RUDN university

The 4th Struchkov Meeting

International Workshop on Chemical Crystallography and Structural Biology

dedicated to the Centenary of Yuri T. Struchkov birthday



Book of abstracts

16-20 November,
Moscow – 2026

**Федеральное государственное автономное
образовательное учреждение высшего образования
«РОССИЙСКИЙ УНИВЕРСИТЕТ ДРУЖБЫ НАРОДОВ
ИМЕНИ ПАТРИСА ЛУМУМБЫ»**



IV СТРУЧКОВСКИЕ ЧТЕНИЯ

**Сборник тезисов Международной конференции
по кристаллохимии и структурной биологии,
посвященной 100-летию со дня рождения
члена-корреспондента АН СССР, профессора
Ю.Т. Стручкова**

Москва, РУДН, 16–20 ноября 2026 г.

The 4th STRUCHKOV MEETING

**Book of Abstracts of International Workshop
on Chemical Crystallography and Structural Biology
dedicated to the Centenary of Yuri T. Struchkov birthday**

Moscow, RUDN University, November 16–20, 2026

**Москва
Российский университет дружбы народов
им. Патриса Лумумбы
2026**

УДК 548.3:577.2(063)
ББК 24.5+28.07
С87

Конференция организована при поддержке
Программы стратегического академического лидерства «Стратегия-2030»

Председатель конференции –
проф. *В.Н. Хрусталев* (РУДН)

ПРОГРАММНЫЙ КОМИТЕТ:
Сопредседатель – акад. *С.М. Алдошин* (МГУ – ИПХФ РАН)
Сопредседатель – акад. *И.Л. Ерёменко* (ИОНХ РАН – ИНЭОС РАН)
акад. *В.П. Анаников* (ИОХ РАН, МГУ)
акад. *Е.В. Антипов* (МГУ, ИОХ РАН)
акад. *С.Н. Калмыков* (МГУ)
акад. *В.П. Федин* (НГУ – ИНХ СО РАН)
акад. *А.Ю. Цивадзе* (РХТУ – ИХФЭ РАН)
член-корр. РАН *И.С. Антипин* (КФУ – ИОФХ РАН)
член-корр. РАН *А.Н. Кузнецов* (МГУ – ИОНХ РАН)
член-корр. РАН *А.В. Шевельков* (МГУ)
проф. *Я.В. Зубавичус* (ИК СО РАН)
Abel Maharramov (Baku State University, Azerbaijan)
Ilia A. Guzei (University of Wisconsin-Madison, WI, USA)
Tatiana Timofeeva (New Mexico Highlands University, NM, USA)
Alex Yanovsky (Pfizer, San Diego, CA, USA)

ОРГАНИЗАЦИОННЫЙ КОМИТЕТ:
А.С. Голубенкова (РУДН), *Е.И. Князева* (РУДН), *Я.В. Султанова* (РУДН), *А.С. Критченков* (РУДН), *А.Г. Цховребов* (РУДН), *А.Н. Биляченко* (РУДН), *Н.Н. Лобанов* (РУДН), *А.А. Невская* (РУДН), *Т.А. Терёшина* (РУДН), *А.Ю. Зуева* (РУДН), *М.Р. Комаровских* (РУДН), *О.В. Репина* (РУДН), *Е.П. Лопашинова* (РУДН)

Секретарь – *Е.В. Доброхотова* (РУДН)

С87 **IV Стручковские чтения = The 4th Struchkov Meeting :** сборник тезисов Международной конференции по кристаллохимии и структурной биологии, посвященной 100-летию со дня рождения члена-корреспондента АН СССР, профессора Ю.Т. Стручкова. Москва, РУДН, 16–20 ноября 2026 г. – Москва : РУДН, 2026. – 103 с. : ил.

Сборник тезисов Международной конференции по кристаллохимии и структурной биологии «IV Стручковские чтения», проведённой 16–20 ноября 2026 г. на базе факультета физико-математических и естественных наук Российского университета дружбы народов им. Патриса Лумумбы, содержит пленарные, ключевые и устные доклады.

Издание призвано популяризовать научно-исследовательскую деятельность в области химии и осветить современные химические проблемы на международном уровне.

Предназначено для ученых, студентов и аспирантов, а также читателей, интересующихся проблемами химии.

The Book of Abstracts of The International Workshop on Chemical Crystallography and Structural Biology "*The 4th Struchkov Meeting*", which was held in November 16–20, 2026 based on the Faculty of Science at RUDN University, includes summaries of Plenary, Keynote, and Oral speakers.

The present publication was designed to popularize scientific research activity in the field of chemistry and to discuss modern chemical problems on the international level.

The digest is intended for scientists, students, postgraduates and for wide range of readers interested in problems in chemistry.

ISBN 978-5-209-15005-3

© Коллектив авторов, 2026
© Оформление. Российский университет дружбы народов, 2026



Memorial plaque of Yuri T. Struchkov at the A.N. Nesmeyanov Institute of Organoelement Compounds (INEOS) of the Russian Academy of Sciences. The text reads: "*Yuri Timofeevich Struchkov, outstanding crystallographer and specialist in organometallic chemistry, worked at INEOS in 1954–1995*"

Dear Colleagues,

Let me start with the words of welcome to the participants of the 4th International Workshop on Chemical Crystallography and Structural Biology, dedicated to the memory of Prof. Yuri T. Struchkov. This is the third time when the RUDN University gets the honor of hosting this vibrant and diverse scientific community, which took its roots from the remarkable achievements of Prof. Struchkov's laboratory in the decades around the turn of the last century and was since diversified both in scientific and geographical sense thanks to the work and enthusiasm of Struchkov's lab alumni as well as their colleagues and students. We are very happy that members of this community will present within our Workshop their interesting results in various fields ranging from nanomaterials and supramolecular chemistry to green chemistry and proteins.

I'd like to stress that this Conference comes in the year which happens to carry two important dates, the 100th anniversary of Prof. Yuri T. Struchkov's birthday, as well as the 75th birthday of Prof. Mikhail Yu. Antipin, who took over the helm of the leader of the laboratory from Prof. Struchkov in 1995 and was heading it up to his untimely death in 2013. It was prof. Antipin, who, in 1997, took initiative along with other former colleagues of Prof Struchkov, organized the first Struchkov Prize Competition thus setting up the annual tradition and initializing the community, which formed around it and which we are welcoming today as participants of our Workshop.

Since 2023, the Struchkov Prize is bestowed by the IUCr every triennium at the IUCr Congress and General Assembly. In August 2026, the Second International Struchkov Prize was awarded to Dr. Erik Svensson Grape (Sweden) at the International Congress of Crystallography in Calgary, Canada. We are hoping that participants of the Workshop will become major champions of the global Struchkov Prize and will nominate their friends and colleagues for the Prize. I'm sure we will eventually see many of them in our future Struchkov Workshops as active participants. And let us also hope we will then see and warmly hug all our old and new friends, live and in person, on the premises of our great RUDN University in our beautiful city of Moscow.

Conference Chair, Prof. Dr. Victor N. Khrustalev



International Workshop
on Chemical Crystallography and Structural Biology
"The Fourth Struchkov Meeting"

dedicated to the Centenary of Yuri T. Struchkov birthday

Moscow • November 16-20, 2026

Scientific Program
(*hybrid format*)

https://struchkovprizeassociation.org/the-4th-struchkov-meeting-2026/

Moscow Time • Japan+6 • China+5 • Kazakhstan+2 • Azerbaijan+1 •
Germany-2 • Portugal-3 • USA-8

International Workshop on Chemical Crystallography and Structural Biology
"The Fourth Struchkov Meeting"
dedicated to the Centenary of Yuri T. Struchkov birthday

Scientific Program
https://struchkovprizeassociation.org/the-4th-struchkov-meeting-2026/

Monday November 16, 2026 (Ordzhonikidze Street, 3, *Science Faculty Club*)

	Workshop Opening
9 30–9 40	***Victor N. Khrustalev*** (Chair of Organizing Committee)
9 40–9 45	***Sergey M. Aldoshin*** (Co-Chair of Program Committee)
9 45–9 50	***Igor L. Eremenko*** (Co-Chair of Program Committee)
9 50–9 55	***Andrei V. Shevelkov*** (Member of Program Committee)
9 55–10 00	***Igor A. Litvinov*** (FRC "Kazan Scientific Center", RAS)
Session A	**Session Chair: Victor N. Khrustalev (Moscow, Russia)**
10 00–10 45	**Historical Lecture** *Yuri Timofeevich Struchkov. On the centenary of his birth* ***Igor A. Litvinov*** Arbuzov Institute of Organic and Physical Chemistry, FRC RAS (Kazan, Russia)
10 45–11 25	**Plenary** *Crystal and electronic structure of polar intermetallic compounds – achievements and challenges on the way to functional materials* ***Andrei V. Shevelkov*** Lomonosov Moscow State University (Moscow, Russia)
11 25–12 05	**Plenary** *Synthesis, structural features, catalytic properties and biological activity of some transition metals complexes with isoxazole and isothiazole ligands* ***Vladimir I. Potkin*** Institute of Physical Organic Chemistry, NAS of Belarus (Minsk, Belarus)
12 05–12 35	**Coffee Break**
Session B	**Session Chair: Andrei V. Shevelkov (Moscow, Russia)**
12 35–13 15	**Plenary** *Structural bonanza of intermetallic phosphide platinides* ***Alexey N. Kuznetsov*** Lomonosov Moscow State University (Moscow, Russia)
13 15–13 55	**Plenary** *Synchrotron radiation facility SKIF: new capabilities for chemical crystallography in Russia* ***Yan V. Zubavichus*** Synchrotron Radiation Facility SKIF (Koltsovo-Novosibirsk, Russia)
13 55–15 00	**Lunch**
Session C	**Session Chair: Vladimir I. Potkin (Minsk, Belarus)**
15 00–15 30	**Keynote** *New chitosan-based polymers* ***Andrei S. Kritchenkov*** Institute of Technical Acoustics, NAS of Belarus (Vitebsk, Belarus)

15 30–15 50	**Oral** *Weak interactions in directing molecular conformation and crystal packing of some azole 3a,6-epoxyisoindole-7-carboxyliates* ***Irina A. Kolesnik*** Institute of Physical Organic Chemistry, NAS of Belarus (Minsk, Belarus)
15 50–16 20	**Coffee Break**
Session D	**Session Chair: Alexey N. Kuznetsov (Moscow, Russia)**
16 20–16 50	**Keynote** *Asymmetric metal-templated synthesis of non-proteinogenic α-amino acids* ***Vladimir A. Larionov*** Nesmeyanov Institute of Organoelement Compounds, RAS (Moscow, Russia)
16 50–17 20	**Keynote** *An analytical approach to modeling small angle scattering curves for nanoparticle and hybrid systems: a case study analysis* ***Artem V. Bakirov*** National Research Center "Kurchatov Institute" (Moscow, Russia)
17 30–18 45	**Round Table** (*Lecture room 208*) ***dedicated to the 75th Birth Anniversary of Mikhail Yu. Antipin*** ***Yuri L. Slovokhotov (Moscow, Russia)***
19 00–21 00	**Welcome Cocktail**

