной и органической фаз 1:1. Концентрацию ионов РЗЭ определяли в водной фазе методом атомно эмиссионной спектроскопии микроволновой индуцированной плазмы (АЭС МИП). Степень извлечения рассчитывается по уравнению:

$$R = \frac{C_0 - C}{C_0} * 100\%$$

Где C_0 – исходная концентрация металла в водной фазе, C – концентрация после экстракции.

На рисунке 1 приведена зависимость степени извлечения ионов РЗЭ от pH водной фазы. Рост степени извлечения при переходе от кислых к слабокислым растворам связан с тем, что в этом интервале pH экстракция осуществляется по катионообменному механизму:

$$M^{3+} + 3[HR]_{org} = [MR_3]_{org} + 3H^+$$

В сильнокислой области водной фазы степень извлечения ионов РЗЭ увеличивается с ростом концентрации HNO_3. По нашему мнению, это связано с тем, что в сильнокислых средах при высоких концентрациях ионов РЗЭ в органическую фазу переходит ионный ассоциат, образованный комплексом иона РЗЭ с протонированной формой лиганда и тремя нитрат ионами:

$$M^{3+} + 3HR_{org} + 3NO_3^- = \{[M(HR)_3]^{3+} \cdot 3NO_3^-\}_{org}$$

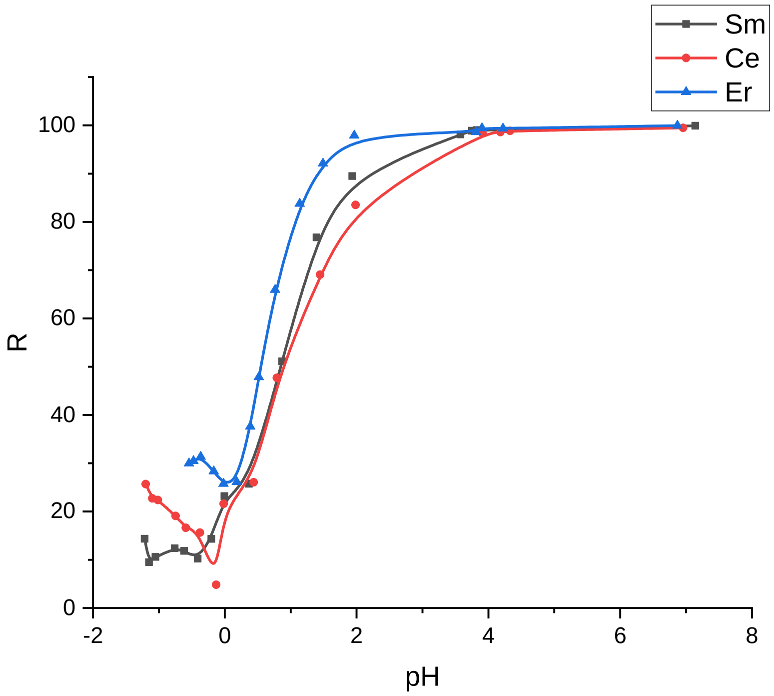


Рис 1. Зависимость степени извлечения ионов Ce^{3+}, Sm^{3+} и Er^{3+} экстрагентом HR от pH водной фазы.

Установлено, что катионы щелочных и щелочноземельных металлов и алюминия(III) не экстрагируются при pH<5 данным экстрагентом. Следовательно O-2-этилгексил-N,N-бис(2-этилгексил)аминометилфосфоновая кислота представляет интерес как реагент для группового концентрирования ионов РЗЭ из растворов, содержащих сопутствующие элементы.

e-mail: redatushared@gmail.com

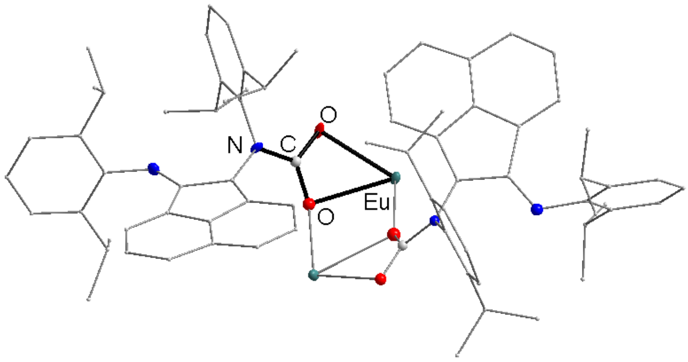
Bisiminoacenaphthene lanthanides complexes: synthesis and reactivity

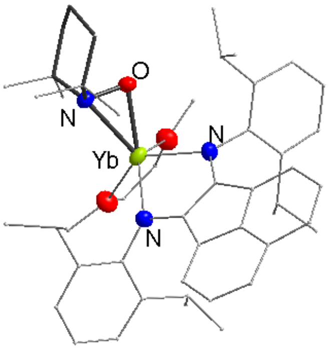
D.S. Yambulatov[a], S.A. Nikolaevskii[a], I.A. Lutsenko[a], M.A. Kiskin[a], I.L. Fedushkin[b]

[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry, 119991, Moscow, RUSSIA*
[b]*G. A. Razuvaev Institute of Organometallic Chemistry, Nizhnii Novgorod, RUSSIA*

Complexes of low-valent lanthanides with redox-active ligands of the diimine series are promising objects for the synthesis of compounds with switchable properties. We are looking for such objects [1,2]. Previously, we have shown that such complexes can form electronic isomers [3] and react with a substrates with labile hydrogen atom [4]. Due to the large ionic radius and the coordinated charged redox-active ligand, divalent lanthanide complexes can be active towards carbon dioxide.

In this work, it is shown that the complex of divalent europium with a dpp-BIAN ligand in the dianion state reacts with CO_2. It was also shown that the ytterbium(II) complex with the same ligand reacts with the free radical TEMPO, forming an adduct with N-Yb and O-Yb bonds. Features of the synthesis and reactivity to other substrates will be discussed during the report.





1. Fedushkin, I.L.; Skatova, A.A.; Yambulatov, D.S.; Cherkasov, A.V.; Demeshko, S.V. Europium complexes with 1,2-bis(arylimino)acenaphthenes: a search for redox isomers. *Russian Chemical Bulletin* **2015**, *64*, 38-43, doi:10.1007/s11172-015-0817-6.
2. Skatova, A.A.; Yambulatov, D.S.; Fedyushkin, I.L.; Baranov, E.V. Europium and Ytterbium Complexes with the Redox Active Acenaphthene-1,2-Diimine Ligand. *Russian Journal of Coordination Chemistry* **2018**, *44*, 400-409, doi:10.1134/S1070328418060064.
3. Fedushkin, I.L.; Yambulatov, D.S.; Skatova, A.A.; Baranov, E.V.; Demeshko, S.; Bogomyakov, A.S.; Ovcharenko, V.I.; Zueva, E.M. Ytterbium and Europium Complexes of Redox-Active Ligands: Searching for Redox Isomerism. *Inorganic Chemistry* **2017**, *56*, 9825-9833, doi:10.1021/acs.inorgchem.7b01344.
4. Yambulatov, D.S.; Skatova, A.A.; Cherkasov, A.V.; Fedushkin, I.L. Addition of phenylacetylene and camphor to the complex [(dpp-bian)Eu(dme)2] (dpp-bian is the 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene dianion). *Russian Chemical Bulletin* **2017**, *66*, 1187-1195, doi:10.1007/s11172-017-1871-z.

Acknowledgements – This work was supported by the Russian Science Foundation (Project 20-13-00061)

e-mail: yambulatov@yandex.ru

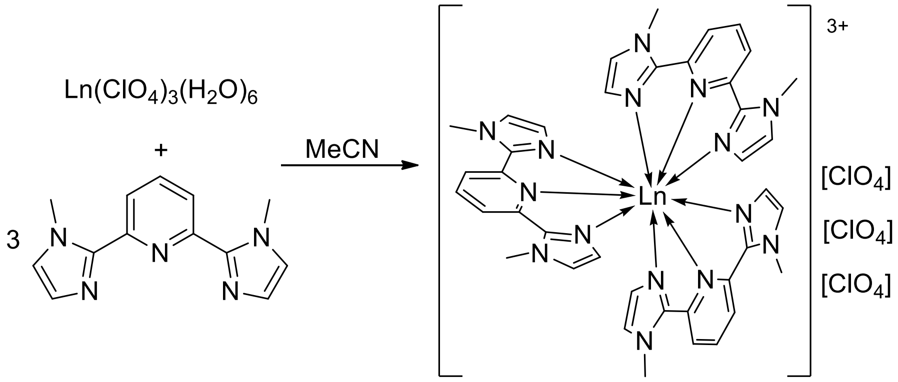
Заочные участники

Ln (III) coordination compounds with neutral pincer ligands and investigation of their luminescent properties

A. Fayoumi,[a] D.M. Lyubov,[b,c] A.A. Trifonov[b,c]

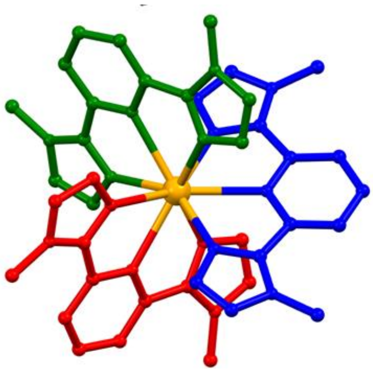
[a]*Atomic Energy Commission of Syria*
[b]*Institute of Organometallic Chemistry of Russian Academy of Sciences, 49 Tropinina str., GSP-445, 630950, Nizhny Novgorod, RUSSIA*
[c]*Institute of Organoelement Compounds of Russian Academy of Sciences, 28 Vavilova str., 119334 , Moscow, RUSSIA*

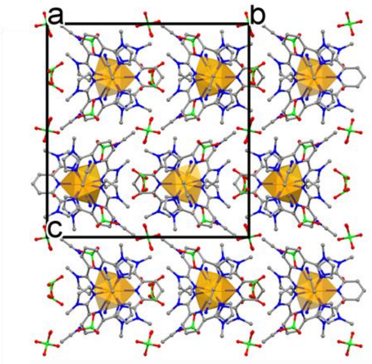
Pincer ligands can be used not only for the preparation of organometallic derivatives of rare earth metals, but also as neutral chelating ligands for the preparation of various classes of lanthanide coordination compounds. In this regard, we investigated the complex formation of bis (imidazolyl) pyridine with lanthanide perchlorates.



Eu, **Tb**, **Dy**, **Er**, **Yb**

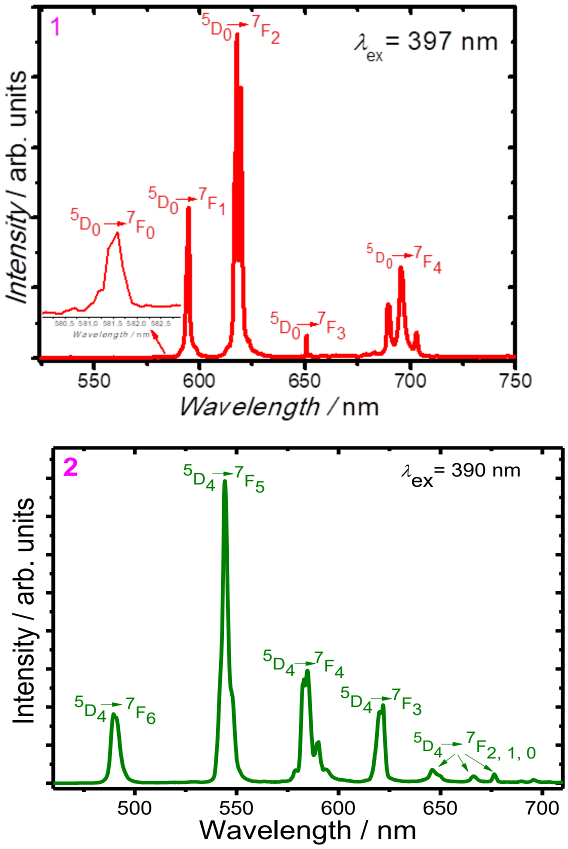
According to X-ray diffraction analysis, the obtained complexes of europium, terbium, dysprosium, erbium, and ytterbium are isostructural and represent separated ion pairs, in which the Ln3 cation is coordinated by three neutral tridentate ligands, and perchlorate anions act as anions.



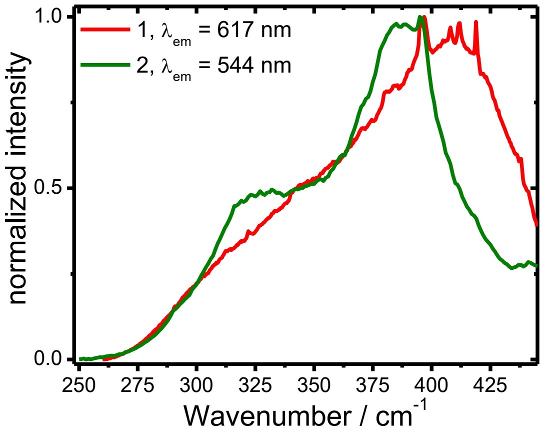


For the series of complexes, were investigated the luminescence properties in solid state. It was found that only the Eu and Tb complexes give excitation in wavelengths light of 397 and 390 nm, respectively, exhibit emission characteristic for Ln (III) ions.

Excitation analyses spectra for Eu and Tb complexes allow to study differences in the mechanisms of their excitation. The excitation spectrum of the Eu complex is characterized by a broad band due to the absorption of the ligand, as well as narrow absorption bands due to internal f-f transitions of Eu ions. Thus, in the case of Eu, the sensitization mechanism includes double excitation both through the ligand and directly through 4f-4f transitions. In the case of the Tb complex, the excitation spectrum contains only a broad band due to the absorption of the organic ligand with maxima at 325 and 390 nm.



Photoluminescence spectra of complexes Eu and Tb. Q = 57% (Eu) and 18% (Tb)



Excitation spectra for Eu and Tb complexes.

Acknowledgments: Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, Russia .Atomic Energy Commission (AECS) of Syria

e-mail: adfu_87@hotmail.com

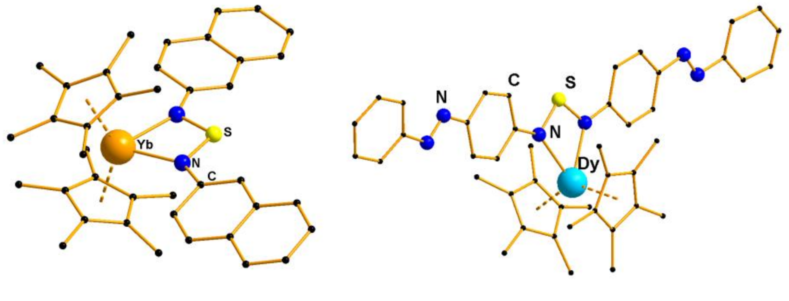
Комплексы лантаноидов с ациклическими тиодиимидами

М.Ю. Афонин, Т.С. Сухих, С.Н. Конченко

Институт неорганической химии им. А.В. Николаева СО РАН, г. Новосибирск

Ациклические тиоодиимиды R-N=S=N-R интересный и очень перспективный класс редокс-активных соединений. Одноэлектронное восстановление которых, приводит к образованию анион-радикальной частицы. Однако координационная химия производных тиодиимида развита слабо. На сегодняшний день опубликовано меньше десяти работ по координационным соединениям производных тиодиимида с переходными металлами и всего одна работа посвящена комплексам лантаноидов [$LnCp^*_2(RN=)_2S$] (Ln = Sm, Eu, Yb; R = $SiMe_3$, Cp* = C_5Me_5) [1]. Все структурно охарактеризованные комплексы, получены с лигандами, в которых в качестве заместителей $SiMe_3$ или *t*-Bu группы. Ни одного комплекса с арильными производными тиодиимида до наших работ структурно охарактеризовано не было. Хотя именно арильные тиодиимиды представляют обширное поле для исследования, в том числе благодаря возможности их функционализации.

Для получения тиодиимидных комплексов самария, европия и иттербия был использован восстановительный подход. Комплексы лантаноидов 2+ [$Cp^*_2Ln(thf)_2$] (Ln = Sm, Eu, Yb; thf = тетрагидрофуран) восстанавливают тиодиимиды до анион-радикальной формы, которая координируется к иону лантаноида. В результате этих реакций был получен ряд соединений состава [$LnCp^*_2(RN=)_2S$] (R = Ph, α-нафтил, β-нафтил, -C_6H_4-N_2-C_6H_5). Оригинальный подход был разработан для лантаноидов, для которых нехарактерна степень окисления 2+. Он основан на восстановительной способности тетрафенилборат-аниона в комплексах [$LnCp^*_2BPh_4$]. Таким образом, были получены соединения [$LnCp^*_2(R1N=)_2S$] (Ln = Dy, Tm, Y; R1 = -C_6H_4-N_2-C_6H_5). Для комплексов [$LnCp^*_2(R1N=)_2S$] (Ln = Sm, Dy, Tm, Y), методом УФ-спектроскопии, была обнаружена обратимая изомеризация. При облучении ультрафиолетовым светом с длиной волны 365 нм происходит изомеризация азо-группы координированного лиганда. Обратная изомеризация происходит медленно под воздействием дневного света или быстро при облучении белым светом LED-лампы.