Tuesday November 17, 2026 (Ordzhonikidze Street, 3, *Lecture room 208*)

Moscow Time • ***Japan+6*** • ***China+5*** • ***Azerbaijan+1*** • ***Germany-2*** • ***Portugal-3*** • ***USA-8***

Session E (online)	**Session Chairs: Yan V. Zubavichus (Novosibirsk, Russia), Alexander G. Tskhovrebov (Moscow, Russia)**
10 00–10 40	**Plenary** *Synthesis and structures of well-defined silsesquioxane* ***Masafumi Unno*** Gunma University (Kiryu, Japan)
10 40–11 20	**Plenary** *Synthesis and assembly mechanism of silver nanoclusters protected by thiacalix[4]arene* ***Zhi Wang*** University of Shandong (Jinan, China)
11 20–12 00	**Plenary** *Extended metal chain complexes (Ni, Co, Cr) and copper(II) coordination polymers based on modulated oligo-α-pyridylamines. Current status and perspectives* ***Rayyat H. Ismayilov*** Nagiyev Institute of Catalysis and Inorganic Chemistry (Baku, Azerbaijan)
12 00–12 40	**Plenary** *How can we trust our crystal structure solutions? Pseudo-homometry and chemical reliability in single-crystal X-ray diffraction* ***Alexander V. Virovets*** Goethe University of Frankfurt (Frankfurt am Main, Germany)

12 40–13 20	**Plenary** *MOFs and selected catalytic applications towards sustainability* ***Armando J. L. Pombeiro*** Instituto Superior Tecnico (Lisbon, Portugal)
13 20–15 00	**Lunch**
Session F (online)	**Session Chairs: Andrei S. Kritchenkov (Vitebsk, Belarus), Maxim S. Molokeev (Krasnoyarsk, Russia)**
15 00–15 40	**Plenary** *Confinement effects in metal–organic frameworks: from crystal structure to advanced functional materials* ***Brij B. Mohan*** Instituto Superior Tecnico (Lisbon, Portugal)
15 40–16 10	**Keynote** *Synthesis and crystal-chemical features of new compounds and solid solutions with the apatite structure* ***Evgeny N. Bulanov*** Lobachevsky State University (Nizhny Novgorod, Russia)
16 10–16 30	**Oral** *Synthesis, crystal structure and spectroscopic properties of the Co(III) complex with 3,5-di-tert-butylsalicylaldehyde acetylhydrazone* ***Perizad A. Fatullayeva*** Nagiyev Institute of Catalysis and Inorganic Chemistry (Baku, Azerbaijan)
16 30–16 50	**Oral** *Electrolyte-dependent crystal chemistry of silver-modified hydroxyapatite synthesized by reaction–diffusion: a powder diffraction and spectroscopic study* ***Olumakinde C. Omiyale*** ITMO University (Saint Petersburg, Russia)
16 50–17 30	**Plenary** *Charging carbon bowls, hoops, and graphene fragments with multiple electrons through the lens of crystallography* ***Marina A. Petrukhina*** University at Albany – State University of New York (Albany, USA)
17 30–18 10	**Plenary** *Current status of Pt-based 1D solids* ***Nikolay N. Gerasimchuk*** Missouri State University (Springfield, USA)

Wednesday November 18, 2026 (Ordzhonikidze Street, 3, *Science Faculty Club*)

Session G	**Session Chair: Yuri L. Slovokhotov (Moscow, Russia)**
10 00–10 40	**Plenary** *Structure and functional properties of metal-organic frameworks* ***Vladimir P. Fedin*** Nikolaev Institute of Inorganic Chemistry, SB RAS (Novosibirsk, Russia)

10 40–11 20	**Plenary** *New electrode materials for metal-ion batteries* ***Evgeny V. Antipov*** Lomonosov Moscow State University (Moscow, Russia)
11 20–12 00	**Plenary** *New materials and X-rays: what to expect when they meet?* ***Vladimir V. Chernyshev*** Lomonosov Moscow State University (Moscow, Russia)
12 00–12 30	**Coffee Break**
Session H	**Session Chair: Vladimir V. Chernyshev (Moscow, Russia)**
12 30–13 00	**Keynote** *Non-classical statistics of structural data* ***Yuri L. Slovokhotov*** Trapeznikov Institute of Control Sciences, RAS (Moscow, Russia)
13 00–13 40	**Plenary** *Obtaining high-quality X-ray crystallographic and functional states on the membrane protein bacteriorhodopsin — 10 years later* ***Valentin I. Borshchevskiy*** Moscow Institute of Physics and Technology (Moscow, Russia)
13 40–14 40	**Lunch**
Session I	**Session Chair: Valentin I. Borshchevskiy (Moscow, Russia)**
14 40–15 20	**Plenary** *Supramolecular cagelike metallasilsesquioxanes: structure and catalytic activity* ***Alexey N. Bilyachenko*** Nesmeyanov Institute of Organoelement Compounds, RAS (Moscow, Russia)
15 20–15 50	**Keynote** *Isomeric forms and spectral behavior of azo-compounds obtained by different methods* ***Olga V. Kovalchukova*** Kosygin State University (Moscow, Russia)
15 50–16 20	**Coffee Break**
Session J	**Session Chair: Igor A. Litvinov (Kazan, Russia)**
16 20–16 50	**Keynote** *A new approach to designing molecular rotors* ***Daut R. Islamov*** Kazan Federal University (Kazan, Russia)
16 50–17 20	**Keynote** *Cyclic Group 11 metal pyrazolates as a rigid matrix for organic structure elucidation and photophysical tuning* ***Alexey A. Titov*** Nesmeyanov Institute of Organoelement Compounds, RAS (Moscow, Russia)
17 20–17 50	**Keynote** *Control over the structure and magnetic properties of 3d-metal clusters supported by (thia)calix[4]arenes* ***Alexander S. Ovsyannikov*** Arbuzov Institute of Organic and Physical Chemistry, RAS (Kazan, Russia)

17 50–18 10	**Oral** *Aggregation-induced emission in supramolecular complexes of a bis(styryl) dye with cucurbiturils* ***Olesya V. Sulimova*** Nesmeyanov Institute of Organoelement Compounds, RAS (Moscow, Russia)

Thursday November 19, 2026 (Ordzhonikidze Street, 3, *Science Faculty Club*)

Session K	**Session Chair: Olga A. Bulavchenko (Novosibirsk, Russia)**
	Young scientist Session
10 00–10 20	**Oral** *Crystal structure and vibrational properties of guanidinium trans-diaquabis(malonato)aluminate(III): experimental and periodic DFT study* ***Daniil V. Kiryak*** Lomonosov Moscow State University (Moscow, Russia)
10 20–10 40	**Oral** *Interpretation of X-ray diffraction data of metal-organic framework polymers [REBTC] (RE = La-Lu, Y; BTC – $C_6H_5(COO)_3$)* ***Daniil A. Valeshnyi*** Russian Technological University MIREA (Moscow, Russia)
10 40–11 00	**Oral** *New BODIPY fluorophores with five-membered heterocycles at the meso-position: design, synthesis and crystal structure* ***Evgeniya R. Shelukho*** RUDN University (Moscow, Russia)
11 00–11 20	**Oral** *Non-covalent interactions in epoxyisoxazoloisoindol derivatives* ***Viktoriya S. Maslova*** RUDN University (Moscow, Russia)
11 20–11 40	**Oral** σ-Hole-driven interactions in phosphine selenides: structural, spectroscopic and computational studies ***Valeriya V. Mulloyarova*** Saint Petersburg State University (Saint Petersburg, Russia)
11 40–12 00	**Oral** *Specifics of evaluating the real composition of single-crystal solid solutions $[Co_{1-x}Ni_x)_3(C_6H_5(COO)_3)_2(H_2O)_{12}]$ based XRD data* ***Anton G. Mushtakov*** RUDN University (Moscow, Russia)
12 00–12 30	**Coffee Break**
Session L	**Session Chair: Alexey A. Titov (Moscow, Russia)**
12 30–13 00	**Keynote** *In situ X-ray diffraction as a basic tool to study oxide and metal oxide catalysts* ***Olga A. Bulavchenko*** Boreskov Institute of Catalysis, SB RAS (Novosibirsk, Russia)

13 00–13 30	**Keynote** *A comparative study of the effect of high-pressure and low temperature on the crystal structure of the salts of purine nucleobases* ***Anna A. Gaydamaka*** Synchrotron Radiation Facility SKIF (Koltsovo-Novosibirsk, Russia)
13 30–14 00	**Keynote** *Synthesis of platinum, palladium and rhodium-based bimetallic complexes: structural and catalytical insights* ***Ilya A. Yakushev*** Kurnakov Institute of General and Inorganic Chemistry, RAS (Moscow, Russia)
14 00–15 00	**Lunch**
Session M	**Session Chair: Mikhail A. Kinzhalov (Saint Petersburg, Russia)**
	Young scientist Session
15 00–15 20	**Oral** *Influence of molecular and crystal structure on photophysical properties in cyclometalled platinum complexes with carboxylate and pyridine ligands* ***Egor A. Sosunov*** Kurnakov Institute of General and Inorganic Chemistry, RAS (Moscow, Russia)
15 20–15 40	**Oral** *Lanthanide 1D coordination polymers with bulky cyclohexanecarboxylate ligands: synthesis, structure and properties* ***Irina A. Sabitova*** Lomonosov Moscow State University (Moscow, Russia)
15 40–16 00	**Oral** X-ray structural analysis of α-$NiSO_4 \cdot 6H_2O$ single crystals doped with low concentrations of Y^{3+} and Ti^{4+} ions ***Levko A. Arbanas*** RUDN University (Moscow, Russia)
16 00–16 30	**Coffee Break**
Session N	**Session Chair: Vladimir A. Larionov (Moscow, Russia)**
16 30–16 50	**Oral** *Metal-induced halogen bonding in Platinum-Group isocyanide complexes* ***Mikhail A. Kinzhalov*** Saint Petersburg State University (Saint Petersburg, Russia)
16 50–17 10	**Oral** *Correlation between the structure and scintillation properties of materials* ***Maxim S. Molokeev*** Kirensky Institute of Physics (Krasnoyarsk, Russia)
17 30–18 30	**Awarding the Winners for the best presentations** **Concluding remarks of the Chairmen and Members of the Program and Organizing Committees**
	Workshop Closing
19 00–22 00	**Banquet**

Plenary Lectures

Yuri Timofeevich Struchkov. On the centenary of his birth

Litvinov I.A.

Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, Kazan, 420088 Russian Federation
e-mail: litvinov@iopc.ru

This year, July 28, marks the 100th anniversary of Yuri Timofeevich Struchkov's birth. Sadly, he passed away 31 years ago, but why, after all these years, do we remember him with respect, gratitude, and deep sadness? What did he accomplish in his short life that, just the following year, his students established a national prize for young crystallographers — a truly public organization, without any governing body. In 2000, a national committee for this prize was established, and in 2007, at a conference dedicated to Yuri Timofeevich's 80th birthday, held in the United States, they agreed to establish the Struchkov Prize Society. Why did world-renowned scientists such as Nobel laureates Linus Pauling, Dorothy Hodgkin, and Roald Hoffman visit Moscow's INEOS X-ray diffraction laboratory to meet with Yuri Timofeevich? Even this brief list leads to the conclusion that Yuri Timofeevich was an extraordinary individual, deserving of our attention and respect. In this report, I will attempt to outline my view on Yuri Timofeevich's role and significance in the development of structural research in the Soviet Union, Russia, and internationally.

Crystal and electronic structure of polar intermetallic compounds – achievements and challenges on the way to functional materials

Shevelkov A.V.

Lomonosov Moscow State University, Department of Chemistry,
Moscow, 119991, Leninskie Gory 1-3
e-mail: shev@inorg.chem.msu.ru

Intermetallics are a broad class of compounds with a vast variety of crystal structures. The diversity of metals that form intermetallic compounds determines not only the variety of crystal structures but also the variability of their electronic structure and properties, which is why these compounds cannot be easily analyzed within the framework of establishing the "composition–structure–property" relationship. Two families of intermetallics with opposite properties can be identified as those for which structure-property relations have been established. At one side, nonpolar "electronic" compounds are described by the Hume-Rothery rules, which relate the concentration of valence electrons to the composition and structure of intermetallic compounds. On the other hand, Zintl phases are essentially ionic intermetallics to which the octet rule applies.

Polar intermetallic compounds occupy an intermediate position; they are formed by a combination of transition metals with metals and metalloids of the p-block and represent an extensive family of compounds, unevenly distributed among approximately eight hundred structural types [1], which often differ strikingly from one another in terms of coordination polyhedra, building blocks, and the type of metal–metal bonds. Only for small, very limited families of polar intermetallic compounds, a description has been proposed that links composition and crystal structure to certain functional properties. In particular, applying the "18−n rule", proposed by Hoffman and substantiated by Frederiksen to certain groups of compounds [2] made it possible to explain and predict transport properties, including non-metallic conductivity, of some intermetallic compounds [3,4].

This work is devoted to the analysis of the relationship between crystal structures and transport and magnetic properties of various types of polar intermetallics. Several structural types of intermetallics will be considered, the crystal structures of which range from the simplest to the most complex. We will show that for some types of polar intermetallics it is possible to establish a relationship between the structure and the properties based on the features of d-p orbital interaction, which define local and extended electronic structure of polar intermetallics [5]. Examined will be their influence on the transport and magnetic properties, including the magnetocaloric effect, thermoelectric figure of merit, and superconductivity.

This work is supported by the Russian science foundation, grant # 25-13-00005

References

[1] Westbrook, J.H., Fleischer R. L. (eds.) Intermetallic compounds. Principles and Practice, John Wiley & Sons, Chichester 1995.
[2] Yannello V.J., Fredrickson D.C. *Inorg. Chem*., **2015**, 54, 11385.
[3] Lim A., Fredrickson D.C. 2023, *Inorg. Chem*., **2023**, 62, 10833.
[4] Verchenko V.Yu., Tsirlin A.A., Shevelkov A.V. *Inorg. Chem. Front*., **2021**, 8, 1702.
[5] Khalaniya R.A., Verchenko V.Yu., Zonov E.M., Stern R., Shevelkov A.V. *Inorg. Chem.*, **2024**, 63, 21099.

Synthesis, structural features, catalytic properties and biological activity of some transition metals complexes with isoxazole and isothiazole ligands

Potkin V.I.,[1] Kolesnik I.A.,[1] Bumagin N.A.,[2] Lider E.V.[3]

[1]*Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, 220072, Minsk, Belarus, Surganova St., 13*
[2]*M.V. Lomonosov Moscow State University, 119991, Moscow, Russia, Leninskii Gory 1/3;*
[3]*Nikolaev Institute of Inorganic Chemistry SB RAS, 630090, Novosibirsk, Russia, Acad. Lavrentiev Ave. 3*
e-mail: potkin@ifoch.bas-net.by

Isoxazole and isothiazole heterocycles are incorporated into the structures of a wide range of bioactive molecules and are capable of coordinating with various transition metals to form metal complexes that exhibit both biological and catalytic activity. The properties of metal complexes and the coordination of the heterocyclic ligand depend significantly on the functional environment of the heterocycle and the nature of the metal. Unlike isoxazole complexes, isothiazole ones are significantly less studied.

We have shown that palladium (II) complexes with isoxazole and isothiazole ligands exhibit very high catalytic activity in cross-coupling reactions [1]. In this respect, they are among the best representatives described in the literature. Moreover, such complexes make it possible to perform C–C cross-coupling in aqueous medium without inert atmosphere. Immobilization of complexes on various carriers allows obtaining reusable catalysts that retain activity even after 10 recycles. Catalytically active azole complexes are characterized by a variety of structures, which are determined by the structure of the ligand, including both classical complexes with N_{ring}-coordinated ligands and unusual structures with different amount of polydentate ligands. A prominent example is the Pd(II) coordination compounds with azolyl-pyridines,[3] where the complexation is accompanied by deprotonation of the amide group and the formation of a Me-N σ-bond, while the number of ligands depends on the length of the linker between the azole and pyridine heterocycles. Earlier, the same coordination pattern was proven by us using X-ray spectroscopy for the complexes with similar in structure azolyl-pyrimidine ligands [2].

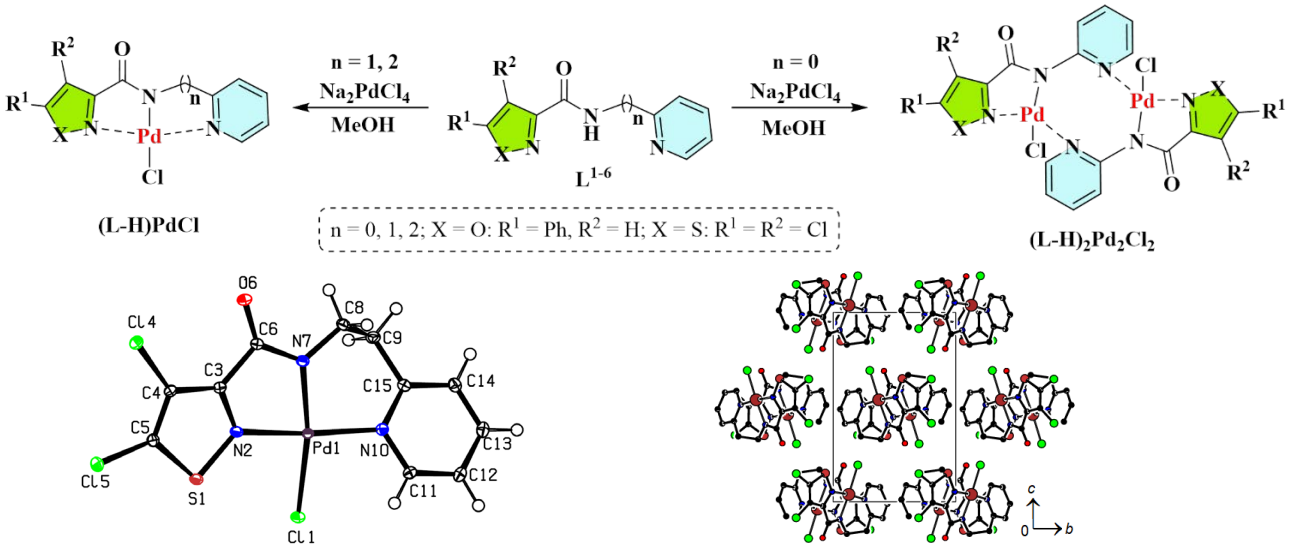


Fig. 1. Structures of Pd(II) complexes with N-(pyridin-2-yl)azole-3-carboxamides

Whereas better catalytic activity was discovered for Pd(II) complexes with isoxazole ligands, valuable biological properties were demonstrated by isothiazole complexes and with another metal. For example, copper(II) carboxylate complexes with 4,5-dichloroisothiazole-3-carboxylic acid (HL) was shown to be able to enhance the activity of insecticides against larvae and imago of the Colorado potato beetle, while mixed Cu(II) complexes with the same acid and N-donor ligands (bipyridine, picoline, phenanthroline) exhibited antitumor activity [3]. Notably, isothiazole-phenanthroline complex [Cu(4,7-dimethyl-1,10-phenantroline)L_2] was found to be more cytotoxic (IC_{50} = 0.97 ± 0.03 μM) than cisplatin (IC_{50} = 9.2 ± 0.5 μM) on the human cancer cell line Hep-2 (larynx carcinoma). X-ray structural analysis revealed interesting features of the described isothiazole carboxylic acid complexes: in addition to the diversity of structures, they are distinguished by the fact that in one complex there are at least two identical isothiazole ligands, for which different coordination modes are realized (exocyclic oxygen only or both exocyclic oxygen and N_{ring} of the heterocycle).

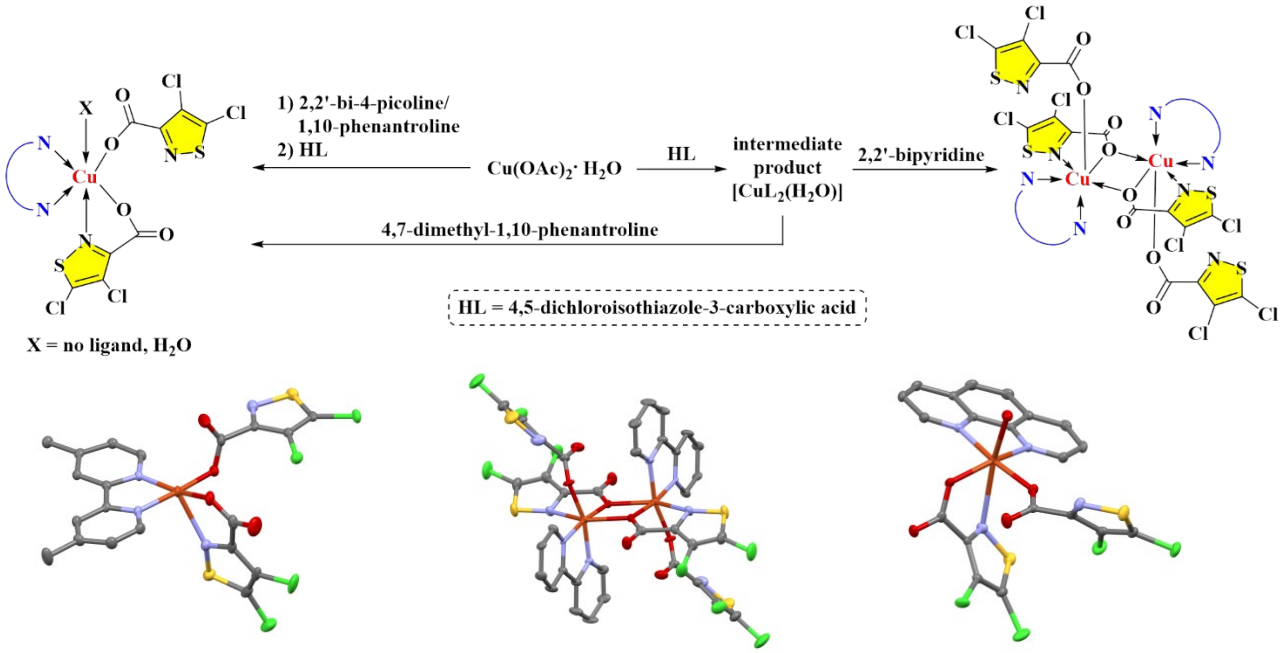


Fig. 2. Synthesis and structures of bioactive Cu(II) complexes with 4,5-dichloroisothiazole-3-carboxylic acid.

This work was supported by the Belarusian Republican Foundation for Fundamental Research (project № X25KI-027)

References

[1] Bumagin, N.A.; Potkin, V.I. *Russ. Chem. Bull.*, **2016**, 65, 321.
[2] Bumagin, N.A.; Kolesnik, I.A.; Potkin, V.I.; Dikusar, E.A.; Lyakhov. A.S.; Ivashkevich, L.S.; Hongwei Zhou; Wenliang Li. *Polyhedron*. **264**, 17249.
[3] Eremina, J.; Lider, E.; Sukhikh, T.; Klyushova, L.; Perepechaeva, M.; Sheven, D.; Berezin, A.; Grishanova, A.; Potkin, V. *Inorganica Chimica Acta*, **2020**, 510, 119778.

Structural Bonanza of Intermetallic Phosphide Platinides

Kuznetsov A.N., Polevik A.Yu., Zakharova E.Yu., Nesterenko S.N., Lyssenko K.A.

Lomonosov Moscow State University, 119991, Moscow, Leninskie Gory 1-3
e-mail: alexei@inorg.chem.msu.ru

Ordered intermetallic compounds are as fascinating objects as one can get in the field of inorganic and solid state chemistry, and they are still expanding. The variety of crystal structures arising from different combinations of metals is simply amazing, with 2166 structure types and just under 21000 unique intermetallic compounds (not counting solid solutions and statistical alloys) characterized by 2015 [1], and yet the field is seriously underinvestigated and undeservedly underrepresented at the top level of scientific publications and major congresses and other exchange platforms. This lack of publicity is rather surprising since various intermetallics feature not only diverse and complex structures, but many exciting and potentially useful functional physical properties, with their range only matched by their structural variety.

Unpredictability of the phase formation and relationships makes systematic study of complex intermetallic systems very difficult, and a 'simple' search for new compounds by investigating a region of phase diagram rather inefficient. Instead, we offer an approach to structural design of new ternary and quaternary intermetallics based on the established and stable fragments. One of the most common structure types among binary intermetallics is the $AuCu_3$ type, the structural unit in $AuCu_3$ is a cuboctahedron, e.g. gold-centered copper cuboctahedron $[Cu_{12}Au]$. In our work, we perform the search for new compounds formed by combining Pt_3M fragments with the $AuCu_3$ structure (M=3d- or p-block metal) with ternary RPt_2P_{2-x} fragments with the $CaBe_2Ge_2$ structure (ordered variant of the $BaAl_4$ type).

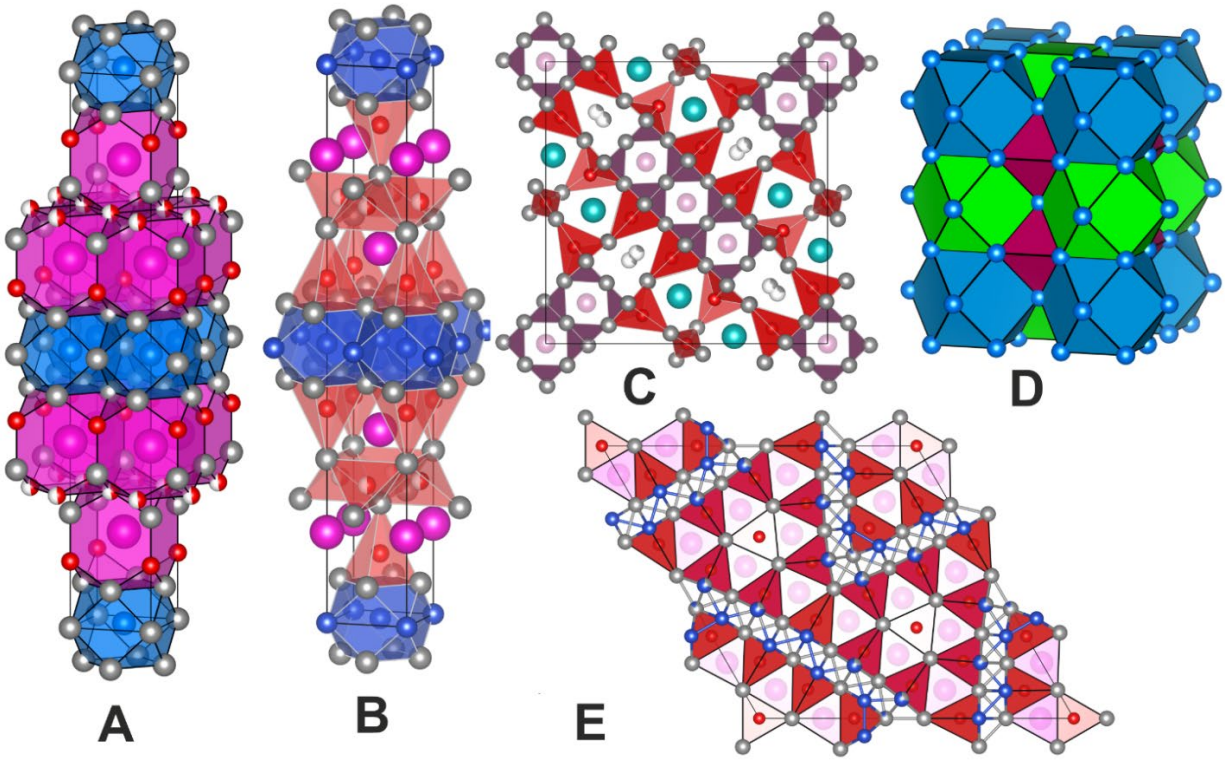


Fig. 1. Main structure types of quaternary phosphide platinides featured in the talk: **A** – $R_2Pt_7MP_{4-x}$, **B** – $R_2Pt_6Cu_2P_{4-x}$, **C** - $Sr_4Pt_{26-x}M_3P_9$, **D** - $R_6Pt_{30-x}Ni_{17+y}P_{22}$, **E** - $R_6Pt_{22-x}Cu_xP_9$.

The search is performed using flux-assisted crystal growth with lead or bismuth as metal fluxes. As a result, a large number of new compounds, both conforming to the concept of

$AuCu_3$/$CaBe_2Ge_2$ intergrowth structures and deviating from it, were synthesized and characterized based on the single-crystal X-ray diffraction data. New quaternary phosphide platinides form 5 families (see Fig. 1).

The first, with the largest number of representatives, is the tetragonal $R_2Pt_7MP_{4-x}$ family (R=Eu, Ca; M=Ti, Cr, Mn, Fe, Co, Ni, Zn, Al, Ga, In; x~ 1; see Fig.1A) [2], it also includes $Eu_2Pt_6Cu_2P_3$ compound (see Fig. 1B). These compounds are built as intrinsic heterostructures with layers of Pt_3M and RPt_2P_{2-x} fragments alternating along the *c* axis ($Eu_2Pt_6Cu_2P_3$ instead of the $AuCu_3$-type block has the AuCu-type block).

Another family is formed when strontium is used as an R element rather than calcium or europium, namely $Sr_4Pt_{26-x}M_3P_9$ (M=Al, Ga, In, Fe; see Fig. 1C). In these tetragonal compounds Pt_3M-type cuboctahedra form columns three-wide, which are joined together by phosphorus-centered platinum pyramids, which represent a hybrid of block-type intergrowth and 3D-framework structures.

Another interesting highly symmetric family of pseudo-cubic phosphide platinides is the $R_6Pt_{30-x}Ni_{17+y}P_{22}$-type compounds (R=Ca, Eu, Sr; see Fig. 1D), featuring complex Russian-doll-like structure based on nested polyhedra [3].

Finally, there is a family of the hexagonal compounds with the general formula of $R_6Pt_{22-x}Cu_xP_9$ (R=Ca, Eu; x=4-8), featuring complex framework where platinum and copper atoms can either form a herringbone pattern (x=8, see Fig. 1E), or an alternating platinum and copper in one part of the framework (x=4).

In the cases where the concept of block-type or hybrid structure failed due to the assumed instability of the fragments, we were still able to synthesize a number of new ternary phosphide platinides (typically without M entering the structure) belonging to either own or established structure types.

Many of the compounds in question, particularly those featuring either europium or europium/3d-metal combination, have interesting magnetic properties, which will also be mentioned in the talk. In this regard, the $R_2Pt_7MP_{4-x}$ family is especially remarkable as these compounds represent magnetic heterostructures, and will be discussed in more detail. The potential to vary the elements in the $AuCu_3$ and $CaBe_2Ge_2$-type fragments makes this family particularly interesting in terms of tunable magnetic properties.

This work was supported by Russian Science Foundation (grant № 25-13-00101)

References

[1] Steurer, W.; Dshemuchadse, J. *Intermetallics: Structures, Properties, and Statistics*, Oxford University Press, 1st edition, **2016**.