[1] S.V. Klementyeva, P.W. Roesky, A.V. Zibarev, S.N. Konchenko at al, *Chem. A Eur.J.* **2017**, 23, 1278-1290.

Благодарности: Работа выполнена при финансовой поддержке РФФИ и Правительства Новосибирской области в рамках проекта № 19-43-543026.

e-mail: afonin@niic.nsc.ru

Phase transformations, peculiarities of Eu^{3+} and Tb^{3+} ions distribution on C_{3i} and C_2 cation positions and excitation channels of photoluminescence centers of C-$Gd_{2(1-x)}Tb_xEu_xO_3$ solid solution

V.V. Bakovets

Nikolaev Institute of Inorganic Chemistry SB RAN, Novosibirsk, RUSSIA

$Gd_{2(1-x)}Tb_xEu_xO_3$ solid solutions are characterized by photoemission (PL) properties, which are determined by the lattice modification of the cubic or monoclinic Gd_2O_3 matrix, Tb^{3+} and Eu^{3+} activator concentrations, impurity phase composition, activator distribution over centrosymmetric C_{3i}, noncentrosymmetric C_2 cation sites of the bixbyite lattice and C_s surface states. During annealing of precursors – products of the sol-gel process $Gd_{2(1-x)}Tb_xEu_x(OH)_y(CO_3)_z{\cdot}n(H_2O)$, x = 1, 2.5 mol.% in the temperature range 700-1200 °C phase transformations with dehydration, dehydroxylation and decomposition of carbonates occur.

Generally formed solid solutions Gd_2O_3:$(Tb^{3+})_x(Eu^{3+})_x$ contain microinclusions of Tb_7O_{12}:Eu^{3+} phase lamellae (Fig. 1). These microinclusions are eliminated by additional annealing in hydrogen by reduction of Tb^{4+} cations to Tb^{3+}. Fig. 2 shows the normalized PL spectra of the samples. The intensity of all PL bands of Eu^{3+} and Tb^{3+} ions increases due to the increase in crystallinity of the samples and the concentration of these ions.

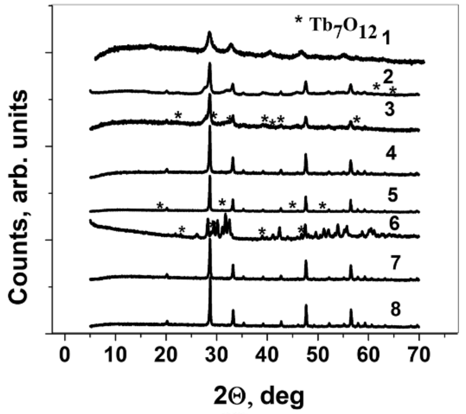
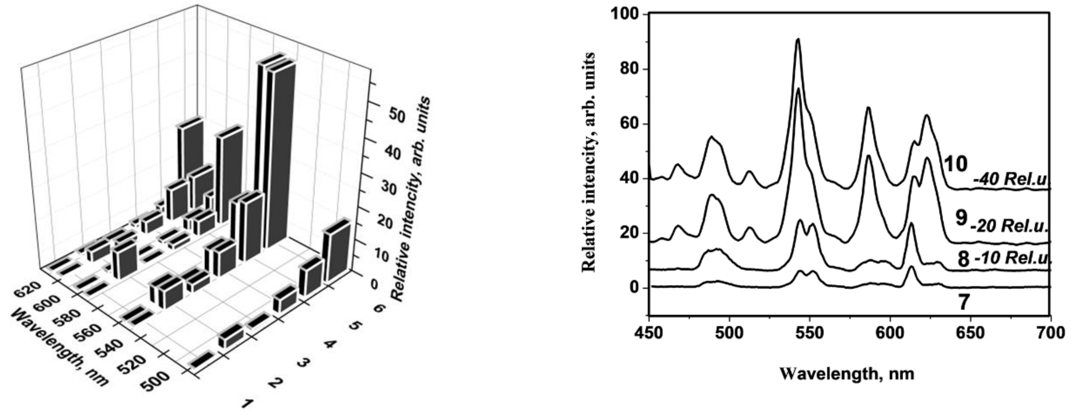


Fig. 1. X-ray patterns of samples: 1% Eu,Tb (700 °C, air), C-Gd_2O_3, $Gd(OH)_3$, $Gd(CO_3)OH$; 2. 1% Eu,Tb (700 °C, H_2), C-Gd_2O_3, Tb_7O_{12}, $Gd(CO_3)OH$; 3. 1% Eu,Tb (900 °C, air), C-Gd_2O_3, Tb_7O_{12}, $TbO_{1.81}$; 4. 1% Eu,Tb (900 °C, H_2), C-Gd_2O_3; 5. 1% Eu,Tb (1200 °C, air), C-Gd_2O_3, Tb_7O_{12}; 6. 1% Eu,Tb (1200 °C, H_2), B-Gd_2O_3, Tb_7O_{12}, 7. 2.5% Eu,Tb (1200°C, air), C-Gd_2O_3, 8. 2.5% Eu,Tb (1200 °C, H_2), C-Gd_2O_3

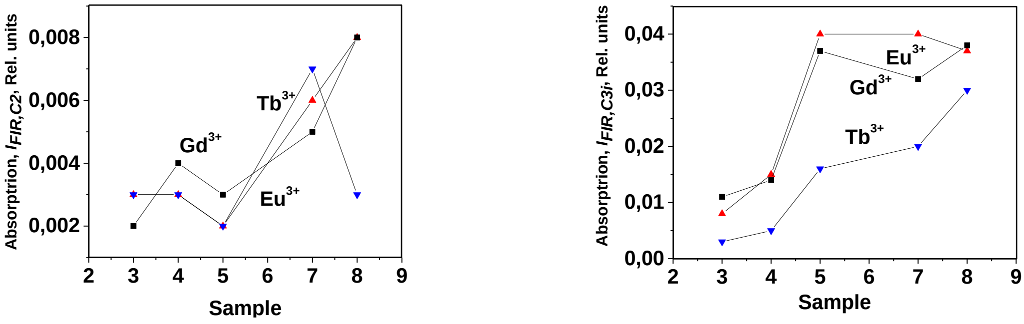


a b

Fig. 2. PL spectra of samples 1 - 6 as a 3D bar diagram of the maxima of the main emission bands 487, 513, 542, 550, 584 nm (Tb^{3+}), 595, 612 and 622 nm (Eu^{3+}) (a) and the general view of the spectra of samples 7-10: sample 9 - sample 6, annealed in air at 1200 °C, B-Gd_2O_3 and sample 10 - sample 5 annealed, in Ar at 1200 °C, B-Gd_2O_3 (b).

Obviously, the short-order structure of the samples changes with variation in the annealing processes, and this is reflected in the FIR spectra (far-IR) (Fig. 3).

Using the results of the analysis of FIR spectra the absorption bands and localization of Gd^{3+}, Eu^{3+} and Tb^{3+} cations at the C_{3i} and C_2 positions of the bixbyite type lattice were identified. The intensities of the bands depending on the processes of obtaining the samples are shown in Fig. 3.



a b

Fig. 3. Intensities of FIR absorption bands caused by movement of cations in the positions: C_2 - region 190 - 230 cm^{-1} (a) and C_{3i} - region 120 - 140 cm^{-1} (b).

As a result of joint consideration of changes in the phase composition and real structure of ceramic polycrystalline samples, as well as their PL and FIR spectra, self-consistent data on the distribution of PL activators on the C_{3i} and C_2 lattice positions of cubic sesquioxide gadolinium as well as on the surface C_S states on the crystallite boundaries were obtained. The redistribution of cations on the above lattice positions is caused by the transition of surface active terbium ions to the boundaries of crystallites and the coexistence of these ions in different oxidation states of Tb^{3+} and Tb^{4+}. In this case, the spectra of PL samples change characteristically . It is shown, that the change in the PL spectra of the samples correlates with the change in the specific surface of S_{cr} crystallites and with the FIR spectra within the framework of the known models for describing these spectra.

Using the obtained correlations of the S_{cr}, PL, and FIR spectra for Eu^{3+} cations with the known correlations of the PL bands with the C_{3i} and C_2 localization positions of these ions, we were first able to describe the most likely transfer channels of Tb^{3+} activator excitation energy to radiative PL transitions of Eu3+ centers.

[1] V.V. Bakovets, I.P. Dolgovesova, T.D. Pivovarova, M.I. Rakhmanova, PSS, **2020**, *62*, 2412–24216 (*FTT*, **2020**, *62*, 2147- 2156)
[2] V.V. Bakovets, I.P. Dolgovesova, T.D. Pivovarova, L.A..Sheludjakova PSS, **2021**, *63*, 2162 - 2170

Acknowledgements The work is supported by Ministry of Education and Science of Russian Federation № 121031700315-2, I express my gratitude to my colleagues on the presented work: I.P. Dolgovesova, L.A. Sheludyakova, M.I. Rakhmanova and T.D. Pivovarova.

e-mail: becambe@niic.nsc.ru

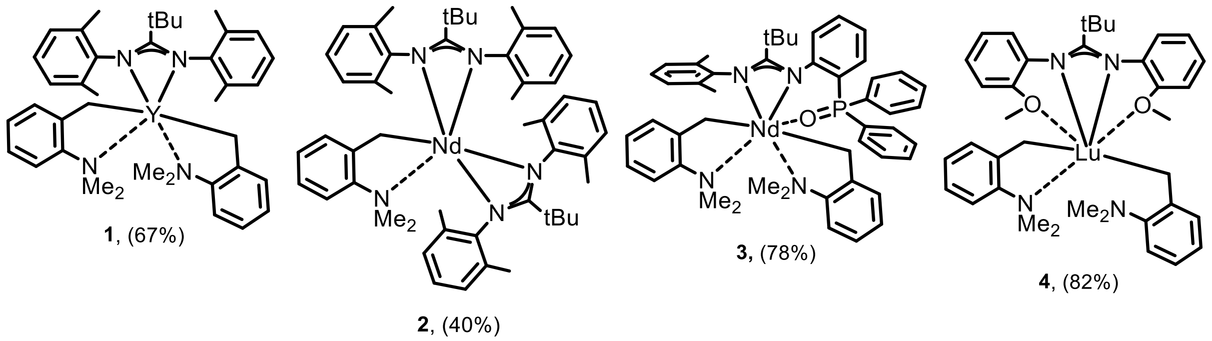
O-N,N-dimethylaminobenzyl complexes of rare-earth metals with polydentate amidinate ligands. Synthesis, structure and study of catalytic activity in the polymerization of isoprene

O.A. Basalova[a], A.A. Trifonov[b]

[a]*G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences,*
Nizhny Novgorod, RUSSIA
[b]*A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences,*
Moscow, RUSSIA

Polymerization of diene monomers, in particular isoprene, is one of the areas where lanthanide compounds are most successfully used. Physical and mechanical properties of polyisoprenes largely depend on factors such as molecular weight, polydispersity, stereoregularity of the structure, the ratio of 1,4-*cis*, 1,4-*trans* and 3,4 units in the polymer chain. A particularly important task is the development of such catalysts that would make it possible to obtain polyisoprene closed to natural in its properties.

A series of new *o*-N,N-dimethylaminobenzyl complexes of lanthanides (Y, Nd, Lu) were obtained and structurally characterized.



Scheme 1.

Bis-(*o*-N,N-dimethylaminobenzyl) complexes turned out to be effective catalysts for isoprene polymerization in ternary systems **1, 3, 4** / [[Ph_3C][$B(C_6F_5)_4$], [$PhNHMe_2$][$B(C_6F_5)_4$]] / AlR_3 (AlR_3=Al^iBu_3, Al^iBu_2H, $AlMe_3$). These systems provide good rates and stereoselectivity of the polymerization process, allowing predominantly cis-1,4 polyisoprene. In addition, the obtained polymer samples have high molecular weights and moderate molecular weight distribution.

Acknowledgements – The authors thank the Russian Science Foundation Grant No. 20-73-10037

e-mail lesek93@mail.ru

Влияние поляризации галоид-анионов, координированных с трехвалентным ионом церия, на фотолюминесценцию его соединений в растворе и твердом виде

Д.И. Галимов,[а] Д.Р. Газеева,[а] С.М. Якупова,[а] К.С. Василюк[а], Р.Г. Булгаков[б]

[а]*Институт нефтехимии и катализа УФИЦ РАН, г. Уфа*
[б]*Институт физики молекул и кристаллов УФИЦ РАН, г. Уфа*

Церий – металл семейства РЗЭ с ярким настоящим и большим будущим. Последнее, главным образом, связано с потенциальной возможностью применения соединений церия в люминесцентной спектроскопии и фотокатализе. В соединениях церий может находиться в двух устойчивых валентных состояниях (III и IV). Однако фотолюминесценция (ФЛ) известна лишь для соединений трехвалентного церия. ФЛ иона Ce(III), в отличии от ФЛ других ионов Ln(III), обусловлена излучательным переходом из не экранированного $5s^2$- и $5p^6$-оболочками $5d^1$-уровня на $4f^1$-уровень. Поэтому ФЛ соединений CeX_3 сильно подвержена влиянию природы аниона X^-, координированного с ионом Ce(III). Так, при переходе от $CeCl_3$ к $CeBr_3$ и CeI_3 наблюдается сдвиг максимумов ФЛ в длинноволновую область. Наряду с этим красным сдвигом ФЛ в ряду соединений $CeCl_3 \rightarrow CeBr_3 \rightarrow CeI_3$ также увеличиваются поляризация анионов X^- и ковалентность связи Ce–X. Таким образом, логично предположить, что поляризация анионов может быть первопричиной красного сдвига ФЛ тригалидов CeX_3. Для подтверждения этого предположения нами изучено влияние поляризации анионов X^- (X = Cl, Br, I) и ковалентности связи Ce–X на положение максимумов ФЛ тригалидов CeX_3; последние были взяты в виде твердых соединений и растворов в тетрагидрофуране (ТГФ).

Спектры ФЛ твердых CeX_3 состоят из двух диффузных полос в синей области, положение которых зависит от природы аниона X^- при катионе церия: 339, 352 (Cl^-), 363, 381(Br^-), 383, 392 нм (I^-). Аналогичные красные сдвиги наблюдаются и для спектров ФЛ CeX_3 в ТГФ: 354, 380 (Cl^-) → 359, 390 (Br^-) → 382, 393 нм (I^-). Для изучения влияния координационного окружения Ce(III) на длинноволновый сдвиг максимумов ФЛ проведена также оценка степени ионности связи Ce–X, используя классическую теорию химических связей. В результате установлено, что ионный характер связи Ce–X уменьшается в ряду Ce–Cl (36%) → Ce–Br (28%) → Ce–I (18%), т.е. ковалентный характер этой связи увеличивается. Обнаруженные сдвиги хорошо коррелируют со средними значениями длин связей Ce–X: Ce–Cl (2.84 Å) → Ce–Br (2.89Å) → Ce–I (3.18 Å), и поляризуемости анионов: Cl^- (1.79 $Å^3$) → Br^- (3.12 $Å^3$) → I^- (4.57 $Å^3$), рассчитанными методом PBE/3ζ (Priroda 11).

На основании полученных корреляционных зависимостей сделан вывод о том, что батохромный сдвиг максимумов в спектрах ФЛ CeX_3, как и для соединений европия EuX_2 [1], обусловлен нефелоксетическим эффектом, т.е. увеличением поляризации анионов X^- и ковалентности связи Ce–X.

[1] D.I. Galimov, S.M. Yakupova, K.S. Vasilyuk, D.Sh. Sabirov, R.G. Bulgakov, *J. Photochem. Photobiol. A*, 2020, 403, 112839.

e-mail:gazeevadilara@mail.ru

Orientation behavior of lyotropic Ln-containing mesogens

A.I. Galeeva, N.M. Selivanova, Yu.G. Galyametdinov

Kazan National Research Technological University, Kazan, RUSSIA

Lyotropic liquid crystals (LLCs) have attraction because of their unique properties that make them applicable in various fields of science and technology, such as biomedical devices, electronic devices and others [1, 2].

Earlier in our group were synthesized and investigated lyotropic liquid crystalline lanthanide (Ln^{III}=La, Eu, Tb) containing systems based on surfactants: $C_{12}H_{25}O(CH_2CH_2O)_{10}H$, $C_{12}H_{25}O(CH_2CH_2O)_4H$, $CH_3(CH_2)_{11}N(O)(CH_3)_2)$, which exhibit stable lyotropic mesophase in various solvents (H_2O, D_2O, H_2O-$C_{10}H_{21}OH$ mixture) [3,4].