[2] Polevik, A.Yu.; Kuznetsov, A.N. *Russ. J. Inorg. Chem.,* **2026**, in press.

[3] Polevik, A.Yu.; Zakharova, E.Yu.; Nesterenko, S.N.; Kazakov, S.M.; Lyssenko, K.A.; Efimov, N.N.; Kuznetsov, A.N. *Inorg. Chem*., **2026**, 65, 11152.

Synchrotron radiation facility SKIF: new capabilities for chemical crystallography in Russia

Zubavichus Y.V., Vinokurov Z.S.

Synchrotron Radiation Facility SKIF, 630559, Koltsovo, Russian Federation,
SKIF Scientific Site 1
e-mail: ya.v.zubavichus@srf-skif.ru

Synchrotron Radiation Facility SKIF is a new large-scale research infrastructure project accomplished in the Science City of Koltsovo, ca. 15 km apart from Novosibirsk (Fig. 1). The 3 GeV electron storage ring designed by specialists from the Budker Institute of Nuclear Physics SB RAS will provide the record low emittance of 75 pm·rad. Major construction works on the SKIF site are finished, integrative commissioning of the SKIF's engineering systems, accelerator complex, and beamlines are currently underway. Furst regular users are expected in the second half of 2027.



Fig. 1. Digital model of SKIF (left) and real aerial photo of the construction site as of mid of July, 2026.

The accelerator complex of the SRF SKIF consists of an electron linear accelerator of 200 MeV, a full-energy synchrotron booster, and a storage ring. The storage of relativistic 3-GeV storage ring electrons, with a circumference of 476 m and an ultralow theoretical horizontal emittance of ca. 75 pm rad will produce synchrotron radiation (SR) in the photon energy range from 10 eV to 150 keV. For a photon energy of 2-5 keV, the source emittance approaches the diffraction limit, providing a high degree of spatial coherence thus expanding the research capabilities of the facility [1].

Currently, there are seven first-priority beamlines with different scientific scopes and aims. The first-priority beamlines of SKIF are as follows: 1-1 "Microfocus," 1-2 "Structural Diagnostics," 1-3 "Fast Processes," 1-4 "XAFS Spectroscopy and Magnetic Dichroism," 1-5 "Hard X-ray Diagnostics and Imaging," 1-6 "Electronic Structure", and 1-7 "Basic synchrotron techniques for students". In total, the SRF SKIF may accommodate up to 30 beamlines; 14 of them will use the radiation of special insertion devices (wigglers and undulators) in straight sections, and 16 will be located at either low-field (0.5 T) or high-field (2.0 T) bending magnets.

The main functional task of the SRF SKIF will be infrastructural support of fundamental and applied research of scientific and educational institutions, as well as industrial companies in order to ensure leadership in the priority lines of scientific and technological development of the Russian Federation.

The SRF SKIF will become a national-level multidisciplinary research and innovative centre. Key directions of the scientific program to be deployed at the SRF SKIF will encompass biomedicine,

green technologies in chemistry and energetics, advanced engineering materials and mechanical engineering technologies.

Chemical crystallography and structural biology are envisaged among major scientific directions of the SKIF. Single-crystal X-ray diffraction (for crystals of both small and macromolecules) will be implemented as a part of the 1-2 “Structural Diagnostics” beamline functionality. The optical scheme of the beamline along with the photo of the diffractometer installed inside the experimental hutch is shown in Fig. 2. A robotic sample changer ans specialized auxiliary equipment for the automated protein crystallization will be available for users in the support Labs building.

The present lecture briefly outlines the history and current status of the SKIF project, its major research directions and plans for the infrastructure development with the emphasis on crystallography-related facilities within SKIF.

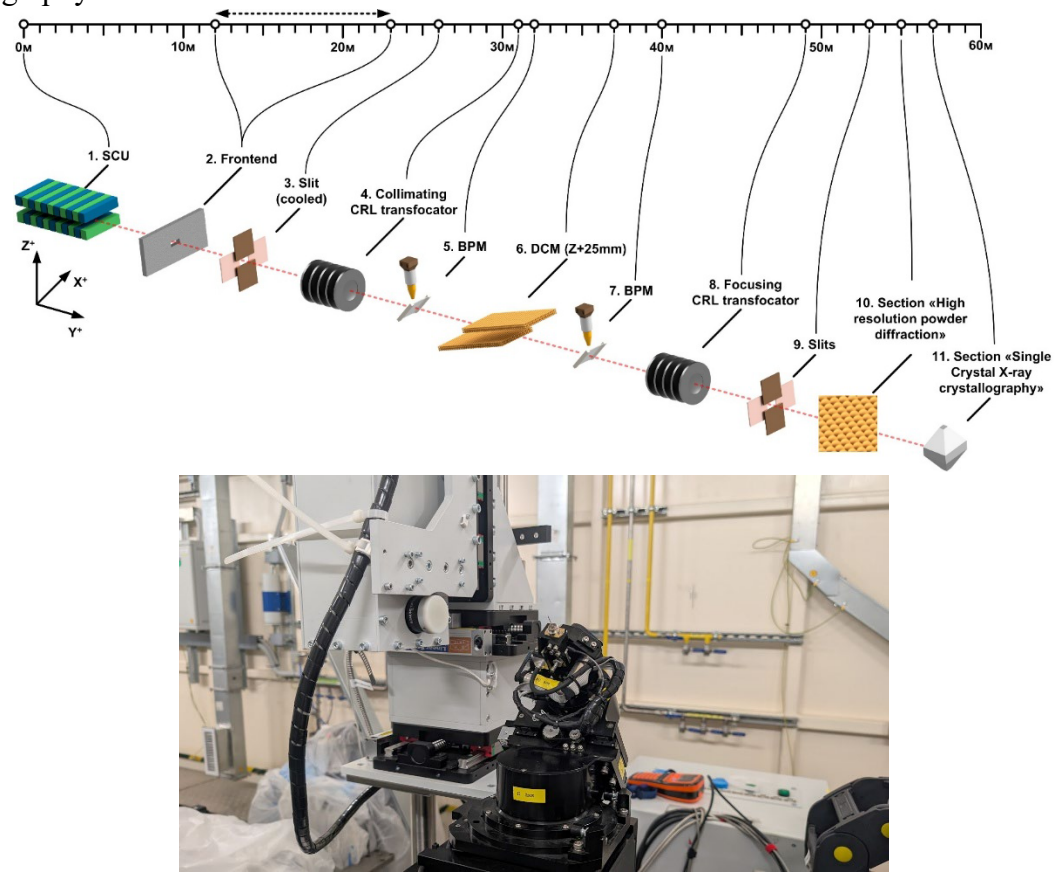


Fig. 2. Optical scheme of the 1-2 “Structural diagnostics beamline (top) and photo of the single-crystal difftactometer unit designed by the Institute of High-Current Electronics SB RAS (bottom).

This work was partially supported by the Ministry of Science and Higher Education of the Russian Federation within the budget project of SRF SKIF, Boreskov Institute of Catalysis, SB RAS

References

[1] Bukhtiyarov, A.V.; Bukhtiyarov, V.I.; Zhuravlev, A.N.; Zolotarev, K.V.; Zubavichus, Y.V.; Levichev, E.B.; Mezentsev, N.A.; Nikolenko, A.D.; Piminov, P.A. Churkin, I.N. “Synchrotron Radiation Facility “Siberian Circular Photon Source” (SRF SKIF),” *Crystallogr. Rep*., **2022**, 67(5), 690-711, doi: 10.1134/S1063774522050029.

Unusual structures of oligosilanes and siloxanes ~crystallographic work

Unno M., Liu Y., Takeda N.

Materials and Environment Division, Faculty of Science and Technology, Gunma University, JAPAN
e-mail: unno@gunma-u.ac.jp

From the early 90's, we have been focusing on the synthesis of novel silicon compounds. Occasionally, crystallographic analysis has revealed totally unexpected structures. In this talk, I will summarize the structures we have determined.

In 1988, our group reported the first synthesis of octasilacubane ($(t\text{-BuMe}_2\text{Si})_8\text{Si}_8$) **1**. This compound and its alkyl-substituted analog exhibit interesting reactions owing to their high strain and electronic properties. As a first example, we show the products of the halogenation reactions of octasilacubane [1]. The most unusual structure was observed in reactions with sulfur or selenium [2]. We also show the products.

The compound that amazed us the most is silicon sesquisulfide cage **2**. This compound can form both adamantane and double-decker structures, and adamantane one can only crystallize with S_8 and benzene. The structure was totally beautiful [3].

We prepared silapericyclynes with different ring sizes, and the largest **3** crystallized into two different structures. Both chair and boat conformations were stable, and we were able to determine the structures [4].

Cyclic silanol 4 is a versatile precursor to cage, ladder, and many novel silsesquioxanes. However, during the first synthesis, three stereoisomers with similar spectra were observed. The preparation of single crystals was difficult; however, we succeeded. The compound co-crystallized with an unusual solvent[5].

Among the well-defined silsesquioxanes, we recently synthesized butterfly cage **5**[6] and bat siloxane **6**[7]. Both compounds contain large D-rings, but their thermal stability is similar to that of T-cages. Within the flexible wings, they can contain guest molecules.

References

[1] M. Unno, K. Higuchi, M. Ida, H. Shioyama, S. Kyushin, M. Goto, and H. Matsumoto, *Organometallics*, **13**, 4633–4635 (1994).
[2] M. Unno, N. Yamashita, and H. Matsumoto, *Phosphorus, Sulfur, Silicon Relat. Elem.*, **186**, 1259–1262 (2011).
[3] M. Unno, Y. Kawai, H. Shioyama, and H. Matsumoto, *Organometallics*, **16**, 4428–4434 (1997).
[4] M. Unno, T. Saito, and H. Matsumoto, *Chem*. *Lett*., **28**, 1235–1236 (1999).
[5] M. Unno, K. Takada, and H. Matsumoto, *Chem. Lett.*, **27**, 489–490 (1998).
[6] R. Kunthom, T. Adachi, Y. Liu, N. Takeda, M. Unno, R. Tanaka, *Chem. Asian J.*, **14**, 4179–4182 (2019).
[7] T. Chaiprasert, Y. Liu, P. Intaraprecha, R. Kunthom, N. Takeda, M. Unno, *Macromol. Rapid Commun*., **42**, 2000608 (2021).

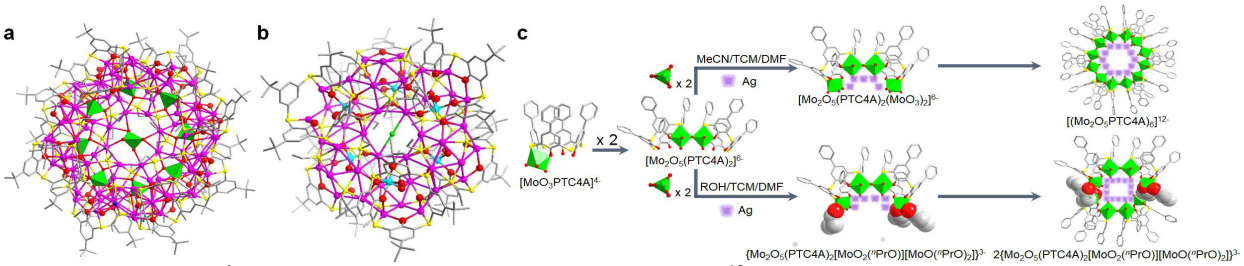
Synthesis and Assembly Mechanism of Silver Nanoclusters Protected by Thiacalix[4]arene

Wang Z., Sun D.

Department of Chemistry, University of Shandong, Shandong province, Jinan, 250100
e-mail: zwang@sdu.edu.cn

Compared with the traditional mono-site ligands, thiacalix[4]arene, composed of phenolic hydroxyl and bridging sulfur groups in proximity of each other, can effectively suppress the coordination dissociation equilibrium during silver cluster assembly and significantly improve their stability. Herein, an anion templated Ag_{88} nanocluster (**Ag88**) built from thiacalix[4]arene was synthesized and characterized. The structure of Ag_{88} can be deconstructed to eight [CrO_4@Ag_{11}] secondary building units (SBU) arranged in an annulus encircling a CrO_4^{2-} in the center. Local and global anion template effects from CrO_4^{2-} are individually manifested in Ag . The hierarchical assembly mechanism from bowl-like Ag_{11} SBU, a semicircular Ag44 fragment to the final circular Ag_{88} supercalix was also revealed by using electrospray mass spectrometry (ESI-MS). Under the guidance of ESI-MS, the author reported the stepwise syntheses of a family of halogen-templated Ag_{42} nanoclusters based on Mo^{VI}-anchored thiacalix[4]arene as a metalloligand. In combination with solvent intervention, the condensation degree of the metalloligand was successfully manipulated at the molecular level. Hexagonal and rectangular Ag_{18} nanoclusters are constructed from the $[Mo_2O_5(PTC_4A)_2]^{6-}$ (H_4PTC4A=p-phenylthiacalix[4]arene) metalloligand through stepwise assembly. The pre-organized metalloligand assembled with silver ions to form two geometrically different Ag_{18} nanoclusters in different solvents. The cyclization from the metalloligand to $[(Mo_2O_5PTC4A)_6]^{12-}$ can be realized without alcohols and otherwise blocked by them. The installation of the thiacalix[4]arene not only provides comprehensive understanding of how the solvents regulate the silver nanocluster structures, but also brings new insights for the controllable ligand metallization and subsequent condensation.

Fig. 1 The crystal structure of Ag88 (a) and Ag42 (b); (c) Silver-assisted cyclization of



$[Mo_2O_5(PTC_4A)_2]^{6-}$ metalloligand to form $[(Mo_2O_5PTC4A)_6]^{12-}$ metallamacrocycle in different solvents.

This work was supported by the National Natural Science Foundation of China (grant № 91961105)

References

[1] Wang, Z.; Su, H.-F.; Gong, Y.-W.; Qu, Q.-P.; Bi, Y.-F.; Tung, C.-H.; Sun, D.; Zheng, L.-S. Nat. Commun., 2020, 11, 308.
[2] Wang, Z.; Su, H.-F.; Zhang, L.-P.; Dou, J.-M.; Tung, C.-H.; Sun, D.; Zheng, L. ACS Nano, 2022, 16, 4500.
[3] Wang, Z.; Li, L.; Feng, L.; Gao, Z. Y.; Tung, C. H.; Zheng, L. S.; Sun, D. Angew. Chem. Int. Ed. 2022, 61, e202200823.

Structural and physicochemical studies of pyrimidine-modulated tripyridyldiamine ligand and its metal complexes

Ismayilova S.Z., Ismayilov R.H., Peng S.M.

"Institute of Chemistry" Public Legal Entity, Ministry of Science and Education of the Republic of Azerbaijan, H. Javid Ave., 113, AZ 1143 Baku, Azerbaijan
e-mail: ismayilov.rayyat@gmail.com

Extended metal atom chain (EMAC) complexes have attracted considerable attention because they provide valuable insight into the fundamental nature of metal–metal interactions and offer promising prospects for applications in molecular-scale electronic devices, particularly as molecular wires and switches [1]. Numerous metal-string complexes containing three, four, five, six, seven, nine, and eleven metal centers have been successfully synthesized and structurally characterized [1-6]. These compounds incorporate various transition metals, including Cu, Ni, Co, Cr, Ru, and Rh, coordinated by oligo-α-pyridylamido ligands.

Using pyrimidine-modulated ligand, N^2-(pyridin-2-yl)-N^6-(pyrimidin-2-yl)pyridine-2,6-diamine (H_2pppmda) a new pentanickel metal string complex [$Ni_5(\mu_5$-pppmda$)_4Cl_2$](**1**) have been synthesized and structurally characterized.

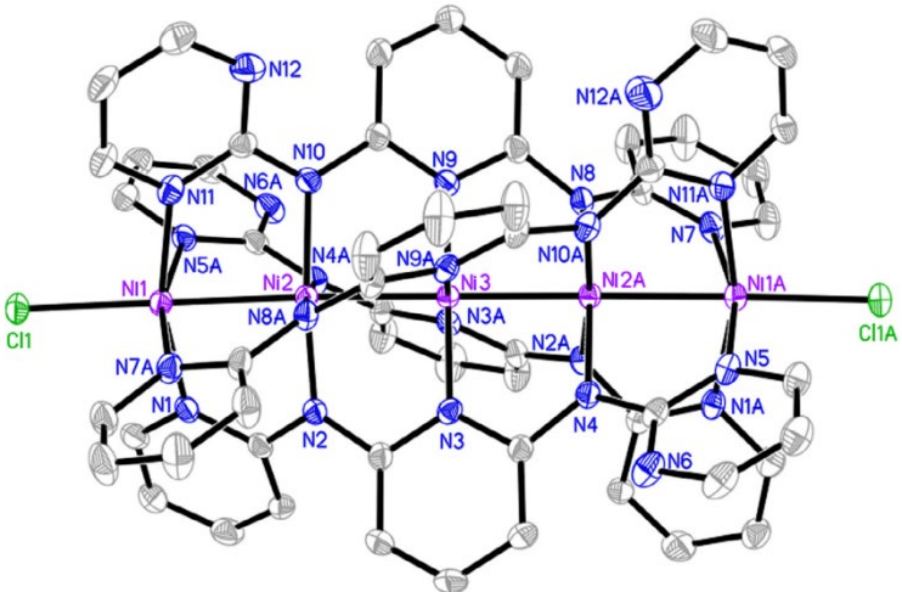


Fig. 1. Crystal structure of [$Ni_5(\mu_5$-pppmda$)_4Cl_2$] in **1** ·2$CHCl_3$ CH_2Cl_2. Thermal ellipsoids are at the 30% probability level, and hydrogen atoms are omitted for clarity. Label A was generated through the symmetry operation (x, y, z + 1/2).

The [$Ni_5(\mu_5$-pppmda$)_4Cl_2$] complex involves a Ni_5 linear chain unit where all the Ni–Ni–Ni angles are nearly 179 °, and which is terminated by the two axial ligands. The pentanuclear linear metal chain is helically wrapped by four syn–syn–syn–syn type $pppmda^2$ ligands. There are two types of Ni–Ni distances in this complex. Terminal Ni–Ni distances bonded with the axial ligand are longer (2.3669(8) Å); the inner Ni–Ni distances are short at 2.2987(6) Å. The terminal Ni(II) ions bonded with the axial ligands are square-pyramidal (NiN_4Cl) with long Ni–N_{av} bonds (2.096 Å), consistent with a high-spin Ni(II) configuration. The inner three Ni(II) ions have short Ni–N_{av} bond distances

(1.902(4)–1.888(4) Å), consistent with a square planar (NiN_4), diamagnetic arrangement of a low-spin Ni(II) configuration. This compound exhibits magnetic behavior similar to $[Ni_5(\mu_5\text{-tpda})_4Cl_2]$, indicating an antiferromagnetic interaction of the two terminal high-spin Ni(II) ions. Electrochemical studies showed that the pentanickel(II) complex can undergo one reversible oxidation at +0.76 V. The introduction of an electron-withdrawing pyrimidine ring to the spacer ligand retarded the oxidation of the pentanickel metal string and stabilized the complex.

A detailed comparison of the structural and magnetic properties of $[Ni_5(\mu_5\text{-pppmda})_4Cl_2]$ (**1**) and its unsubstituted analogue, $[Ni_5(\mu_5\text{-tpda})_4Cl_2]$, indicates that the pentanickel complexes supported by H_2pppm and H_2tpda exhibit closely comparable structural and magnetic behavior. In contrast, their electrochemical properties differ significantly. Complex **1** displays a single reversible one-electron oxidation wave at a relatively positive potential (+0.76 V), suggesting that incorporation of the electron-withdrawing pyrimidine moiety into the supporting ligand makes oxidation of the metal chain more difficult and consequently enhances the stability of the complex.

References

[1] (a) J. Berry, F. Cotton, L. Daniels, C. Murillo, J. Am. Chem. Soc. 124 (2002) 3212; (b) S.-Y. Lin, I.-W.P. Chen, C.-H. Chen, M.-H. Hsieh, C.-Y. Yeh, T.-W. Lin, Y.-H. Chen, S.-M. Peng, J. Phys. Chem. B 108 (2004) 959; (c) I.-W.P. Chen, M.-D. Fu, W.-H. Tseng, J.-Y. Yu, S.-H. Wu, C.-J. Ku, C.-H. Chen, S.-M. Peng, Angew. Chem., Int. Ed. Engl. 45 (2006) 5414.

[2] (a) S.-Y. Lai, T.-W. Lin, Y.-H. Chen, C.-C. Wang, G.-H. Lee, M.-H. Yang, M.-K. Leung, S.-M. Peng, J. Am. Chem. Soc. 121 (1999) 250; (b) F.A. Cotton, L.M. Daniels, C.A. Murillo, X. Wang, Chem. Commun. (1998) 39; (c) X. López, M.-Y. Huang, G.-C. Huang, S.-M. Peng, F.-Y. Li, M. Bénard, M.-M. Rohmer, Inorg. Chem. 45 (2006) 9075.