In this work new thin films with nanoorganized lanthanide ions from aligned and non-aligned lyotropic systems are researched. For creation aligned samples were used polymeric orientantes: nylon N6, polyamide AL 1254, Jals-2021-R2. The influence of aligned samples on lanthanide nanoorganization and its environment were investigated complex of methods: AFM, SEM, TEM, SAXS, luminescence, contact angle measurement. X-ray diffraction by small-angle study was carried out to clarify the way of metal ions organization in mesophase and for orientating properties exploring. The surface free energy of orientate was determined by the method of geometrical mean approximation based on Foaks conception and Owens-Wendt equations. The data of oriented polymer surfaces wetting (contact angles) with testing liquids were used. Important difference in the magnitudes of the surface energy characteristics for planar and homeotropic orientantes has been revealed. The LLC based on nonionic surfactant was shown to demonstrate higher wettability to be compared with the nematic mesogens. Orientations of the surface by it rubbing leads to wetting reduce because of the surface layer reorientation. The best wetting was reached on the substrates covered with ITO. The work of adhesion LLC to studied surfaces was calculated using Young equation and the data of wetting and LLC surface tension measurements. It was established that the system which forms from nematic phase show more poor adhesion to the surfaces investigated than the systems with hexagonal and lamellar mesophases. The adhesion to polyimide is higher than to nylon for any type of mesophases. This offered approach allows estimating the efficiency of polymer – LLC interaction and surface nanolayers self-organization. The results obtained of the orientation behavior new materials are useful for new electronic devices creation.

[1] Saadat, Y. Imran, O. Q. Osuji, C.O. Foudazi R. Lyotropic liquid crystals as templates for advanced materials, *J. Mater. Chem. A*, **2021**, 9, 21607–21658.
[2] Selivanova, N.M. Galeeva, A.I. Galyametdinov, Yu.G. Biocompatible delivery systems based on κ-carrageenan and nonionic surfactants, *Liq. Cryst. and their Appl*., **2020**, 20, 2, 23-34.
[3] Selivanova, N. M. Galeeva, A. I. Vandyukov, A. E. Galyametdinov, Yu.G. New Liquid-Crystalline Complex C12DMAO/LaIII with the Nematic Phase. Russ, *Chem. Bull*, **2010**, 59, 469– 472.
[4] Selivanova, N. M. Galeeva, A. I. Gubaydullin, A.T. Lobkov, V.S. Galyametdinov, Yu.G. Mesogenic and Luminescent Properties of Lyotropic Liquid Crystals Containing Eu(III) and Tb(III) Ions, *Journal of Physical Chemistry B*, **2012**, 116, 2, 735-742.

Acknowledgements – Authors thank Russian Science Foundation (grant 18-13-00112-П) for financial support.

e-mail: galeeva-alija@mail.ru

Разработка методики определения РЗЭ в бурых углях масс-спектрометрическим методом

А.В. Гапонько, С.С. Шацкая

Институт химии твёрдого тела и механохимии СО РАН, Новосибирск

Современная военная промышленность и энергосберегающие технологии требуют создания новых функциональных материалов с заданными свойствами. В связи с этим в нашей стране и за рубежом возрос спрос на редкоземельные элементы. Они незаменимы при создании электродвигателей, применяемых в автомобилестроении и космических кораблей, компьютерных дисплеев, оптоволоконных кабелей.

В многочисленных литературных источниках сообщается о том, что угли и золоотвалы содержат высокие концентрации редкоземельных элементов и других элементов-примесей. Данные объекты многие рассматривают в качестве источников редких элементов и благородных металлов.

Для определения содержания редкоземельного потенциала в породах долгое время использовались не деструктивные методы. Однако они имеют недостаточно низкие пределы обнаружения или несут определенные ограничения по набору элементов. На сегодняшний день масс-спектрометрия с индуктивно-связанной плазмой стала одним из основных методов для определения низких концентраций редкоземельных элементов.

Нами была разработана методика масс-спектрометрического определения редкоземельных элементов в углях и золоотвалах с различным содержанием силикатной части, определена зольность и влажность данных образцов углей. Концентрации редкоземельных элементов определяли методом масс-спектрометрии с индуктивно-связанной плазмой количественным и полуколичественным вариантами с разными коэффициентами разбавлений. Относительное стандартное отклонение при определении РЗЭ полуколичественным методом составляет не более 15 %, количественным методом – не более 8 %. Полученные результаты были проверены методом добавок.

Для подтверждения правильности результатов, полученных методом масс-спектрометрии, определено содержание суммы редкоземельных элементов в угле Азейского месторождения колориметрическим методом с арсеназо (III). Суммарное содержание РЗЭ, полученное обоими методами, совпадает.

Благодарности: выражаем особую признательность д. г.-м. н., профессору Томского политехнического университета, Арбузову Сергею Ивановичу за предоставление образцов угля.

e-mail: andrejgaponko@gmail.com

A new gadolinium-based contrast agent: synthesis and MRI research

V. O. Glavinskaia, R. O. Matsenko, V. V. Zheltova, M. G. Osmolowsky, N. P. Bobrysheva,
O. M. Osmolowskaya

Saint Petersburg State University, Saint Petersburg, RUSSIA

Gadolinium is known for its unique properties. Its compounds are currently actively used in medical diagnostics as contrast agents for magnetic resonance imaging (MRI) – a modern diagnostic method that allows visualization of internal organs and tissues for the diagnosis of a wide range of diseases.

To this day, contrast agents based on gadolinium chelate complexes are the only approved contrast agents for magnetic resonance imaging worldwide. However, free gadolinium ion itself is toxic and, if ingested, can cause serious side effects.

In this work, we propose to use gadolinium-doped hydroxyapatite nanoparticles as contrasting agents. Main advantages of such material are biocompatibility of hydroxyapatite, which is the main inorganic component of human bone tissue, as well as the energy efficiency of the synthesis process and economic benefits.

Hydroxyapatite nanoparticles doped with gadolinium were obtained by precipitation and hydrothermal treatment at different temperatures by varying the composition of the reaction medium. These synthesis methods allow the dopant to enter inside crystal lattice of the matrix without the formation of additional phases. The morphological parameters and surface composition of the obtained powders were studied by X-ray, TEM, and IR spectroscopy methods, and their specific surface area was also determined by the BET method. It was found that the obtained nanoparticles are rod-shaped and varying in thickness from 12 to 33 nm and 34 to 81 nm in length.

The imaging capabilities of gadolinium-doped hydroxyapatite nanoparticles were studied by MRI. For this purpose, their suspensions in agarose gel were prepared. The presence of contrast relative to agarose was observed in all samples. This indicates that the obtained material has contrasting properties and can be used in MRI. The results of the studies showed that the relaxation times T1 and T2 increase with increasing nanoparticle size. Relaxation times, signal intensity and image contrast are comparable with the data obtained earlier in studies of magnetite. Also, the obtained samples of doped nanoparticles were compared with the contrasting effect of the contrast agent "Omniscan" based on gadodiamide trihydrate.

Acknowledgements – Scientific research was performed using the equipment of the Research Park of St. Petersburg State University (Centre for X-ray Diffraction Studies, Chemical Analysis and Materials Research Centre, Centre for Innovative Technologies of Composite Nanomaterials, Centre for Optical and Laser Materials Research, Centre for Magnetic Resonance).

The first author of the paper expresses gratitude to the St. Petersburg State University Alumni Association for the financial support of the research

e-mail: vladaglavinskaia@mail.ru

Использование эффекта плазмонного резонанса для увеличения электролюминесцентных свойств комплексов тербия

А.Ю. Гладких[а], М.И. Козлов[б], А.А. Ващенко[в], В.В. Уточникова[г]

[а]Факультет наук о материалах МГУ имени М.В. Ломоносова, 119991, Москва, РОССИЯ
[б]Физический институт имени П. Н. Лебедева РАН, 119333, Москва, РОССИЯ
[в]Химический факультет МГУ имени М.В. Ломоносова, 119991, Москва, РОССИЯ

Органические светоизлучающие диоды на основе координационных соединений (КС) лантанидов демонстрируют непревзойденную чистоту цвета OLED из-за чрезвычайно узких эмиссионных полос, характерных для ионов лантанидов. Однако в данный момент эффективность и яркость OLED на основе комплексов лантанидов существенно уступает аналогам на основе КС иридия и материалам TADF. В нашей научной группе было выявлено, что определяющим фактором, ограничивающим максимальные характеристики в OLED, являются большие времена жизни возбуждённого состояния ионов лантанидов в КС [1].

На примере эмиттеров других классов было продемонстрировано, что введение наночастиц золота (AuGNP) в дырочно-инжектирующий слой PEDOT:PSS позволяет увеличить эффективность OLED в результате возникновения следующих эффектов: поверхностного плазмонного резонанса, усиления выхода света из устройства и улучшения инжекции носителей заряда (Рис. 1б). Целью данной работы стало изучение влияния плазмонного резонанса на время жизни возбуждённого состояния и электролюминесцентные свойства КС тербия. Объектами исследования стали комплексы тербия Tb(czb)3 и Tb(czb)3TDZP (Рис. 1а), где в качестве анионного лиганда был выбран ароматический карбоксилат (czb-), обладающий высокой дырочной подвижностью [2], а в качестве нейтрального лиганда – TDZP, комплексы тербия с которыми показали рекордную яркость в OLED [3].

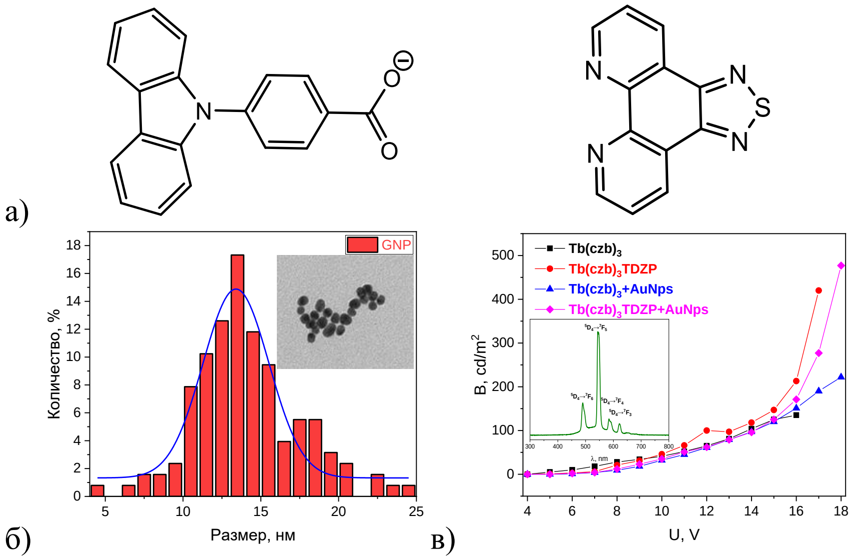


Рис.1. а) Структурные формулы лигандов: czb- и TDZP; б) Распределение размера и ПЭМ изображение (во вкладке) наночастиц золота; в) ВЯХ и спектр электролюминесценции (во вкладке) полученных OLED

Комплексы Tb(czb)$_3$ и Tb(czb)$_3$TDZP были синтезированы по обменной методике. Состав полученных соединений подтверждали по совокупности методов РФА, ЯМР-спектроскопии, ТГА и ИК-спектроскопии. Изучение фотолюминесцентных свойств показало, что оба полученных комплекса обладают эффективной фотолюминесценцией, характерной для иона тербия. Квантовый выход фотолюминесценции комплекса Tb(czb)3 составил 37%, а время жизни – 0,73 мс, в то время как для Tb(czb)3TDZP – 16% и 0,49 мс соответственно. Видно, что введение нейтрального лиганда снижает квантовый выход, но также и время жизни возбуждённого состояния.

Наночастицы золота были синтезированы по методу Френса, они представляют собой однородные сферообразные структуры, средний размер которых по результатам просвечивающей электронной микроскопии составляет 13,5±2 нм (Рис. 1б).

Полученные КС тербия были протестированы в качестве эмиссионного слоя (EML) в OLED с гетероструктурой ITO/PEDOT:PSS/poly-TPD/EML/TPBi/LiF/Al. Максимальная яркость OLED на основе комплекса Tb(czb)3 достигла 140 кд/м2 при 16 В, а для Tb(czb)3TDZP – 420 кд/м2 при 18 В (Рис. 1в). Для изучения влияния плазмонного резонанса синтезированные AuGNP в слой PEDOT:PSS. Введение наночастиц золота позволяет увеличить максимальную яркость светодиода на основе Tb(czb)3 до 220 кд/м2, а на основе Tb(czb)3TDZP – до 480 кд/м2. Комплекс Tb(czb)3TDZP с наночастицами золота в смеси с PEDOT:PSS продемонстрировал рекордную яркость для OLED на основе комплексов тербия, эмиссионный слой которого нанесён из раствора.

[1] V. V Utochnikova et al., “Identifying lifetime as one of the key parameters responsible for the low brightness of lanthanide-based OLEDs,” Dalt. Trans., vol. 50, no. 37, pp. 12806–12813, 2021, doi: 10.1039/D1DT02269E.

[2] M. I. Kozlov et al., “Towards efficient terbium-based solution-processed OLEDs: Hole mobility increase by the ligand design,” J. Alloys Compd., vol. 887, p. 161319, 2021, doi: 10.1016/j.jallcom.2021.161319.

[3] E. Girotto et al., “Efficient terbium complex based on a novel pyrazolone derivative ligand used in solution-processed OLEDs,” J. Lumin., vol. 208, no. September 2018, pp. 57–62, 2019, doi: 10.1016/j.jlumin.2018.12.027.

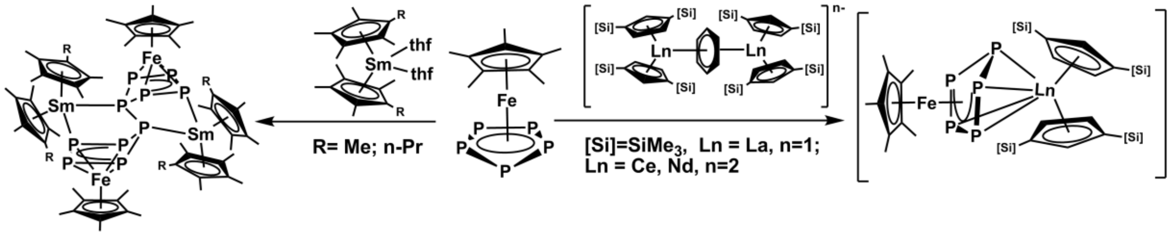
e-mail: yugladkikh1246@gmail.com

Hetero-d/f-metallic polyphosphide complexes containing lanthanides of the second half of the series

A.D. Demkin[a], T.S. Sukhikh[a], S.N. Konchenko[a,b]

[a]Nikolaev Institute of Inorganic Chemistry SB RAN, Novosibirsk, RUSSIA
[b]Novosibirsk State University, Novosibirsk, RUSSIA

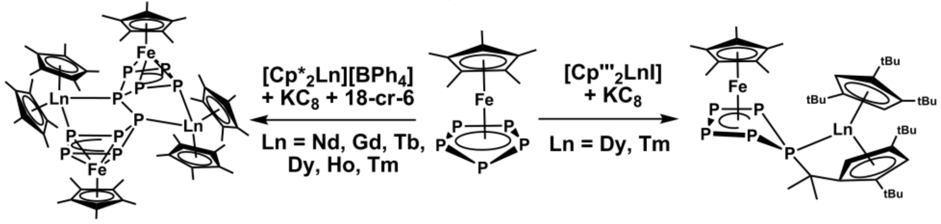
Lanthanide polyphosphide complexes, despite the fact that they are promising starting compounds for the preparation of functional materials [1], are still rather rare examples of such a combination of elements. The general method for synthesis these compounds is the reduction of phosphorus-containing substrates with Ln(II) complexes. In works [2,3] it was shown that the reduction of [Cp*FeP$_5$] with cyclopentadienyl complexes of Ln(II) leads to the formation of heterometallic *d/f* polyphosphide complexes of various nuclearity (Scheme 1).



Scheme 1. Methods for the synthesis of polyphosphide complexes of lanthanides.

However, to date, polyphosphide complexes have been obtained only for the first half of the lanthanide series. In an attempt to expand the number of involved lanthanides, we studied reactions of [Cp*FeP$_5$] with [Cp*$_2$Ln][BPh$_4$] (Ln = Nd, Gd, Tb, Dy, Ho, Tm) within the reduction by KC$_8$, as well as with “[Cp‴$_2$Ln]” (Ln = Dy, Tm; Cp‴= $C_5H_2{}^tBu_3$) generated in solution by reduction of [Cp‴$_2$LnI].

It was found that the reactions of [Cp*FeP$_5$] with [Cp*$_2$Ln][BPh$_4$]/KC$_8$ lead to reductive dimerization of P_5^-. As a result, a number of hetero-*d/f*-metallic complexes [{Cp*$_2$Ln}$_2$(P$_{10}$)(FeCp*)$_2$] were obtained (Scheme 2, left side). The reactions of “[Cp‴$_2$Ln]” with [Cp*FeP$_5$] lead not to reduction, but to a nucleophilic attack of the P$_5$ ring by the carbon atom of the deprotonated *tert*-butyl substituent in Cp‴ (Scheme 2, right side). The report discusses the features of the studied chemistry and structures of the obtained complexes.



Scheme 2. The synthesis of polyphosphide complexes of the second half of lanthanide series.

[1] A. T. Rowley and I. P. Parkin, J. Mater. Chem., **1993**, 3, 689-692
[2] T. Li, M. T. Gamer, M. Scheer, S. N. Konchenko and P. W. Roesky, Chem. Commun., **2013**, 49, 2183-2185
[3] N. Reinfandt, N. Michenfelder, C. Schoo, R. Yadav, S. Reichl, S. N. Konchenko, A. N. Unterreiner, M. Scheer and P. W. Roesky, Chem. – A Eur. J., **2021**, 27, 7862-7871

Acknowledgements – Authors thank RFBR (projects 19-03-00568) and Ministry of Education and Science of Russian Federation for financial support.

e-mail: demag@niic.nsc.ru

Lanthanide complexes based on substituted 1,2,3-triazole

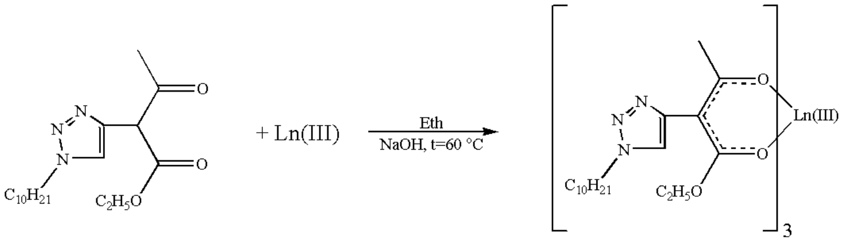
M.V. Zimina[a], N.M. Selivanova[a], V.E. Semenov[b], Y.G. Galyametdinov[a,c]

[a]*Kazan National Research Technological University, Kazan, RUSSIA*
[b]*A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, RUSSIA*
[c]*E.K. Zavoisky Kazan Institute of Physics and Technology, RUSSIA*

The triazole compounds are of significant interest due to their physical - chemical properties: ease of bonding with biomolecules, organic and inorganic compounds, as well as high biological activity. Triazoles and their derivatives are widely used in supramolecular, coordination chemistry and biochemistry. Many compounds of the triazole class exhibit various biological activities, such as antibacterial, antiviral, antifungal, antituberculous, anticonvulsant, anti-inflammatory, antitumor. High coordination potential of the triazoles allow use their as bidentant ligands in click chemistry to obtain metal complexes and functionalize biomolecules.

Lanthanide ions Ln(III), due to their unique optical properties, are widely used in molecular electronics, OLEDs, as bioprobes, paramagnetic probes, sensors and bioindicators. The formation and optimization the sensory function of the lanthanide complexes, is possible at the expense of the selection organic ligand and mixed ligand complexation [1,2]. In this aspect, substituted triazoles are of interest as an organic ligands for Ln(III) complexes with high potential for biomedical applications.

The purpose of this work was to synthesize the lanthanide complexes Ln = (La, Dy, Tb, Gd) with 1-decyl-4- (ethyl 3-oxobutaonate-2-yl) -1,2,3-triazole.
Previously the solubility of the substituted triazole for further development of the lanthanide complexes was evaluated. The solvents were selected based on their polarity. The ligand with a 1,3-diketone unit dissolves in H_2O, CH_3OH, $C_2H_6O_2$, C_2H_5OH at 25° C. The solubility was investigated according to polarization optical microscopy. The scheme of the synthesis lanthanide complexes based on substituted triazole shown in scheme 1.



Scheme 1. The scheme of the synthesis Ln(III) lanthanide complexes based on substituted 1,2,3-triazole

The intermolecular interactions of the obtained complexes evaluated by FTIR spectroscopy. However, the interpretation of the IR spectra is difficult due to the superposition the vibration bands of the ligand individual groups coordinated by the Ln(III) ion, in particular the oscillations C=O «free» β-diketone at 1558-1600 cm^{-1}. The appearance of the C-C bond absorption band at 1521 cm^{-1} and at 1400 cm^{-1} at the IR spectra the obtained complex, indicates the complexation.

Thus, a new complexes of lanthanides have been synthesized, which, bearing in mind bioactivity of the ligand, can be use as potential objects for biomedical use.

[1] N. M. Selivanova, Y. G. Galyametdinov, *Chemosensors*, **2021**. *9 (6)*, 134.
[2] N. M. Selivanova, K. Vasilieva, Y.G. Galyametdinov, *Luminescence*, **2014**, *29 (3)*, 202-210.

Acknowledgements – This research was funded by Russian foundation for basic research, grant number 20-03-00620.

e-mail: marina-ls@list.ru

Anisometric Eu(III) and Tb(III) complexes as thermosensitive luminescent materials

R.M. Ziyatdinova[a], A.A. Leshcheva[a], A.S. Krupin[a], D.V. Lapaev[b], A.A. Knyazev[a], Y.G. Galyametdinov[a,b]

[a]*Federal State Budgetary Educational Institution of Higher Education «Kazan National Research Technological University»*
[b]*Zavoisky Physical-Technical Institute is a separate structural subdivision of the Federal State Budget Scientific Institution «Federal Research Centre «Kazan Scientific Centre of the Russian Academy of Sciences»*

Among non-contact methods, temperature measurement is more interesting because of several advantages over traditional thermometers, such as rapid response, high sensitivity, superior spatial and temporal resolution, etc. [1]. Intensive luminescence, long service life and low environmental sensitivity are the main characteristics required for a temperature sensor to operate. B-diketonate complexes Eu^{3+} and Tb^{3+} due to their unique properties, meet these criteria [2]. Unfortunately, relatively low photostability in UV irradiation is a major disadvantage that prevents the use of film materials based on the β-diketonate complexes Eu^{3+} and Tb^{3+} as working elements for fluorescent temperature sensors. Therefore, the creation of photo and thermostable materials with a high sensitivity of luminescence in a wide range of temperatures is a current task.

In this work photostable fluorescent thermosensors based on mesogenic complexes Eu^{3+} and Tb^{3+} were obtained and described (Fig. 1).

The proposed sensors are vitrified films of Eu^{3+} or Tb^{3+} complexes (depending on the ranges of determined temperatures) obtained by melting between two quartz substrates. Film materials have high transmission (more than 90%) in the entire visible and near-IR wavelength range (450-800 nm) and effectively absorb light in the UV region (Fig. 2a).

The Eu^{3+} and Tb^{3+} complexes exhibit intense red and green photoluminescence at a wavelength of 612 nm by irradiation with UV light (Fig. 2b) and 545 nm (Fig. 2c), respectively.

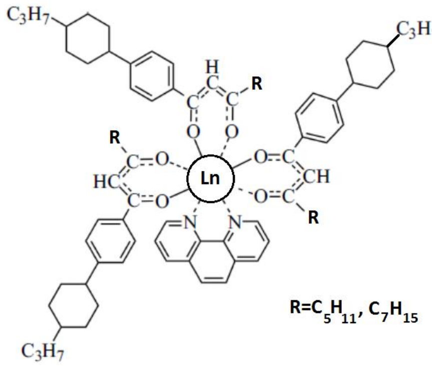
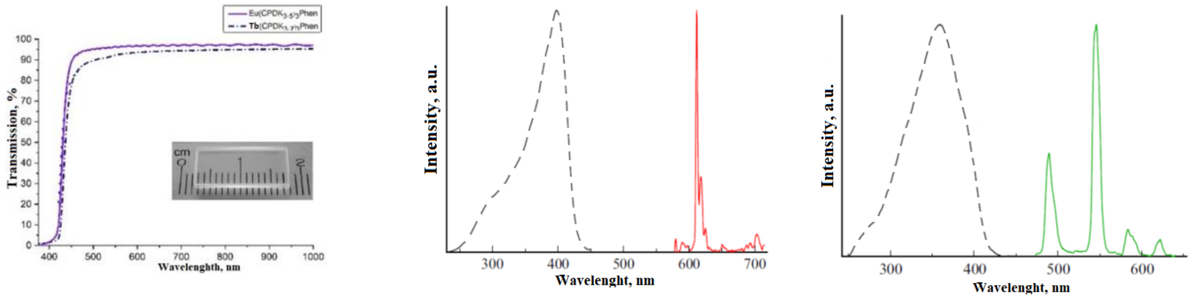


Fig. 1 – Structural formulas of β-diketonate complexes Ln(III), Ln=Eu, Tb



a b c

Fig. 2 – Spectra of transmission (a) and excitation (bar), luminescence (solid line) films of Eu^{3+} (b) and Tb^{3+} (c) complexes

The influence of temperature on optical properties of vitrified films based on Eu^{3+} and Tb^{3+} complexes was studied (Fig. 3).

The sensors have a high sensitivity of luminescence to a temperature of -6.5 μs K^{-1} in the range 298-348 K for the Eu^{3+} complex and -3.3 μs K^{-1} in the range 143-253 K for the Tb^{3+} complex and are capable of reversing the intensity and attenuation time of Eu^{3+} and Tb^{3+}.

The resultant materials are photo- and thermostable and withstand multiple cycles of heating and cooling (Fig. 4).

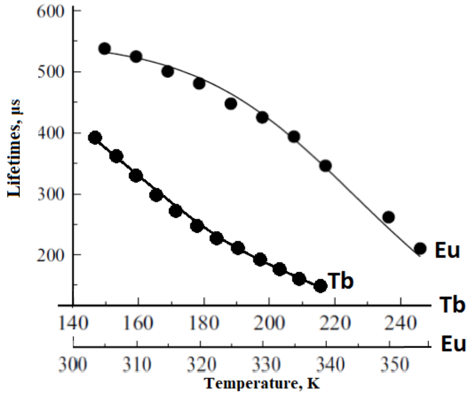


Fig. 3 – Temperature dependence of lifetime on 612 nm and 545 nm films of Eu^{3+} (a) and Tb^{3+} (b) complexes, respectively

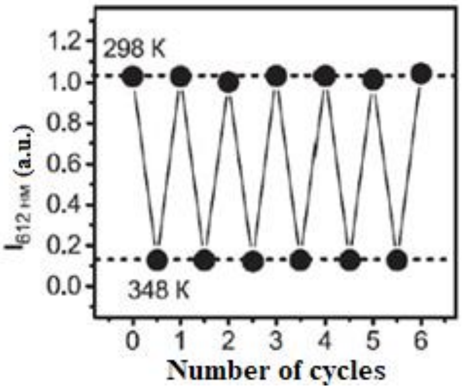


Fig. 4 – Invertible changes of τ_{att}. luminescence (when excited by λ_{exc}=337 nm) in successive heating and cooling cycles

[1] Zhao Y., Wang X., Zhang Y., Li Y., Yao X. 2020. Journal of Alloys and Compounds. 2020. V. 817. P. 152691.
[2] Lapaev D.V., Nikiforov V.G., Lobkov V.S., Knyazev A.A., Ziyatdinova R.M., Galyametdinov Yu.G., 2020, Journal of Materials Chemistry C. №18. 6273-6280.

Acknowledgments: Work carried out with financial support of RSF, grant №18-13-00112-P

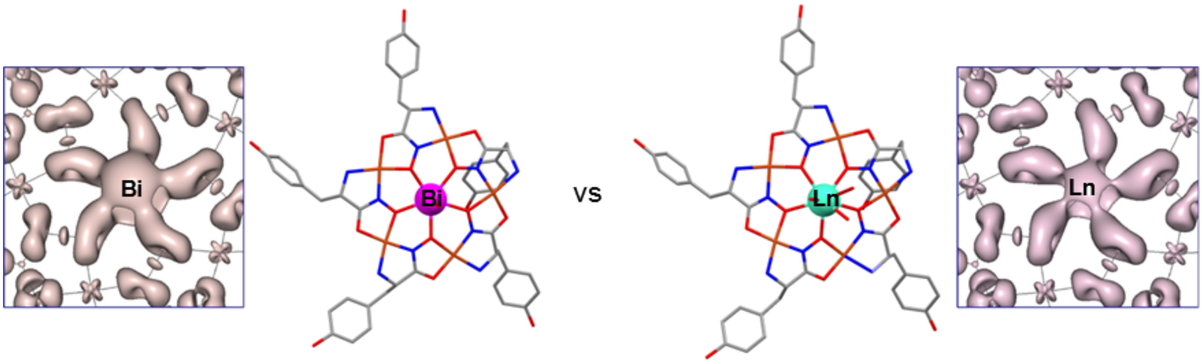
e-mail: ruzannochka95@mail.ru

Polynuclear Metallamacrocyclic Complexes of Bismuth(III) and Lanthanides(III): Similar But Not Equal

M.A. Katkova, M.S. Muravyeva, R.V. Rumyantcev, G.Y. Zhigulin, S.Yu. Ketkov

G.A. Razuvaev Institute of Organometallic Chemistry RAS, Nizhny Novgorod, RUSSIA

Among numerous examples of the polynuclear metallamacrocyclic compounds named as metallacrowns, the popularity of Ln(III)-Cu(II) 15-MC-5 complexes is largely due to their fascinating architectures and potential applications. A relevant aspect of these structures is that the metallamacrocyclic scaffold prefers early lanthanides characterized by the same charge and similar ionic radii as Bi^{3+}. Based on this analogy, we have designed and isolated novel examples of the Bi(III)-Cu(II) metallamacrocyclic complexes of the 15-MC-5 type [1,2]. The single crystal X-ray diffraction measurements confirmed the classic metallamacrocyclic 15-MC-5 configuration with the neutral ring consisting of five [Cu(II)-N-O] repeating units, and the five hydroximate oxygen atoms encapsulating the Bi^{3+} ion within the central cavity. Scalar relativistic DFT investigations predict similarity between the molecular structures of the model bismuth(III) and lanthanum(III) 15-metallacrowns-5. At the same time analysis of the electronic structures reveals stronger donor-acceptor interactions between the central ion and the metallamacrocycle in the case of the lanthanum analogue (Scheme 1).



Scheme 1. Deformation Electron Density isosurfaces at 0.01 a.u. in the region of the central ion and the five oxime oxygen atoms for $[Bi(15\text{-}MC_{Cu(II)Tyrha}\text{-}5)]^{3+}$ (left) and for $[La(15\text{-}MC_{Cu(II)Tyrha}\text{-}5)]^{3+}$ (right). In the center: top views of the X-ray structures of the Bi(III) [2] and Gd(III) [3]complexes. All hydrogen atoms, uncoordinated NO_3^- and solvate water molecules are omitted for clarity.

[1] G.S. Zabrodina, M.A. Katkova, E.V. Baranov, G.Yu. Zhigulin, S.Yu. Ketkov, *Macroheterocycles*, **2019**, *12*, 300-306.
[2] M.A. Katkova, G.Y. Zhigulin, R.V. Rumyantcev, G.S. Zabrodina, V.R. Shayapov, M.N. Sokolov, S.Y. Ketkov, *Molecules **2020**, 25, 4379.*
[3] A.D. Cutland, R.G. Malkani, J.W. Kampf, V.L. Pecoraro, *Angew. Chem. Int. Ed*., **2000**, *39*, 2689–2692.

Acknowledgements - This work was supported by the Russian Science Foundation (project 18-13-00356).

e-mail: marina@iomc.ras.ru

Металлоидные кластеры германия как лиганды в комплексах двухвалентных лантаноидов

С.В. Клементьева

Институт неорганической химии Университета Тюбингена, ГЕРМАНИЯ

Анионные металлоидные кластеры германия $Ge_9Hyp_3^-$ (**1**) and $Ge_9Hyp_2^{2-}$ (**2**, Hyp = $Si(SiMe_3)_3$), [1-3] в которых кластерное ядро окружено пространственно экранированными заместителями, стабильны в инертных условиях и имеют достаточно хорошую растворимость в органических растворителях в отличие от большинства металлических кластеров, а потому представляют несомненный интерес для изучения реакционной способности таких объектов, лежащих на стыке между молекулярными соединениями и конденсированными фазами. В частности, благодаря тому, что кластерное ядро лишь частично экранировано объемными лигандами, и некоторые грани открыты для взаимодействия, возможны реакции комплексообразования, что было ранее показано для переходных металлов. [4-7]

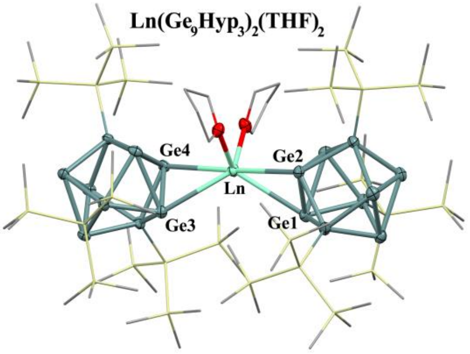


Рис. 1 Молекулярная структура $[(THF)_2Ln(Ge_9Hyp_3)_2]$ (Ln = Eu, Sm)

Недавно нам впервые удалось получить комплексы двухвалентных лантаноидов с металлоидными германиевыми кластерами в качестве лигандов. Соединения $[(THF)_2Ln(Ge_9Hyp_3)_2]$ (Ln = Eu, Sm) (Рис. 1) были выделены из реакции соответствующих дийодидов $(THF)_2LnI_2$ с двумя эквивалентами KGe_9Hyp_3.[8] Необходимо отметить, что получить комплекс иттербия в аналогичных условиях не удается, ввиду существенно меньшего размера иона Yb^{2+}. Реакции с менее экранированным германиевым кластером **2** приводят к соединениям с общей формулой $[(THF)_5Ln(Ge_9Hyp_2)]$ (Ln = Eu, Sm, Yb), в которых кластерный лиганд координирован различным образом на металл. Так в комплексе иттербия наблюдается η^1-координация, а в комплексах европия и самария как η^2- так и η^3-координация металлоидного кластера германия **2**. Для всех новых соединений самария и европия исследованы магнитные свойства, а для комплексов европия измерены спектры люминесценции, однозначно подтверждающие наличие двухвалентных лантаноидов.