[3] (a) C.-H. Chien, G.-H. Lee, Y. Song, S.-M. Peng, Dalton Trans. (2006) 3249; (b) C.-H. Chien, J.-C. Chang, C.-Y. Yeh, G.-H. Lee, J.-M. Fang, S.-M. Peng, Dalton Trans. (2006) 2106.

[4] (a) Y.-H. Chen, C.-C. Lee, C.-C. Wang, G.-H. Lee, S.-Y. Lai, S.-M. Peng, Chem. Commun. (1999) 1667; (b) S.-Y. Lai, C.-C. Wang, Y.-H. Chen, C.-C. Lee, Y.-H. Liu, S.-M. Peng, J. Chin. Chem. Soc. 46 (1999) 477; (c) W.-Z. Wang, R.H. Ismayilov, G.-H. Lee, I.P.-C. Liu, C.-Y. Yeh, S.-M. Peng, Dalton Trans. (2007) 830.

[5] (a) S.-M. Peng, C.-C. Wang, Y.-L. Jang, Y.-H. Chen, F.-Y. Li, C.-Y. Mou, M.-K. Leung, J. Mag. Magn. Mater. 209 (2000) 80; (b) R.H. Ismayilov, W.-Z. Wang, R.-R. Wang, C.-Y. Yeh, G.-H. Lee, S.-M. Peng, Chem. Commun. (2007) 1121.

[6] R.H. Ismayilov, W.-Z. Wang, G.-H. Lee, R.-R. Wang, C.-Y. Yeh, S.-A. Hua, Y. Song, M.-M. Rohmer, M. Benard, S.-M. Peng, Angew. Chem., Int. Ed. 50 (2011) 2045.

How can we trust our crystal structure solutions? *Pseudo*-homometry and chemical reliability in single-crystal X-ray diffraction

Virovets A.V.

Faculty of Biochemistry, Chemistry, Pharmacy, Goethe-Universität Frankfurt, 60438 Frankfurt am Main, Max-von-Laue-Str. 9
e-mail: a_v_virovets@yahoo.com

Since the 1980s, progress in single-crystal X-ray diffraction (SCXRD) has made it one of the main methods of characterization in synthetic chemistry. In the USSR, Yuri Timofeyevich Struchkov (1926–1995) undoubtedly played an outstanding role in this process. My personal way to SCXRD began in his lab in 1987. This unique experience crucially influenced my further professional career.

Summarizing more than 30 years in experimental structural chemistry, I decided to look closely at the basic principles of SCXRD that none of us place in doubt. One of them, intuitively obvious, states that the given set of structural amplitudes, $|F|_{hkl}$, corresponds to a unique structural model (the set of atomic coordinates, occupancy factors, and displacement parameters). In other words, *the structure solution is unique*. To the best of my knowledge, there is no formal mathematical proof for this. The structures that give the same diffraction pattern can be called *homometric* [1]. Moreover, diffraction intensities are always measured within some accuracy, and the structural model from a non-linear least-squares procedure features some confidence interval. Let us call two crystal structures *pseudo-homometric* if corresponding structural models, statistically different in the *chemical composition* and/or *constitution* (*connectivity*), give experimentally indistinguishable $|F|_{hkl}$ values. If such structures (potentially) exist, the validity of chemical connectivity as one of the most chemically essential, sensitive results of SCXRD can be questioned.

Different base scenarios of *pseudo*-homometry are possible: models differ in the translational and/or point symmetry (scenario I); the symmetry is the same, but $|F|_{hkl}$ are still not sensitive to chemically significant changes in the model (scenario II); crystallographic disorder 'mixes' chemically different atomic structures, making it impossible to determine the connectivity (scenario III). For example, weak reflections may hide the superstructural ordering, resulting in a chemically wrong model (scenario I). The presence of chemical elements with similar atomic scattering factors leads to scenario II. In some cases, a disordered atomic pattern may allow contradictory interpretations. Crystal structures of giant metal-based supramolecules provide excellent examples of how disorder 'merges' dozens and even millions of isomers in a single crystallographic position (scenario III) [2, 3].

In this presentation, we will discuss practical examples of *pseudo*-homometric structures. We will see how additional information from other physical methods together with chemical data, as well as knowledge of structural chemistry, helps us to solve crystal structures accurately.

References

[1] Farkas-Jahnke, M.; Dornberger-Schiff, K. *Acta Cryst*. **1969**, A25, 35.
[2] Heindl, C.; Peresypkina, E.V.; Virovets, A.V.; Bushmarinov, I.S.; Medvedev, M.G.; Krämer, B.; Dittrich, B.; Scheer, M. *Angew. Chem. Int. Ed*., **2017**, 56, 13237.
[3] Virovets, A. V.; Peresypkina, E.; Scheer, M. *Chem. Rev*. **2021**, 121, 14485.

MOFs and Selected Catalytic Applications towards Sustainability

Pombeiro A.J.L.

Centro de Química Estrutural, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisbon, and Academy of Sciences of Lisbon, Rua da Academia das Ciências 19, 1249-122 Lisbon, Portugal
e-mail: pombeiro@tecnico.ulisboa.pt

Metal-organic frameworks (MOFs) and coordination polymers (CPs) concern metal architectures with a diversity of compositions (including metal centres, ligands and linkers), structures and properties that can be exploited for a variety of applications. They can exhibit controlled organic functionalities, high surface areas in porous architectures, confined chemical environments, low solubility in common solvents, etc., that control their applications, namely in catalysis, gas and liquid adsorption, chemical sensing, drug delivery, etc.

This talk addresses mainly the synthesis, structure and catalytic applications for selected reactions, in fields aligned with some of the UN Sustainable Developments Goals. The MOFs, CPs or related assemblies are based on metals (eg, transition metals of the first row of the Periodic Table) and other elements that are not at current risk of availability and sustainability due to conflict resources.

The selected reactions include hydrocarbon functionalization (by oxidation and carboxylation) and CO_2 utilization for the synthesis of valuable organic compounds, as well as water splitting reactions. Examples of other types of applications can also be mentioned.

Acknowledgments: The co-authors of the publications are gratefully acknowledged. The work was financially supported by LA/P/0056/2020 (IMS DOI https://doi.org/10.54499/LA/P/0056/2020) and CQE UID/00100/2025 (https://doi.org/10.54499/UID/00100/2025), UID/PRR/100/2025 (https://doi.org/10.54499/UID/PRR/00100/2025) and UID/PRR2/00100/2025 (https://doi.org/10.54499/UID/PRR2/00100/2025) funded by national funds through FCT/MECI (PIDDAC).

References

[1] “Science for Sustainability”, A.J.L. Pombeiro (Ed.), World Scientific, 2027. Chs 1, 25, 26 and 32.
[2] B. Mohan, S. Wei, E. Ahmadov, I.M. Garazade, N. Raghav, A.J.L. Pombeiro, “MOFs Engineered for the Capture and Conversion of Carbon Dioxide”, Ch. 25, Vol. 3, in [1].
[3] A.N. Bilyachenko, M.F.C. Guedes da Silva, A.J.L. Pombeiro, “Cage Copper- and Manganese-Silsesquioxanes: Synthesis, Structure, and Catalysis under Mild Conditions”, Ch. 32, Vol. 4, in [1].
[4] N. Reis Conceição, K.T. Mahmudov, M.F.C. Guedes da Silva, A.J.L. Pombeiro, ¨Alkane Functionalization: Recent Advances”, *Coord. Chem. Rev*., 2025, *522*, 216175.
[5] “Catalysis for a Sustainable Environment”, A.J.L. Pombeiro, M. Sutradhar, E.C.B.A. Alegria (Eds.), John Wiley & Sons, 2024. Chs. 1, 20 and 38.
[6] "Synthesis and Applications in Chemistry and Materials", A.J.L. Pombeiro, K.T. Mahmudov, M.F.C. Guedes da Silva (Eds.), World Scientific, 2024, Chs. 7, 8, 9 and 33.

Confinement Effects in Metal-Organic Frameworks: From Crystal Structure to Advanced Functional Materials

Mohan B.B.

Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, Lisboa, 1049-001, Portugal
e-mail: brij.mohan@tecnico.ulisboa.pt

Metal–organic frameworks (MOFs) offer precisely controlled nanospaces for confining molecules, ions, and nanoparticles, significantly impacting coordination, electronic interactions, molecular organization, diffusion, adsorption, and reactions. Understanding how crystal structure influences these effects is crucial for designing advanced MOF materials. This talk explores how pore architecture, topology, functionality, defects, and flexibility affect confined-species behavior, including host–guest interactions, stabilization of reactive species, local electronic changes, and transport. Examples with molecular, metal, and hybrid structures demonstrate how confinement enhances selectivity, reactivity, and transport. This approach broadens MOF applications from passive hosts to customizable nanoscale environments that enable new functions, advancing fields like sensing, catalysis, separation, and energy, and guiding the development of next-generation functional materials.

Charging carbon bowls, hoops, and graphene fragments with multiple electrons through the lens of crystallography

Petrukhina M.A.

Department of Chemistry, University at Albany, State University of New York, Albany, NY
e-mail: mpetrukhina@albany.edu

Recent advances in synthetic organic chemistry provided access to a great variety of novel molecular nanocarbons and nanographenes with precise dimensions, compositions and controlled placement of non-hexagonal rings. The resulting large non-planar polyarenes attract significant attention from chemists and theoreticians due to their unique structures and properties. These nanosize π-scaffolds could acquire multiple electrons in stepwise reduction reactions, showing potential for energy storage applications. Studies of structures and electronic properties of π-conjugated molecules in response to gradual build-up of negative charge become the focus of our research program. Using a combination of X-ray crystallography, spectroscopy, and theory, we unravel changes in molecular geometry, aromaticity and spin localization for a diverse range of molecular nanographenes. By charging the design π-hosts with multiple electrons we reveal their unusual core rearrangements and original coupling pathways which could be charge- and topology-dependent. Several π-systems having different carbon frameworks [1-3], dimensions and symmetry will be discussed, stimulating our fundamental understanding of curved polyaromatics and advancing their material chemistry applications.

References

[1] Stawski, W.; Zhu, Y.; Rončević, I.; Wei, Z.; Petrukhina, M.A.; Anderson, H.L. *Nat. Chem*., **2024**, *16,* 998.
[2] Zhou, Z.; Petrukhina, M.A. *Chem. Sci*. *Perspective,* **2025**, *16*, 468.
[3] Zhu, Y.; Petrukhina, M.A. *Chem. Soc. Rev.,* **2026**, *55*, 3061.

Current status of Pt-based 1D solids

Gerasimchuk N.