[1] A. Schnepf, *Angew. Chem., Int. Ed.* **2003**, 42, 2624. [2] F. Li, S. C. Sevov, *Inorg. Chem.* **2012**, 51, 2706. [3] O. Kysliak, A. Schnepf, *Dalton Trans.* **2016**, 45, 2404. [4] O. Kysliak, C. Schrenk, A. Schnepf, *Chem. Eur. J.* **2016**, 22, 18787. [5] F. Henke, C. Schenk, A. Schnepf, *Dalton Trans.* **2009**, 9141. [6] C. Schenk, F. Henke, G. Santigo, I. Krossing, A. Schnepf, *Dalton Trans.* **2008**, 4436. [7] C. Schenk, A. Schnepf, *Angew. Chem., Int. Ed.* **2007**, 46, 5314. [8] S. V. Klementyeva, C. Schrenk, M. Zhang, M. M. Khusniyarov, A. Schnepf, *Chem. Comm.* **2021**, 57, 4730.

Благодарности: Выражаю мою искреннюю благодарность профессору А. Шнепфу за возможность выполнять проект в его рабочей группе и Фонду Александра фон Гумбольдта за предоставленную стипендию.

e-mail: sklementyeva@yahoo.com

Люминесцентная термометрия на основе нанокристаллических частиц, легированных редкоземельными ионами

И.Е. Колесников,[а] Д.В. Мамонова[а], Е.В. Афанасьева[б]

[а]*Санкт-Петербургский государственный университет*
[б]*Санкт-Петербургский политехнический университет Петра Великого*

Температура является одним из фундаментальных параметров, характеризующих системы, процессы и явления. Понятие температуры хорошо установлено с точки зрения термодинамики и используется для характеризации различных систем (газ, жидкость, твердые фазы, микро- и макрообъекты) в термодинамическом равновесии. Точное измерение температуры необходимо для надежной характеризации и контроля процессов в различных областях от биологии и медицины до промышленного производства. Необходимо отметить, что прямое определение температуры невозможно, однако ее можно измерить путем контроля различных характеристик, таких как объем, давление, проводимость, которые монотонно коррелируют с изменением температуры. Все методы измерения температуры можно разделить на три категории в зависимости от характера контакта между датчиком и объектом анализа: 1) контактные; 2) полуконтактные и 3) бесконтактные.

Быстрый технический прогресс и ограничения существующих контактных термометров для небольших систем субмикронного масштаба требуют разработки новых бесконтактных температурных сенсоров с микро- и наноразмерным пространственным разрешением. Среди бесконтактных спектроскопических методов определения температуры люминесцентная термометрия является одним из наиболее перспективных. Этот метод обеспечивает измерения температуры на основе мониторинга температурной зависимости излучения люминофора (например, интенсивности люминесценции (или соотношения интенсивностей полос люминесценции - LIR), положения спектральной линии, ширины полосы, времени жизни возбужденного состояния и поляризации излучения). Люминесцентная термометрия сочетает в себе высокую относительную тепловую чувствительность (> 1% K^{-1}) и пространственное разрешение (<10 мкм), а также быстрый сбор данных (< 1 мс). Кроме того, люминесцентная термометрия может успешно использоваться в биологических объектах и в сложных условиях окружающей среды (например, в сильных электромагнитных полях).

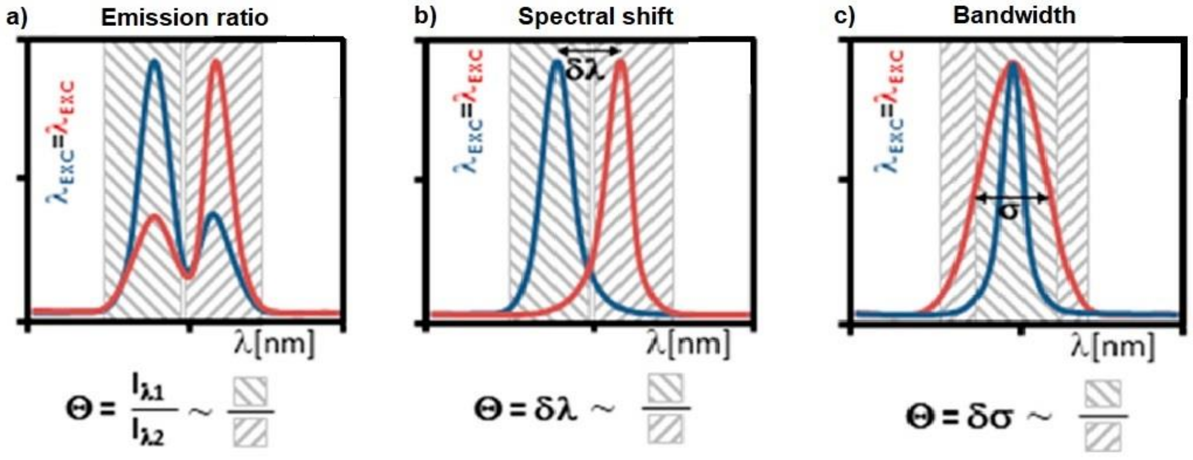


Рис. 1. Различные способы реализации люминесцентной термометрии.

Материалы, легированные редкоземельными ионами (РЗИ), являются стабильными узкополосными люминофорами, покрывающими большую часть спектра, с, как правило, высокими квантовыми выходами люминесценции. В последнее десятилетие были изучены термометры на базе хелатных комплексов, металлоорганических каркасов, полимеров, органо-неорганических гибридов и неорганических наночастиц с РЗИ, охватывающие широкий диапазон температур от криогенных (T <100 K) до технологических (до 1200 K). Данная работа посвящена исследованию принципов люминесцентной термометрии на основе оксидных нанокристаллических частиц, активированных различными РЗИ В качестве температурно-чувствительных люминесцентных параметров, было использовано соотношение интенсивностей люминесцентных полос, спектральное положение линий люминесценции и ширина полосы люминесценции (Рис. 1).

Благодарности: Работы выполнена при поддержке гранта Российского Научного Фонда (№ 21-79-10018). Экспериментальные исследования выполнены на оборудовании Научного Парка СПбГУ в РЦ «Оптические и лазерные методы исследования вещества», РЦ «Рентгенодифракционные методы исследования» и «Междисциплинарном ресурсном центре по направлению "Нанотехнологии"».

e-mail: ie.kolesnikov@gmail.com

Аналитические возможности метода атомной эмиссионной спектроскопии микроволновой индуцированной плазмы при определении редкоземельных элементов.

Е.К. Конькова, Е.О. Чибирев, А.Р. Гарифзянов

Казанский (Приволжский) федеральный университет, Химический институт им. А.М. Бутлерова, г. Казань

Методы атомной спектроскопии являются самыми распространёнными методами анализа редкоземельных элементов (РЗЭ) в минералах и рудах. Наиболее часто для анализа РЗЭ применяется атомно-эмиссионная спектроскопия индуктивно-связанной плазмы благодаря низким пределам обнаружения для большинства элементов в сравнении с другими способами определения содержания металлов, а также быстроте анализа. Однако этот метод является достаточно дорогостоящим, поэтому немаловажной задачей является поиск более доступных методов анализа, не уступающих при этом в эффективности. В этом отношении представляется перспективным использование атомной эмиссионной спектроскопии микроволновой индуцированной плазмы (АЭС МИП). Этот относительно новый вариант эмиссионной спектроскопии может являться более доступной альтернативой атомно-эмиссионной спектроскопии индуктивно-связанной плазмы (АЭС ИСП) за счёт более низкой стоимости спектрометра и меньших эксплуатационных расходов при использовании азота в качестве плазмообразующего газа вместо аргона.

В настоящей работе исследованы аналитические возможности этого варианта эмиссионной спектроскопии для решения сложной аналитической задачи – определения РЗЭ при совместном присутствии. Измерения проводились на приборе Agilent 4100M.

При выборе аналитических линий для исследуемых элементов было установлено, что для всех РЗЭ в азотной микроволновой плазме наибольшая интенсивность наблюдается для резонансных линий однократно ионизированным атомам. В частности, для **La*(II)*** – 394,9 нм, **Ce*(II)*** – 446,0 нм, **Gd*(II)*** – 342,2 нм, **Er*(II)*** - 337,3 нм.

Градуировочные зависимости, построенные при выбранных длинах волн, приведены на рис. 1. По этим данным были рассчитаны пределы обнаружения (ПО) с использованием уравнения:

$$Cпо = \frac{3\sigma}{I} \times C$$

Для расчёта среднеквадратического отклонения σ был измерен аналитический сигнал фона при той же длине волны, при которой измерялся аналитический сигнал элемента.

Табл. 1. Рассчитанные величины ПО (мг/л) методом АЭС МИП в сравнении с ПО методом АЭС ИСП [1]

	Лантан	Церий	Эрбий	Гадолиний
Среднеквадратическое отклонение σ	28	3,8	68	16
ПО АЭС МИП	$2{,}8\cdot10^{-3}$	$2{,}9\cdot10^{-3}$	$1{,}2\cdot10^{-2}$	$1{,}1\cdot10^{-3}$
ПО АЭС ИСП	$4{,}1\cdot10^{-3}$	$2{,}5\cdot10^{-2}$	$8{,}2\cdot10^{-3}$	$3{,}3\cdot10^{-3}$

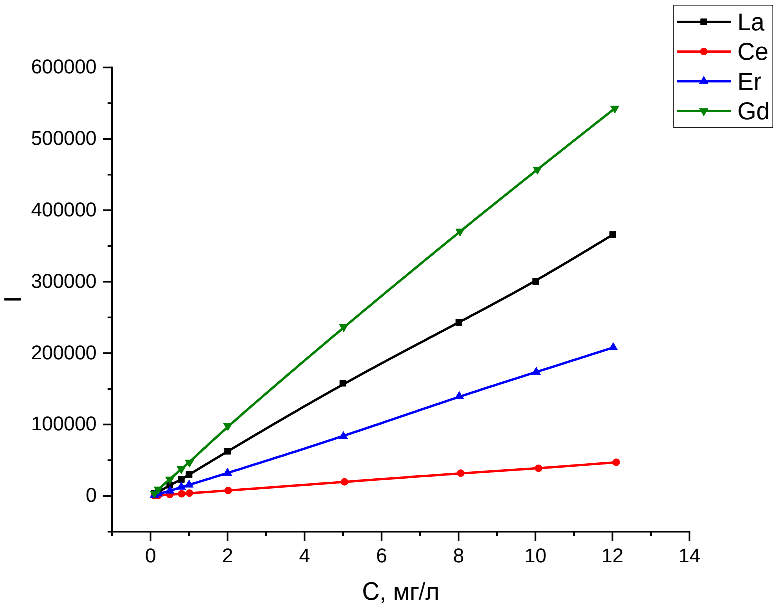


Рис. 1. Градуировочные зависимости интенсивности сигнала от концентрации (мг/л) для лантана, церия, эрбия и гадолиния.

Исходя из полученных результатов, можно сделать вывод о том, что метод АЭС МИП при определении РЗЭ по метрологическим характеристикам не уступает более дорогостоящему методу АЭС ИСП.

[1] Baghaliannejad R., Aghahoseini M., Amini M. K. Determination of rare earth elements in uranium materials by ICP-MS and ICP-OES after matrix separation by solvent extraction with TEHP // Talanta. – 2020. – V. 222. doi:10.1016/j.talanta.2020.121509

e-mail: redatushared@gmail.com

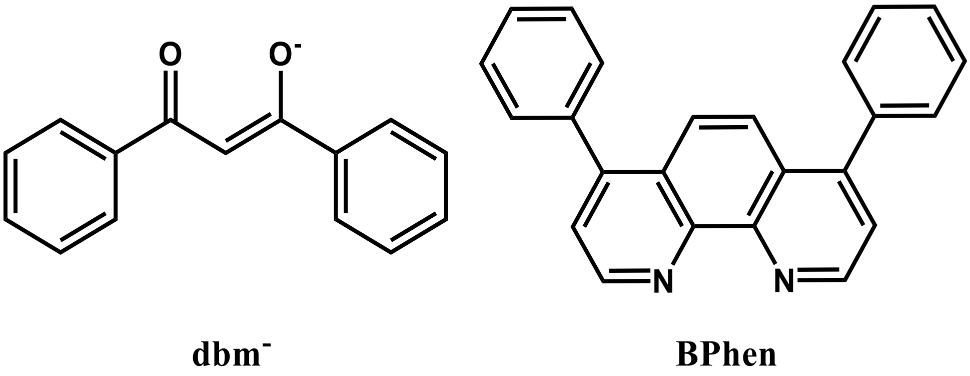
Dual red-NIR emissive OLED based on Eu-Yb bimetallic complexes for oximetry

A.I. Kornikov[a], M.I. Kozlov[b], V.V. Utochnikova[a]

[a]*Lomonosov Moscow State University, Chemistry Department, Moscow, RUSSIA*
[b]*Lomonosov Moscow State University, Department of Materials Science, Moscow, RUSSIA*

Lanthanide coordination compounds are promising materials for emission layers of organic light-emitting diodes (OLEDs), since lanthanide ions, due to their special electronic structure, demonstrate narrow luminescence bands. One of the forward-looking applications of OLED is oximetry, a non-invasive spectrophotometric method of determining the degree of oxygen saturation in the blood. However, a big challenge to OLED technology for oximetry is obtaining OLEDs with luminescence in both visible and near-infrared ranges. The use of bimetallic rather than separate monometallic complexes will allow creating an oximeter, which uses one light-emitting diode instead of two. Even though europium and ytterbium ions have ideal narrow luminescence bands for oximetry, lanthanide-based oximeters have not been obtained yet. Thus, it was proposed to study the luminescent properties of bimetallic complexes of europium and ytterbium, possessing two emission bands in both the red and infrared regions of the spectrum.

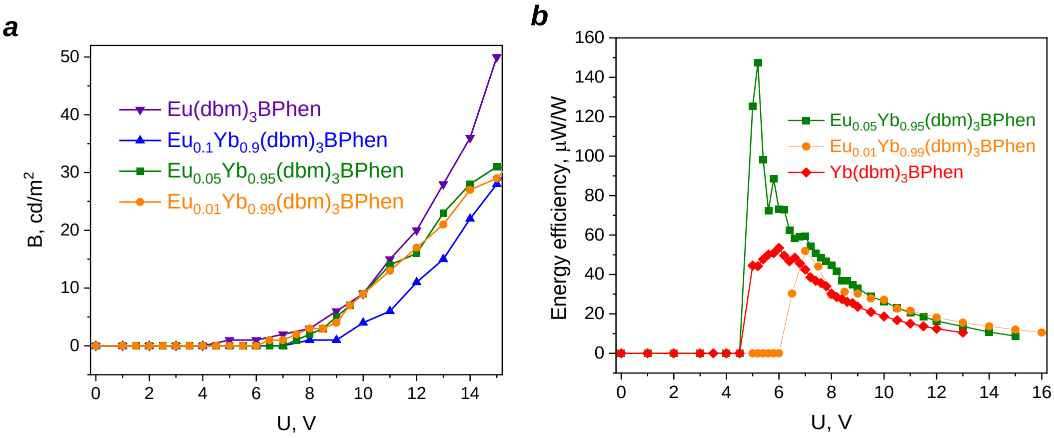
Bathophenanthroline (BPhen) (Scheme 1), which is capable of sensitizing Eu^{3+} ion luminescence and providing high electron mobility, was chosen as a neutral ligand [1]. The dibenzoylmethanate anion (dbm^-) (Scheme 1) was chosen as the anionic ligand (Scheme 1), since its europium complex shows intense luminescence. Thus, the objects of the study are mixed-ligand complexes $Eu_xYb_{1-x}(dbm)_3BPhen$, as well as $Eu_xLa_{1-x}(dbm)_3BPhen$ and $La_xYb_{1-x}(dbm)_3BPhen$ (x = 0; 0.01; 0.02; 0.05; 0.1; 1). The aim of this work was to obtain an efficient OLED with dual emission of europium and ytterbium and to study the energy transfer from the europium ion to the ytterbium ion.



Scheme 1. Structural formulas of the ligands

The composition of the obtained compounds was determined by the thermogravimetric analysis, IR spectroscopy, ^1H NMR spectroscopy, and scanning electron microscopy with EDX. The quantum yields of the ytterbium complexes photoluminescence reached 0,9%, which is rather high, and the individual europium complex demonstrated a quantum yield of 32%. The decrease in the observed lifetimes of europium with an increase in the fraction of ytterbium indicates the presence of energy transfer from the europium ion to the ytterbium ion in the obtained complexes. The obtained complexes $Eu_xYb_{1-x}(dbm)_3BPhen$ (x = 0; 0.01; 0.05;

0.1; 1) were tested in OLEDs, which demonstrated intense electroluminescence in the visible and near-infrared regions, as well as high luminance and energy efficiency values (Scheme 2). The energy efficiency of $Eu_{0.05}Yb_{0.95}(dbm)_3BPhen$ reached 147 μW/W, which is one of the highest values for ytterbium-based OLED. Thus, complex $Eu_{0.05}Yb_{0.95}(dbm)_3BPhen$ is a promising compound for applications in oximetry.



Scheme 2. a) Luminance and b) energy efficiency of the OLED with heterostructure ITO/PEDOT:PSS/poly-TPD/$\mathbf{Eu_xYb_{1-x}(dbm)_3(BPhen):CBP}$/TPBi/LiF/Al.

[1] Kozlov M.I. et al. On the development of a new approach to the design of lanthanide-based materials for solution-processed OLEDs // Dalton Trans., 2019, 48(46), 17298–17309.

e-mail: andrey.i.kornikov@gmail.com

Термоэлектрические свойства твёрдых растворов $CuCr_{0.99}Ln_{0.01}S_2$ (Ln = La...Lu)

Е.В. Коротаев

Институт неорганической химии им. А.В. Николаева СО РАН, Новосибирск

Твёрдые растворы на основе дисульфида меди-хрома $CuCr_{1-x}M_xS_2$ (M – редкоземельный или переходной металл, x=0-0.40) в настоящее время рассматриваются в качестве перспективных функциональных материалов для современной электроники. Данные материалы обладают рядом свойств, перспективных для практического применения: ионная проводимость, термоэлектрические свойства, магнитные свойства, колоссальное магнетосопротивление, фазовый переход металл-диэлектрик. Особо важной задачей является выявление взаимосвязи электронного строения и термоэлектрических свойств химических соединений с целью направленного синтеза наиболее перспективных функциональных материалов с требуемыми свойствами. Катионное замещение $CuCrS_2$-матрицы позволяет в широких приделах варьировать физические свойства $CuCr_{1-x}M_xS_2$. Исходная $CuCrS_2$-матрица является перспективным термоэлектрическим материалом, и демонстрирует высокие значения термоэлектрической добротности ZT~2. Вместе с тем, термоэлектрические свойства и электронное строение катион-замещенных твердых растворов $CuCr_{1-x}M_xS_2$ изучены недостаточно. В этой связи, в рамках представленной работы, было проведено комплексное исследование электронного строения широкого ряда катион-замещенных дисульфидов $CuCr_{0.99}Ln_{0.01}S_2$ (Ln = La…Lu), а также их термоэлектрических свойств в температурном диапазоне 100-740K. Было установлено, что переход порядок-беспорядок в $CuCrS_2$ и твердых растворах на его основе приводит к исчезновению энергетической щели вследствие локализации атомов в октаэдрических позициях, что приводит к возникновению аномалии на температурных зависимостях коэффициента Зеебека $CuCr_{0.99}Ln_{0.01}S_2$ при высоких температурах (T~700K). Увеличение коэффициента Зеебека при катионном замещении вероятно вызвано уменьшением общей плотности состояний у потолка валентной зоны, которое обусловлено следующими факторами:

– электронная плотность атомов лантаноидов вносит меньший вклад в общую плотность состояний, в сравнении с атомами хрома;

– парциальные вклады состояний атомов лантаноидов локализованы в глубине валентной зоны.

Наиболее сильные изменения термоэлектрических свойств наблюдаются для лантан-замещенной системы $CuCr_{0.99}La_{0.01}S$, что позволяет рассматривать данный состав наравне с исходным дисульфидом хрома-меди в качестве перспективного материала для термоэлектрических приложений.

Благодарности: Исследование выполнено за счёт гранта Российского научного фонда (проект № 19-73-10073)

e-mail: korotaev@niic.nsc.ru

Novel heteroleptic amido Ca(II) and Yb(II) NHC pincer complexes

I.V. Lapshin[a], A.A. Trifonov[a,b]

[a]*G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences,*
Tropinina str. 49, 603950 Nizhny Novgorod, RUSSIA
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences,*
Vavilova str.28, 119991 Moscow, RUSSIA

The molecular design of N-heterocyclic carbene ligands with new properties is an essential problem in the chemistry of coordination compounds. Important directions in alkaline-earth and lanthanide coordination chemistry are investigation of their NHC complexes, structural modification of carbene ligands and creation of polydentate NHC-ligands. In the present work, picolyl-functionalized carbene ligands and methods for the synthesis of NHC alkaline-earth and lanthanide complexes were studied. Two novel isostructural heteroleptic amido Ca(II) and Yb(II) complexes bearing NHC pincer ligand have been synthesized. Reaction of 1,3-bis(2-picolyl)-4,5-dimethylimidazolium chloride with $M(N(SiMe_3)_2)_2(THF)_2$ (M = Ca, Yb) led to in situ deprotonation of the imidazolium salt and activation of CH-acidic picolyl group resulting in the dearomatization of one of the pyridine rings and formation of $((NHC)CaN(SiMe_3)_2)_2$ (**2**) and $((NHC)YbN(SiMe_3)_2)_2$ (**3**). NMR and XRD studies of dimer pincer amido complexes **2** and **3** revealed their unique structural features, such as bridging carbenes, which is a first example in alkaline earth and lanthanide metals chemistry.

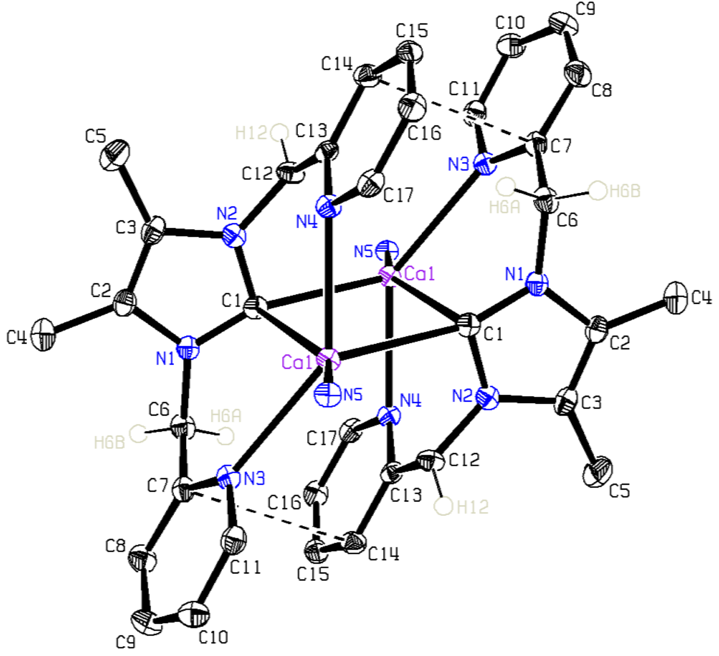


Fig. 1. The molecular structure of heteroleptic amido calcium complex **2**.

[1] I. V. Lapshin, A. V. Cherkasov and A. A. Trifonov, Russ Chem Bull, 2021, 70, 1957–1963.

Acknowledgements – Authors thank Russian Science Foundation (project 17-73-20262-П) for financial support.

e-mail: student.unn@gmail.com

Synthesis, structures, photoluminescent and magnetic properties of three-blade propeller homoleptic lanthanide complexes $[LnL_3](ClO_4)_3{\cdot}H_2O{\cdot}2MeCN$ (L = 2,6-bis(1-methyl-imidazol-2-y1)pyridine)

Dmitry M. Lyubov,[a,b] Albano N. Carneiro Neto,[c] Ahmad Fayoumi,[a]
Vladislav M. Korshunov,[d] Ilya V. Taydakov,[b,d] Yannick Guari,[e] Joulia Larionova,[e]
Luis D. Carlos,[c] Jérôme Long,[e,f] Alexander A. Trifonov[a,b]

[a] *IOMC RAS, Tropinina 49, 603950, Nizhny Novgorod, RUSSIA*
[b] *INEOS RAS, 28 Vavilova str., 119334, Moscow, RUSSIA*
[c] *Department of Physics and CICECO, University of Aveiro, PORTUGAL*
[d] *LPI RAS, Leninskiy Prospect 53, 119991, Moscow, RUSSIA*
[e] *ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, FRANCE.*
[f] *Institut Universitaire de France (IUF), Paris Cedex 05, FRANCE*

We report the synthesis, structures, magnetic and luminescent properties of a series of three-blade propeller homoleptic lanthanide complexes $[LnL_3](ClO_4)_3{\cdot}H_2O{\cdot}2MeCN$ (Ln = Eu (**1**), Tb (**2**), Dy (**3**), Er (**4**), Yb (**5**), Gd (**6**); L = 2,6-bis(1-methyl-imidazol-2-yl)pyridine). The Eu, Tb, and Dy analogues exhibit the characteristic lanthanide-based luminescence. Remarkably, the mixed Eu/Tb complex with a metal ratio (1:10) can be used as a ratiometric thermometer in the solid-state in the temperature range 130–220 K with the maximum value of $S_r = 5.3$ $\%{\cdot}K^{-1}$ within the range of 150–170 K. Theoretical calculations allow not only to model the luminescence properties of pure complexes but also rationalize the performances of the mixed Eu/Tb thermometers.

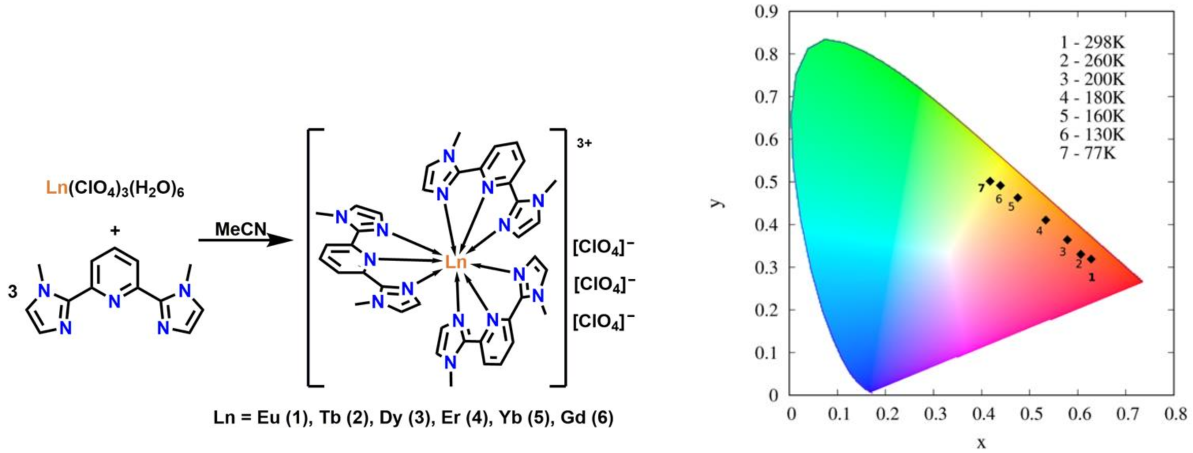


Fig. 1. a) synthesis of $[LnL_3](ClO_4)_3{\cdot}H_2O{\cdot}2MeCN$; b) CIE chromaticity coordinates for the $\mathbf{Eu_{0.09}Tb_{0.91}}$ mixed complex at different temperatures.

Acknowledgements – The financial support of the Russian Science Foundation is highly appreciated (project № 17-73-30036-П).

e-mail: trif@iomc.ras.ru; jerome.long@umontpellier.fr; luboffdm@rambler.ru

Synthesis and regularities of changing in thermodynamic properties for compounds based on bismuthates of rare earth elements

N.I. Matskevich[a], A.N. Semerikova[a], D.A. Samoshkin[a,b], S.V. Stankus[b], E.N. Tkachev[a], V.A. Trifonov[a]

[a]*Nikolaev Institute of Inorganic Chemistry SB RAN, Novosibirsk, RUSSIA*
[b]*Kutateladze Institute of Thermal Physics SB RAN, Novosibirsk, RUSSIA*

Compounds based on bismuthates of rare earth elements are promising materials for environmental technologies, in particular, for application in ceramic oxygen generators [1-2]. They have high ionic conductivity at medium temperatures. Doping by various elements is applied, in particular, by rare earth elements and transition metals to increase the stability of delta form of bismuth oxide.

In this work, we synthesized compounds based on bismuth oxide with following compositions: $Bi_{12.5}Er_{1.5}FeO_{22.5}$, $Bi_3Nb_{0.2}R_{0.8}O_{6.2}$ (R = Sm, Dy, Er, Lu). The compounds were synthesized by solid phase reactions from corresponding oxides. Characterization of compounds was performed by X-ray powder diffraction and confirmed individuality of compounds. Reaction and differential scanning calorimetry were used to determine thermodynamic properties [3-6]. The standard formation enthalpies for all compounds were determined by reaction calorimetry. Based on obtained standard formation enthalpies, the lattice enthalpies were calculated. The heat capacity of $Bi_3Nb_{0.2}R_{0.8}O_{6.2}$ compounds was measured in the temperature range of 320–1000 K using DSC 404 F1 calorimeter.

It was shown that standard formation enthalpy and lattice enthalpy of $Bi_{12.5}Er_{1.5}FeO_{22.5}$ compound were greater in absolute value than for analogous compound with cobalt, which was explained by smaller iron radius. It was shown that standard formation enthalpies and lattice enthalpies for $Bi_3Nb_{0.2}R_{0.8}O_{6.2}$ compounds were increasing in absolute value with decreasing rare earth element radius. This was explained using formulas derived by authors that related lattice enthalpies and formation enthalpies for low doping by rare earth elements with radii of rare earth elements. For all $Bi_3Nb_{0.2}R_{0.8}O_{6.2}$ compounds, the phase transitions were found at temperatures above 500 K, which was associated with transition of cubic phase to tetragonal one.

[1] R. Punn, A.M. Feteira, D.C. Sinclair, C. Greaves, *J. Am. Chem. Soc.*, **2006**, *128*, 15386-15387.
[2] N.I. Matskevich, Th. Wolf, C. Greaves, A.N. Bryzgalova, *J. Alloys Compd.*, **2014**, *582*, 253-256.
[3] N.I. Matskevich, V.N. Shlegel, A.N. Semerikova, D.A. Samoshkin, V.D. Grigorieva, S.V. Stankus, V.A. Kuznetsov, S.A. Ponomareva, V.P. Zaitsev, A.Yu. Novikov, *Dalton Transactions*, **2021**, *50*, 2130-2136.
[4] N.I. Matskevich, V.N. Shlegel, D.A. Samoshkin, S.V. Stankus, V.P. Zaitsev, V.A. Trifonov, *J. Chem. Thermodyn.*, **2022**, *165*, 106643.
[5] E.N. Tkachev, N.I. Matskevich, D.A. Samoshkin, V.N. Shlegel, S.V. Stankus, *Physica B: Phys. Cond. Matter*, **2021**, *612*, 412880.
[6] N.I. Matskevich, V.N. Shlegel, A.A. Chernov, D.A. Samoshkin, S.V. Stankus, V.D. Grigorieva, V.P. Zaitsev, E.N. Tkachev, *J. Phys.: Conf. Series*, **2021**, *2057*, 012048.

Acknowledgements – Authors thank RSF (projects 19-19-00095) for financial support.

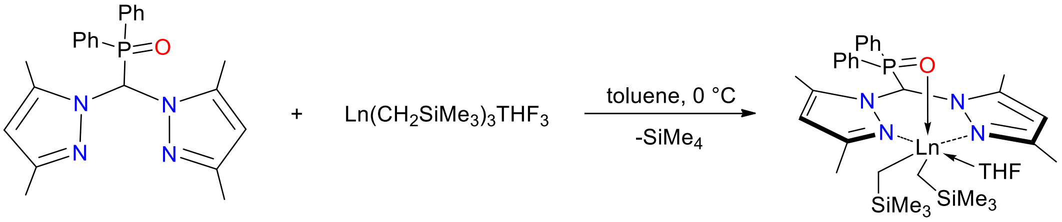
e-mail: nata.matskevich@yandex.ru

Synthesis, structure and catalytic activity of bis(alkyl) rare-earth-metal complexes bearing oxophosphine heteroscorpionate ligand

N. Yu. Rad’kova[a], A. A. Trifonov[a,b]

[a]*G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences,*
Tropinina str. 49, 603950 Nizhny Novgorod, RUSSIA
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences,*
Vavilova str.28, 119991 Moscow, RUSSIA

A tridentate bispyrazolylmethanide ligand containing oxophosphine Ph2P=O group at the methanide carbon atom $\mathrm{Pzl^{Me2}{}_2CHP(O)Ph_2}$ (**1**) was prepared according to previously published methods [1]. $\mathrm{Pzl^{Me2}{}_2CHP(O)Ph_2}$ (**1**) reacted with $\mathrm{Ln(CH_2SiMe_3)_3(THF)_2}$ (Ln = Sc, Y, Er, Lu) in toluene affording bis(alkyl) species $\mathrm{[Pzl^{Me2}{}_2CP(O)Ph_2]Ln(CH_2SiMe_3)_2THF}$ (Scheme 1).



Ln = Sc (63 %) 2, Y (70%) **3**, Er (72%) **4**, Lu (69%) **5**

Scheme 1. Preparation of bis(alkyl) complexes **2**–**5**.

The bis(alkyl) compounds **2**–**5** were evaluated as precatalysts for α-olefins and isoprene polymerization. The ternary systems **2**–**5**/Borate/$\mathrm{AliBu_3}$ were active in the polymerization of 1-nonene and isoprene under very mild conditions.

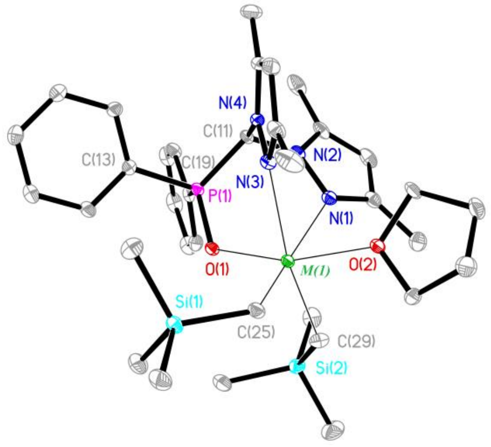


Fig. 1. Molecular structure of bis(alkyl) complexes **2**–**5**.

[1] S. Krieck, A. Koch, K. Hinze, C. Müller, J. Lange, H. Görls and M. Westerhausen, European Journal of Inorganic Chemistry, 2016, 2332–2348.

Acknowledgements – This work was supported by the Russian Science Foundation (Project No 20-73-10037).

e-mail: udilova.n@mail.ru

Перенос энергии и особенности строения координационных полиэдров некоторых жидкокристаллических комплексов лантаноидов(III) в возбужденном состоянии по данным квантово-химического моделирования

К.А. Романова, Ю.Г. Галяметдинов

Казанский национальный исследовательский технологический университет, Казань, РОССИЯ

Отличительные по своему строению жидкокристаллические (ЖК) комплексы лантаноидов(III) (Ln(III)) обладают комплексом уникальных оптических, ЖК и магнитных свойств, являются редким примером термостабильных полиморфных металломезогенов. Наличие иона Ln(III) не только обеспечивает им эффективные люминесцентные свойства, но также увеличивает анизотропию магнитной восприимчивости и оптическую чувствительность полифункциональных материалов на их основе. В то время, как ион Ln(III) подбирается вместе с лигандным окружением на стадии синтеза, строение получаемых координационных полиэдров, в том числе при фотовозбуждении молекул, установлено достаточно неоднозначно. В данной работе представлены результаты квантово-химического моделирования с использованием теории функционала плотности некоторых ЖК β-дикетонатных комплексов Ln(III) с основаниями Льюиса. Рассмотрена взаимосвязь между геометрическими параметрами молекул, особенностями строения координационных полиэдров комплексов и их ЖК свойствами. Установлены значения анизотропии геометрии молекул, при которых наблюдаются ЖК мезофазы. При этом основание Льюиса определяет наличие ЖК свойств у комплексов, а строение β-дикетонов и их заменителей - количество и тип мезофаз. Для оптимизированных геометрий комплексов в основном и триплетном возбужденном состоянии были рассчитаны параметры полиэдров Вороного-Дирихле. Установлено, что природа иона Ln(III) и его первой координационной сферы влияют на анизотропию свойств комплексов. Изменения параметров полиэдров при переходе в ряду от La(III) к Lu(III) коррелируют с изменениями в температурах их фазовых переходов. Рассчитанные энергии лигандно-локализованных возбужденных состояний были использованы для определения каналов внутримолекулярной передачи энергии. В результате было выявлено, что магнитные свойства комплексов определяются в основном координационным полиэдром, ЖК свойства - лигандным окружением, а люминесценция - обоими из этих факторов.

Благодарности: Квантово-химические расчеты были проведены с использованием суперкомпьютеров МВС-10П и МВС-100К «Межведомственного суперкомпьютерного центра РАН». Работа выполнена при финансовой поддержке проекта № ГСГК-0064/21. Проект реализуется победителем Конкурса на предоставление грантов преподавателям магистратуры благотворительной программы «Стипендиальная программа Владимира Потанина» Благотворительного фонда Владимира Потанина.

e-mail: romksenia@kstu.ru

Highly nucleophilic heterobimetallic K-Yb^{II}, Li-Sm^{II} and K-Ca anionic benzhydryl complexes in intermolecular hydroamination of multiple bonds

A.N. Selikhov[a,b], A.A. Trifonov[b,a]

[a]*G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, 603950, Tropinina str, 49, Nizhny Novgorod, RUSSIA*
[b]*A.N. Nesmeyanov Institute of Organoelement Compounds, RAS, Vavilova str. 28, Moscow, 119334, RUSSIA*

Amines and their functionalized derivatives are widespread structural fragments of a large number of natural compounds, drugs, and complex molecules that perform a variety of biological functions. Therefore, the development of new methods for the formation of C-N bonds is certainly an urgent task. Intermolecular hydroamination is a fundamental chemical process of adding N-H bonds of nitrogen-containing substrates to multiple bonds of unsaturated compounds with electrophilic properties: alkenes, acetylenes, diene hydrocarbons, conjugated enyns, proceeding in 100% atom-economical mode in the presence of a catalyst. In this work, two types of heterobimetallic (*ate*-) complexes of divalent Yb^{II}, Sm^{II} and redox-inert calcium were synthesized in the form of contact $[(p\text{-}t\mathrm{BuC_6H_4})_2\mathrm{CH}]_3\mathrm{MK}$ (**A**, **B**, Fig.1), and separated ion pairs $[(p\text{-}t\mathrm{BuC_6H_4})_2\mathrm{CH}]_3\mathrm{SmLi(Base)}$ (**C**, **D**, Fig. 1).

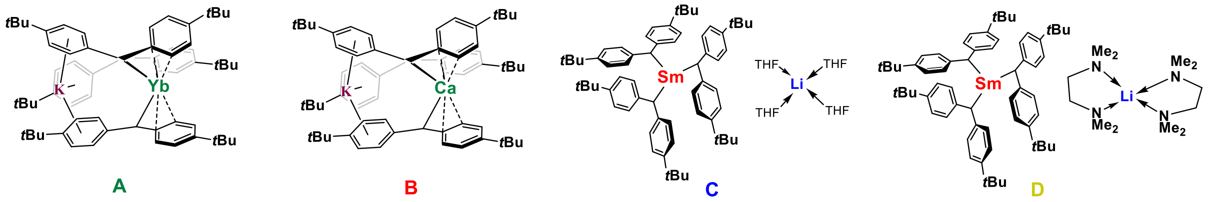


Fig. 1. Synthesized heterobimetallic *ate*-complexes of Yb, Sm, Ca.

Heterobimetallic complexes of type **A** and **B** have demonstrated unprecedented catalytic activity in hydroamination of multiple bonds of styrene, α-methyl-substituted styrene, internal diarylacetylenes, internal double bonds of norbornadiene and *trans*-stilbene with a wide range of primary and secondary amines under mild conditions (room temperature-80 ^{o}C). For the first time, the oxidation of Yb^{II}-Yb^{III} during the catalytic cycle was proved by NMR spectroscopy and X-Ray, which leads to a four-coordinate heterobimetallic complex and a sharp drop in the activity of the catalyst. In the case of redox-inert calcium, no decrease in activity was detected, which emphasizes the key role of the coordination number and the environment of the metal center.

Acknowledgements – Authors thank Russian Science Foundation (grant № 21-73-00107).

e-mail: alselikhov89@yandex.ru

A π-carbazolyl supported alkyl and borohydride half-sandwich Dy(III) complexes, showing single-molecule magnet behavior

A.N. Selikhov[a,b], A.A. Trifonov[b,a], Jérôme Long[c]

[a]*G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, 603950, Tropinina str, 49, Nizhny Novgorod, RUSSIA*
[b]*A.N. Nesmeyanov Institute of Organoelement Compounds, RAS, Vavilova str. 28, Moscow, 119334, RUSSIA*
[c]*Institut Charles Gerhardt, Equipe Ingé nierie Molé culaire et Nano-Objets, Universitéde Montpellier, FRANCE*

The ability of a coordination complex to present bistable magnetic states continues to attract attention of chemists and physicists since the discovery of this phenomenon nearly thirty years ago. In this sense, the field of Single-Molecule Magnets (SMMs) has taken an upturn with the use of lanthanide ions to design highly magnetically anisotropic complexes exhibiting exceptional performances, making such molecular systems potential candidates for applications in datastorage, spintronics or quantum computing. In this work we have reported the synthesis, structures and magnetic investigations of two half-sandwich hetereleptic Dy(III) complexes with alkyl (dimethylaminomethyl) and BH_4 ligands, showing an unprecedented η5 coordination mode of the carbazolyl ligand with a trivalent lanthanide ion resulting in the appearance of an axial crystal field and a zero-field SMM behavior (Fig. 1).[1,2]

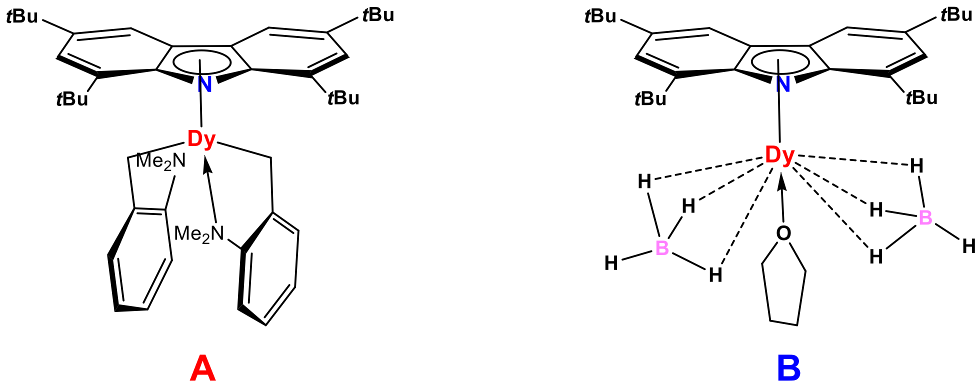


Fig. 1. Half-sandwich hetereleptic Dy(III) complexes with a π-coordination of carbazolyl ligand

[1] J. Long, A. N. Selikhov, K. A. Lyssenko, Y. Guari, J. Larionova, A. A. Trifonov, *Organometallics* **2020**, *39*, 2785−2790.
[2] J. Long, A. N. Selikhov, N. Y. Rad’kova, A. V. Cherkasov, Y. Guari, J. Larionova, A. A. Trifonov. *Eur. J. Inorg. Chem*. **2021**, 3008–3012.

Acknowledgements – Authors thank Russian Science Foundation (grant № 17-73-30036-П).

e-mail: alselikhov89@yandex.ru

Особенности формирования валентной полосы и термоэлектрические свойства катион-замещённых твёрдых растворов $Ln_xMn_{1-x}S$ на основе сульфида марганца

М.М. Сыроквашин

Институт неорганической химии им. А.В. Николаева СО РАН, Новосибирск

В настоящее время одним из наиболее активно развивающихся направлений материаловедения является поиск высокоэффективных термоэлектрических материалов. Использование подобных материалов для создания высокоэффективных термоэлектрических генераторов, позволяющих преобразовывать тепловую энергию в электрическую. К таким материалам относятся сульфиды 3d-металлов, допированные ионами редкоземельных металлов (РЗМ) свойствами которых можно управлять путем варьирования типа и концентрации замещающих атомов, что позволяет проводить направленный поиск и синтез соединений, обладающих требуемыми физическими свойствами. К данному классу соединений относятся катион-замещённые растворы $Ln_xMn_{1–x}S$ (Ln – редкоземельный металл) на основе α-MnS-матрицы, которые демонстрируют высокие значения коэффициента Зеебека, а также и другие практически значимые эффекты: смена типа проводимости и переход металл-диэлектрик. Вместе с тем, электрофизические свойства, в частности коэффициент Зеебека (S) полупроводниковых материалов в существенной степени определяются их электронным строением (плотностью состояний у потолка валентной зоны и дна зоны проводимости):

$$S = -\frac{k}{e} \cdot \left(\frac{\left(ln\frac{N_c}{n}+2\right) \cdot n\mu_n - \left(ln\frac{N_v}{p}+2\right) \cdot p\mu_p}{n\mu_n + n\mu_p} \right),$$

где k – константа Больцмана, e – заряд электрона, n и p – концентрации электронов и дырок соответственно, μ_n и μ_p – подвижность электронов и дырок соответственно, N_c и N_v – эффективная плотность состояний у дна зоны проводимости и потолка валентной зоны, соответственно. В случае $Ln_xMn_{1–x}S$ особенности электронного строения связаны с характером заполнения $3d$-оболочки атомов марганца и $4f$-оболочки атомов РЗМ. В рамках данной работы электронное строение $Ln_xMn_{1–x}S$ (Ln = Dy, Tm, Yb; x = 0.01; 0.05) было изучено экспериментально (РФЭС-спектры валентной полосы) и с привлечением методов квантовой химии (парциальные вклады состояний (DOS) в структуру валентной зоны), а затем сопоставлено с полученными температурными зависимостями коэффициента Зеебека.

Было установлено, что катионное замещение приводит к увеличению значений коэффициента Зеебека $Ln_xMn_{1–x}S$ относительно исходной MnS-матрицы, что согласно данным квантово-химических расчётов обусловлено вкладами f-состояний лантаноидов в структуру потолка валентной зоны. Подобие характеров полученных температурных зависимостей коэффициента Зеебека для твёрдых растворов с Tm и Yb и их отличие от соответствующих зависимостей для твердых растворов с Dy вероятно обусловлено особенностями распределения f-состояний лантаноидов в валентной зоне и зоне проводимости. Увеличение концентрации атомов Ln приводит к снижению величины коэффициента Зеебека, что вероятно связано с возникновением концентрационного перехода металл-диэлектрик.

Было установлено, что основной вклад в плотность занятых состояний в валентной зоне обусловлен вкладами состояний атомов марганца, а вклад состояний лантаноидов смещается в область потолка валентной зоны с увеличением порядкового номера. Характер распределения вкладов состояний коррелирует с полученными температурными зависимостями коэффициента Зеебека для $Ln_xMn_{1–x}S$. Установленные корреляции между электронным строением и термоэлектрическим свойствами позволяют заключить, что использование лантаноидов начала ряда перспективно с точки зрения целенаправленной модификации дна зоны проводимости, в то время как использование лантаноидов конца ряда позволяет изменять электронную структуру потолка валентной зоны.

e-mail: syrokvashin@niic.nsc.ru

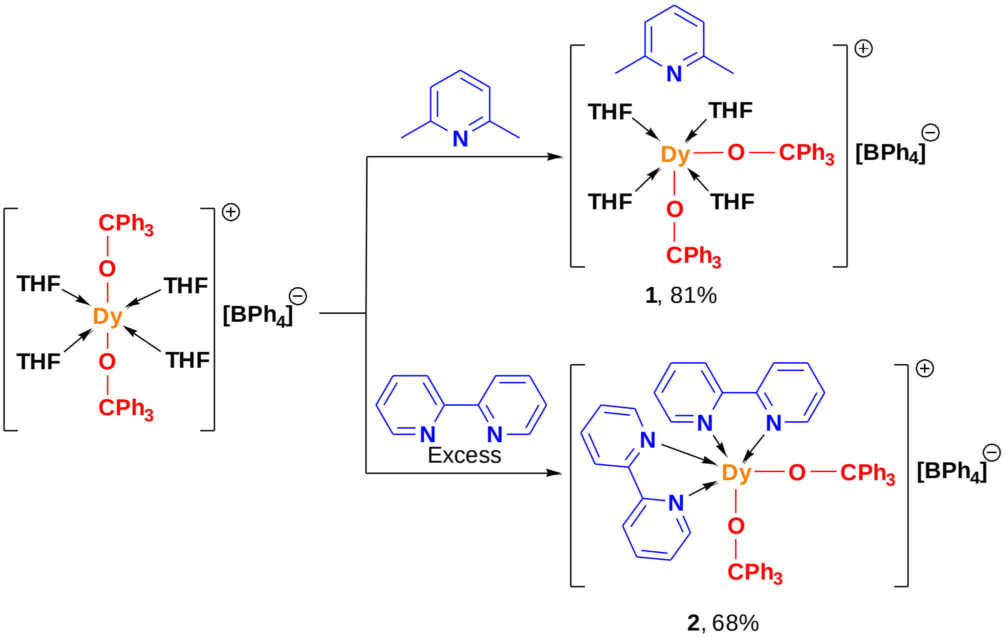
New cationic dysprosium alkoxide complexes. Synthesis and investigation of magnetochemical properties.

A.O. Tolpygin,[a,b] A.A. Kissel,[b] R.R. Saifutiarov,[b] A.A. Trifonov,[a,b] J. Long[c]

[a]*IOMC RAS, Tropinina 49, GSP-445, 603950, Nizhny Novgorod, RUSSIA*
[b]*INEOS RAS, Vavilova str. 28, 119334, Moscow, RUSSIA*
[c]*Institut Charles Gerhardt, Equipe Ingé nierie Molé culaire et Nano-Objets, Universitéde Montpellier, FRANCE*

Complexes that demonstrate slow relaxation of magnetization (SMM) due to their unique properties are of interest to the development of quantum computers, molecular spintronics and ultra-high-density data storage devices. In this regards great attention is focused on development of ligand environment enable to increase of blocking temperature as well as anisotropic barrier of SMM.

It was shown that the replacement of four THF molecules in $Dy(OCPh_3)_2(THF)_4[BPh_4]$[1] by 2 molecules of α,α’-bipy leads to the migration of –OC(Ph$_3$) ligands from the axial to *cis*-positions of the octahedron (O-Dy-O 107.17°). Recrystallization from 2,6-$Me_2C_5H_3N$ also leads to a similar change in the geometry of the cationic alkoxide complex (O-Dy-O 102.69°).



The magnetochemical properties of the resulted complexes **1** and **2** were investigated.

References: [1] J. Long, A. O. Tolpygin, E. Mamontova, K. A. Lyssenko, D. Liu, M. D. Albaqami, L. F. Chibotaru, Y. Guari, J. Larionova, A A. Trifonov, Inorg. Chem. Front., 2021, 8, 1166.

Acknowledgements: The financial support of the Russian Science Foundation is highly appreciated (project № 17-73-30036-П).

e-mail: toao2@yandex.ru, trif@iomc.ras.ru, jerome.long@umontpellier.fr

Участие состояний переноса заряда "лиганд-металл" в тушении люминесценции карбоксилатов европия, содержащих π-избыточный гетероцикл

В.И. Царюк, К.П. Журавлев, В.А. Кудряшова

Институт радиотехники и электроники им. В.А. Котельникова РАН, г. Фрязино Московской обл.

Изучены процессы возбуждения люминесценции индол-3-карбоксилатов $Ln(ICA)_3·3.5H_2O$, индол-3-ацетатов $Ln(IAA)_3·1.5H_2O$ и индол-3-пропионатов $Ln(IPA)_3·H_2O$ (Ln = Eu, Tb), а также серии тройных индолкарбоксилатов европия и тербия с 1,10-фенантролином и 2,2′-бипиридином [1]. Рассмотрены пиррол-2-карбоксилаты $Ln(PCA)_3·3H_2O$ (Ln = Eu, Tb) [2]. Исследованы спектры люминесценции и возбуждения люминесценции соединений европия и тербия, времена жизни электронных состояний $^5D_0$ (Eu^{3+}) и $^5D_4$ (Tb^{3+}) и интенсивность люминесценции. Колебательные ИК спектры и данные рентгеноструктурного анализа свидетельствуют об одинаковом строении двойных соединений европия и тербия с каждой из карбоновых кислот. Сравнение спектроскопических характеристик изоструктурных соединений легко восстанавливаемого иона Eu^{3+} и легко окисляемого иона Tb^{3+} облегчает идентификацию состояний переноса заряда "лиганд-металл" (LMCT).

Продемонстрирована определяющая роль состояний LMCT в передаче энергии возбуждения к иону Eu^{3+} и тушении люминесценции карбоксилатов европия, содержащих индольный или пиррольный фрагмент. Сопряжение параллельно ориентированных орбиталей неподелённой пары электронов атома азота и системы π-электронов ароматического фрагмента лиганда создаёт избыток электронной плотности, которая может сместиться к иону Eu^{3+} с образованием низкоэнергетических состояний LMCT. В индол-3-ацетатах и индол-3-пропионатах формирование состояний LMCT модифицировано метиленовыми мостиками. В исследованных соединениях европия, содержащих π-избыточный гетероцикл, активны два канала тушения люминесценции с участием LMCT. Для большинства соединений европия характерно тушение, обусловленное безызлучательной дезактивацией $^5D_0$-состояния иона Eu^{3+} через низкоэнергетическое состояние LMCT. Но в некоторых тройных соединениях состояние переноса заряда, будучи более высокоэнергетическим, участвует в опустошении возбуждённых электронных состояний лиганда.

[1] В.И. Царюк, К.П. Журавлев, *Опт. и спектр.*, **2022**, *130*, 121.

[2] K.P. Zhuravlev, Ł. Michnik, P. Gawryszewska, V.I. Tsaryuk, V.A. Kudryashova, *Inorg. Chim. Acta*, **2019**, *492*, 1.

Благодарности: Работа выполнена в рамках государственного задания Министерства науки и высшего образования Российской федерации.

e-mail: vtsaryuk@mail.ru

Стекла системы GeS_2-Ga_2S_3-Sb_2S_3:Pr как материалы для активной волоконной оптики

Х.Я. Шахбазова, Е.И. Грошовкин, А.С. Тверьянович

Санкт-Петербургский государственный университет, институт Химии

Халькогенидные стекла допированные редкоземельными ионами имеют неоспоримые преимущества в качестве материалов для оптических сенсоров ИК диапазона для химических, медицинских, биологических и т.д. применений. Использование различных редкоземельных ионов (РЗИ) позволяет создавать набор широкополосных источников излучения перекрывающих спектральную область от видимого диапазона до 12 мкм. При этом эти материалы могут быть получены в объемном, планарном состоянии и в виде оптоволокна. Одной из проблем, возникающих при разработке данных материалов, является высокое концентрационное тушение люминесценции РЗИ.

Данная работа направлена на установление закономерностей связывающих структурно-химическое строение матрицы халькогенидного стекла с однородностью распределения в ней РЗИ. Ранее было показано, что введение в матрицу стекла Ga_2S_3 приводит к существенному повышению растворимости РЗИ, за счет образования комплексной структурной единицы GaS_4^-, компенсирующей заряд РЗИ.

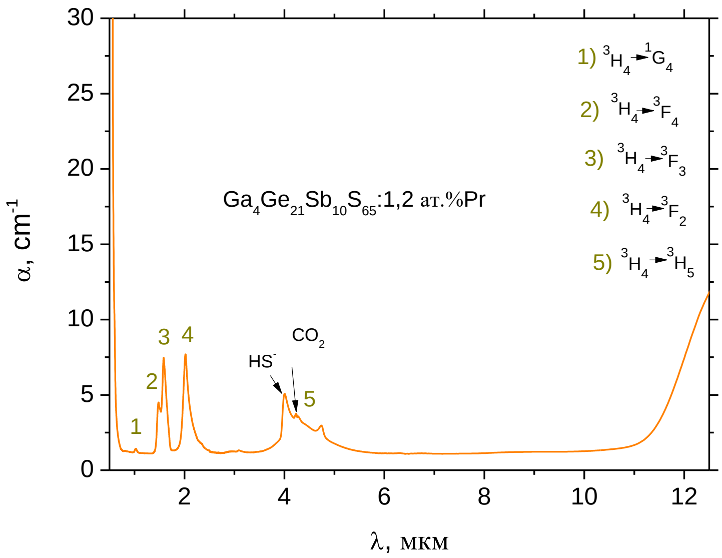
Поэтому, в качестве халькогенидной матрицы для введения РЗИ, в основном исследовали квазибинарную систему Ga_2S_3- GeS_2. Однако недостатками этой системы являются высокая температура синтеза и высокая кристаллизационная способность, что особенно важно при вытягивании оптических волокон. Для уменьшения этих негативных факторов стеклообразующая система была усложнена добавлением Sb_2S_3. В качестве РЗИ был выбран Pr^{3+}, который интересен не только благодаря люминесценции на одной из длин волн информационных линий связи (1,3 мкм), но и благодаря широкополосной люминесценции в средней ИК области спектра от 3,5 до 5,2 мкм, что позволяет создавать, например, сенсоры на CO_2.

Для изучения влияния состава матрицы на характер распределения ионов Pr^{3+} были выбраны 5 составов из вышеуказанной псевдо тройной системы Ga_2S_3-GeS_2-Sb_2S_3, в которые вводилось от 0.1 до 2 ат% Pr. Синтез проводили путем сплавления чистых компонентов в откачанных кварцевых ампулах в несколько стадий в постоянно качающейся печи.

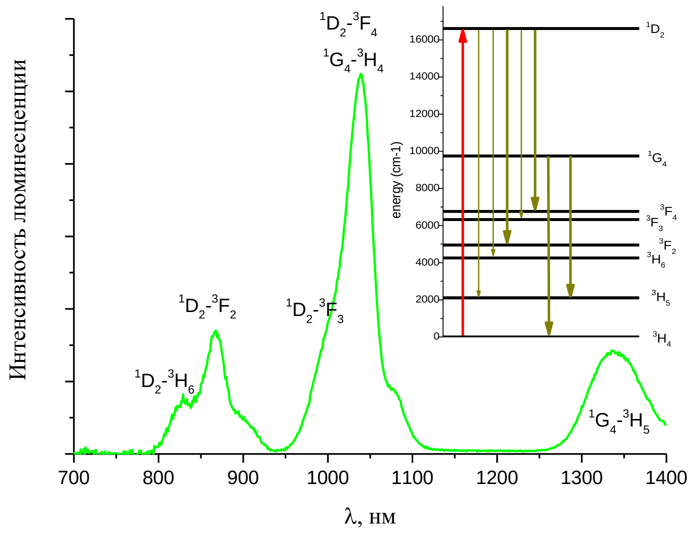
Для указанных составов были изучена структура стекол с помощью комбинационного рассеяния, спектры оптического поглощения, спектры люминесценции при возбуждении излучением с длиной волны 607 нм. Кроме того, для состава проведено тестовое получение оптоволокна в кварцевой оболочке диаметром 80 мкм.

Согласно спектрам КР структура стекол определяется следующими структурными единицами $GeS_{4/2}$, $S_{3/2}Ge – GeS_{3/2}$ $SbS_{3/2}$, причем тетраэдры $GeS_{4/2}$ могут быть соединены, как ребрами $S_{2/2}GeS_2GeS_{2/2}$, так и вершинами $S_3Ge – S – GeS_3$. Ga замещает Ge в данных структурных единицах.

При изменении состава матрицы и концентрации Pr изменяется спектральное положение края фундаментального и фононного поглощения. Примесное оптическое поглощение вблизи переходов Pr^{3+} в средней ИК области спектра определяется присутствием в стеклах групп HS^-, а также CO_2.



При возбуждении излучением с длиной волны 607 нм (3H4->1D2) оптическая релаксация происходит на все промежуточные уровни. Кроме того, наблюдаются два дополнительных пика в области 900 и 1080 нм, которые, по-видимому, обусловлены присутствием примеси Nd^{3+}. На рис. приведен спектр люминесценции стекла $Ga_{9.5}Ge_{13.1}Sb_{9.1}S_{68.3}$ с 0.6 ат.% Pr.



Увеличение относительного содержания Sb_2S_3 приводит к резкому увеличению стеклообразующей способности, смещению области прозрачности в длинноволновую область спектра, увеличению показателя преломления и уменьшению порога концентрационного тушения. В то время, как увеличение Ga_2S_3 приводит к строго обратному эффекту.

Благодарности: Исследование выполнено за счет гранта Российского научного фонда № 22-23-00074, https://rscf.ru/project/22-23-00074.

e-mail: hristka11@yandex.ru

Activation of the Sm (III) → Sm (II) reduction process under the combined action of a chemical reductant and UV irradiation

S. M. Yakupova[a], K. S. Vasilyuk[a], D.I. Galimov[a], and R.G. Bulgakov[b]

[a]*Institute of Petrochemistry and Catalysis, UFIC RAS, RUSSIA*
[b]*Institute of Physics of Molecules and Crystals, UFIC RAS, RUSSIA*

In order to develop new effective methods for the synthesis of compounds of divalent lanthanides, which are promising as catalysts and one-electron reducing agents, we have studied the effect of a significant acceleration of the reduction of Sm (III) to Sm (II) under the combined action of a reducing agent - diisobutylaluminum hydride $^iBu_2AlH$ and UV irradiation on the bulk complex $SmCl_3{\cdot}(THF)_x$–$^iBu_2AlH$ [1]. This complex is a product of the interaction of the crystal hydrate $SmCl_3{\cdot}6H_2O$ with an excess of $^iBu_2AlH$ in THF.

The study of the kinetics of the reduction of Sm (III) to Sm (II) by increasing the optical density of the absorption band of Sm (II) at 586 nm in the reaction of $SmCl_3{\cdot}6H_2O$ with $^iBu_2AlH$ without the use of UV irradiation showed that the time of complete reduction of samarium is 2 hours. The kinetics of samarium reduction changes dramatically upon UV irradiation (λmax = 365 nm, light flux intensity $5.02{\cdot}10^{16}$ photons$\cdot$s^{-1}) of a homogeneous reaction solution formed after interaction in the $SmCl_3{\cdot}6H_2O$-$^iBu_2AlH$-THF system, and complete reduction of Sm(III) to Sm(II) is carried out in a record 15 minutes. The rate constants of Sm (III) reduction were determined: $k_1 = (4.12\pm0.37){\cdot}10^{-4}$ s^{-1} (without irradiation) and $k_2 = (2.25\pm0.18){\cdot}10^{-3}$ s^{-1} (with UV irradiation) from the slope of linear anamorphoses in coordinates Ln ([Sm(III)]-f(t). The ratio of these constants $k_2/k_1 = 5.5$ quantitatively characterizes the effect of acceleration of the Sm (III) reduction under UV irradiation. Quantum yield of photoreduction Sm(III)→Sm(II), defined as the ratio of the amount of formed Sm (II) to the number of absorbed photons, turned out to be $\phi = 0.27 \pm 0.03$.

Based on the experimental data obtained, a mechanism for the reduction of Sm (III) was proposed, including the photolysis of the Al–H bond in the $^iBu_2AlH$ hydride with the formation of atomic hydrogen H, which is a stronger reducing agent than $^iBu_2AlH$.

[1] D.I. Galimov, S.M. Yakupova, R.G. Bulgakov, J. Photochem. Photobiol. A, 2022, 425, 113711.

e-mail: eliseevasm@yandex.ru

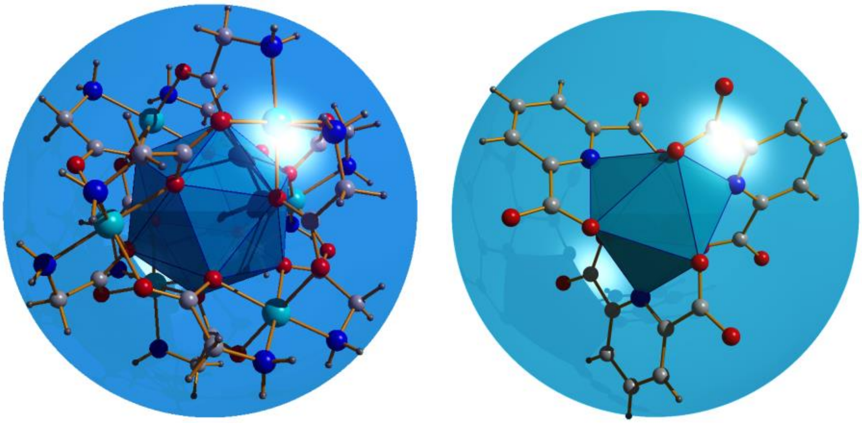
$[LnNi_6(Gly)_{12}][Ln'(dpa)_3]$ complexes, where Ln=Ce, Pr; Ln' = Tb, Eu

Yastrebova E.O., Dolzhenko V.D.

Department of Chemistry, Lomonosov Moscow State University

Polynuclear 3d-4f cluster complexes attract much attention due to their structural diversity and unique physical properties. They can be used as molecular magnets, ion detectors, precursors for the synthesis of mixed 3d-4f oxides. Earlier in our laboratory technique for obtaining polynuclear cation complexes of composition $[LnNi_6(AA)_{12}]^{3+}$ (AA = Gly, Ala) was established. These cations crystalize with large three-charged anions $[Ln(NO_3)_6]^{3-}$.

This work is devoted to gaining $[LnNi_6(Gly)_{12}][Ln'(dpa)_3]$ (Ln = Ce, Pr; Ln' = Tb, Eu; dpa = 2,6-pyridinedicarboxylate) complexes and improving synthetic conditions, the composition and structure of occupied compounds were confirmed by set of physicochemical methods. The choice of lanthanide in cation stemmed from stability of that complex compounds. Tb and Eu were picked due to high luminescence intensity of $[Ln'(dpa)_3]^{3-}$, it can be applied for studying the qualitative composition of the obtained compounds by complementary means. The great feature for solid specimen was discovered: the intensity of anion luminescence falls below device detecting limit. The luminescence signal in solution was recorded. Owing to $\{Ni_6(Gly)_{12}\}$ framework hardness and relatively high inertness of the nickel(II) complexes the compounds with selective distribution of REE over cationic and anionic positions were obtained.



e-mail: eugeniastr@mail.ru

Научное издание

Всероссийская конференция
«VI Российский день редких земель»

РДРЗ-2022

Сборник тезисов

Ответственный за выпуск:
д. х. н. НАУМОВ Николай Геннадьевич

Техническое редактирование и верстка
к. х. н. Пушкаревский Н. А.

Подписано к печати и в свет 10.02.2022.
Формат 60x84/8.
Гарнитура «Times New Roman». Печ. л. 17,9. Уч.-изд. л. 17,4.
Тираж 110 экз. Заказ № 13.
Федеральное государственное бюджетное учреждение науки
Институт неорганической химии им. А.В. Николаева Сибирского отделения РАН.
Просп. Акад. Лаврентьева, 3. Новосибирск, 630090.

ЗОЛОТОЙ СПОНСОР

ЛАБТЕСТ

LABTEST

БРОНЗОВЫЙ СПОНСОР

Primelab