Missouri State University, Department of Chemistry and Biochemistry, Springfield, MO 65897. USA
e-mail: NNGerasimchuk@MissouriState.edu

Since discovery of $[Pt(NH_3)_4][PtCl_4]$, "green salt" by Gustav Magnus, interest to unusual self-aggregating Pt-based compounds grew considerably and resulted in intense investigations of similar compounds that show preferable extension in one dimension. In general, these structures received name 1D solids and their thus far observed motifs are presented in Figure 1.

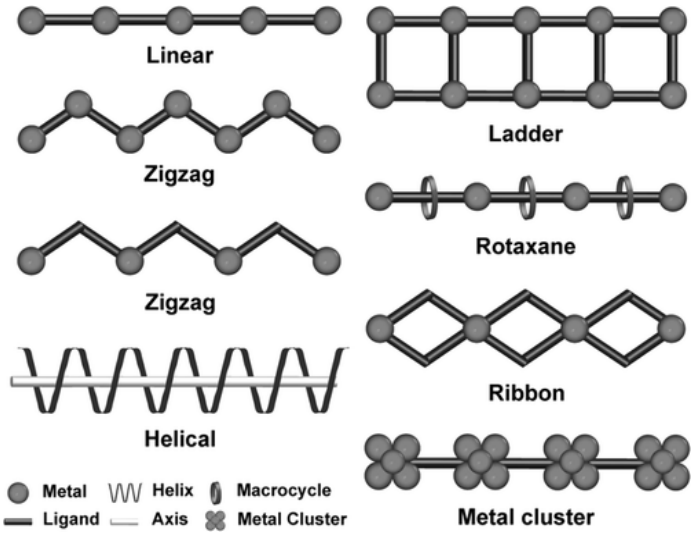


Fig. 1. Repetitive structural patterns of solids extended in one dimension.

The most interesting feature of such solid structures involving platinum ions is metallophilic interactions [1] that facilitate formation of "Pt-wires" with direct short intermetallic contacts. Very often these solids were found to be mixed valence compounds that show a variable degree of electrical conductivity. Naturally, organic counterparts in such Pt-wires play key role in the formation of these 1D polymers that very often represent formations referred as "poker chip" stacks. Recently a pronounced red photoluminescence of these formations gained significant attention. One of the main reasons was effect of an external stimuli (pressure, temperature, vapours of volatile compounds) on intensity and wavelength of observed photoemission [2].

A brief review of current trends in the ligands' design, structural chemistry, physical properties of Pt-based 1D solids is provided in this presentation.

References

[1] Pyykkö P. Strong closed-shell interactions in inorganic chemistry. Chem. Rev. (1997) 97 (3), 597-636.

[2] Wenger O. Vapochromism in organometallic and coordination complexes: chemical sensors for volatile organic compounds. Chem. Rev. 2013, 113, 5, 3686–3733.

Structure and functional properties of metal-organic frameworks

Fedin V.P.

Nikolaev Institute of Inorganic Chemistry SB RAS, 630090, Novosibirsk, 3 Lavrentiev Ave.
e-mail: cluster@niic.nsc.ru

Metal–organic frameworks (MOFs) represent a prominent class of coordination polymers where metal nodes are linked by bridging organic ligands into ordered porous networks. A defining feature of MOFs is their intrinsic porosity, offering accessible channels for guest molecule encapsulation. Consequently, these materials are intensively investigated due to the unique capability to tailor their functional properties for targeted applications [1-5].

While frameworks with permanent porosity are widely utilized for molecular separation and selective detection, chiral MOFs (CMOFs) have emerged as a particularly compelling subclass. Unlike other chiral nanomaterials (e.g., nanoparticles or carbon nanotubes), CMOFs possess well-defined chemical compositions and crystalline structures, which are crucial for elucidating the precise mechanisms of enantioselective recognition. Although the application of luminescent CMOFs in enantioselective fluorescent sensing has only recently begun to explore, it holds immense potential.

This work aims to synthesize novel, rationally designed chiral MOFs that exhibit distinct photoluminescent responses upon selective interactions with different analyte enantiomers. The integration of X-ray diffraction analysis and theoretical modeling will provide a molecular-level understanding of the host–guest interactions governing this efficient enantioselective recognition.

This work was supported by the Russian Science Foundation (grant № 26-13-00002)

References

[1] Sapchenko S.A. et al. *Nature Commun*., **2025**, 16, 1578.
[2] Pavlov D.I. et.al. *J. Amer. Chem. Soc*., **2026**, 148, 17240.
[3] Burlak P.V. et al., *Dalton Trans*., **2026**, 55, 2937.
[4] Yu X. et al. *Inorg. Chem*., **2025**, 64, 6356.
[5] Yu X. et al. *J. Amer. Chem. Soc*., **2026**, 148, 14197.

New Electrode Materials for Metal-ion Batteries

Antipov E.V.

Faculty of Chemistry, Moscow State University named after M.V. Lomonosov
Skolkovo Institute of Science and Technology
Institute of Organic Chemistry RAS named after N.D. Zelinsky
e-mail: evgeny.antipov@gmail.com

Lithium-ion battery production is rapidly expanding, with the market projected to reach 8-10 TWh by 2030. These energy storage devices were originally developed for portable devices but are now widely used as stationary energy storage devices, in electric vehicles and other applications. At the same time, sodium-ion batteries, which offer several advantages over lithium-ion batteries, are actively researched and have already been manufactured at large scale.

The specific energy characteristics of lithium-ion and sodium-ion batteries are primarily determined by the properties of the electrode materials employed. Investigating these materials using various diffraction-based (X-ray and neutron) and spectroscopic techniques—conducted *in operando* — yields vital information regarding the mechanisms of intercalation processes, phase transformations, changes in the oxidation states of transition metals, and more.

The presentation will cover the current state and development trends of lithium-ion battery production globally and in Russia, the prospects for sodium-ion batteries, and the results of our research into novel electrode materials (such as $NaNbV(PO4)_3$, $NaVPO_4F$, $NaVP_2O_7$ and etc.) for batteries—with a particular focus on the interrelationships between chemical composition, synthesis conditions, crystal structure, and the electrochemical properties of these materials.

This work was completed as part of Moscow State University's State Assignment No. AAAA-A21-121011590088-4

New materials and X-rays: what to expect when they meet?

Chernyshev V.V.

Chemistry Dept. M.V. Lomonosov Moscow State University, Leninskie Gory, 1-3, 119234 Moscow
e-mail: vladimir@struct.chem.msu.ru

Nowadays, it is impossible to imagine the emergence of a new solid-state material that has not undergone comprehensive X-ray analysis. X-ray radiation used for scientific purposes causes virtually no damage to the sample itself. Moreover, the widespread availability and ease of use of experimental X-ray equipment enable the rapid execution of numerous studies that are essential during the initial stages of new material development — such as classical phase analysis; analysis of thin and ultrathin films and multilayer coatings; analysis of nanoscale powders and materials; nanoparticle size distribution analysis via small-angle X-ray scattering; detection of phase transitions accompanying changes in sample crystal structure parameters; determination and refinement of unit cell parameters; and the identification of unknown crystal structures..

This lecture will focus on the challenges encountered when working with new powder materials during the determination of crystal structures directly from powder diffraction data. Structure determination from powder diffraction (SDPD) methods have been actively evolving for decades and have established themselves as a reliable source of new crystal structures—a fact confirmed by the tens of thousands of such structures listed in the Cambridge Structural Database. However, the development of new SDPD techniques does not eliminate the need to address long-standing challenges frequently encountered by researchers developing new functional materials. These challenges include, among others: the sample may contain several new crystalline phases; poor crystallinity of the new target phase; sample instability upon exposure to air or other external factors (such as temperature or X-ray radiation); extremely limited sample quantities; and discrepancies between the sample's elemental composition (which almost invariably includes an amorphous phase) and the actual composition of the crystalline phase under study. Alongside a brief overview of the current capabilities of SDPD methods, the lecture will examine possible ways to overcome the problems mentioned above.

In conclusion, the critical importance of high-resolution synchrotron diffraction in the structural characterization of new materials will be demonstrated, and practical examples of successful application of SDPD methods to various inorganic and organic materials will be presented.

Obtaining high-quality X-ray crystallographic and functional states on the membrane protein bacteriorhodopsin — 10 years later.

Borshchevskiy V.I.

Moscow institute of physics and technology
e-mail: borshchevskiy@gmail.com

Seven-transmembrane α-helical proteins connect two fields recognized by Nobel Prizes in the twenty-first century. This shared architecture links receptors targeted by more than one-third of approved drugs with proteins that enable to control neuronal activity using light. Understanding their function requires reliable structural models and experimental approaches that capture the conformational changes underlying ion transport and cellular signaling.

This talk traces our research from bacteriorhodopsin to human GPCRs, focusing on advances in membrane protein structural biology. Modern synchrotron methods and X-ray free-electron lasers provide access to high-resolution structures, while time-resolved experiments capture transient intermediates and assemble structural snapshots into molecular movies. Together, these approaches reveal how local changes at a chromophore or ligand-binding site are coupled to larger conformational rearrangements. Studies of G protein-coupled receptors illustrate how structural information explains ligand recognition and receptor selectivity, providing a foundation for drug discovery.

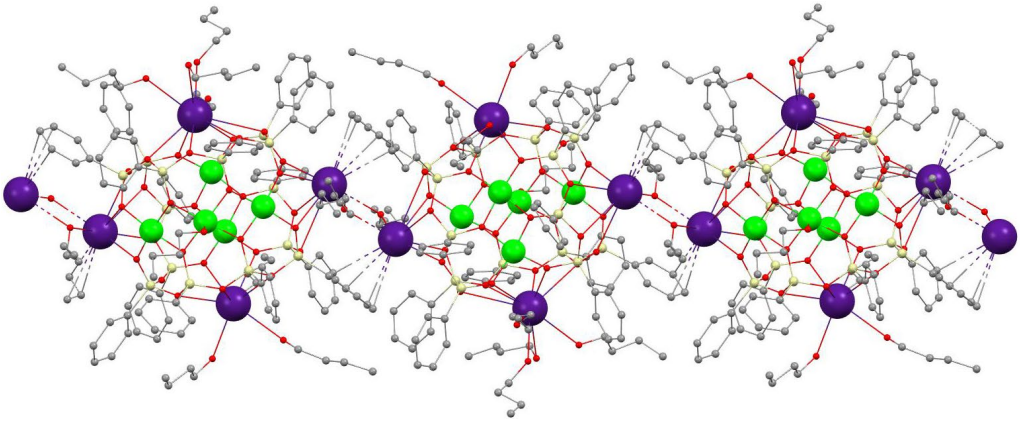
From static structures to molecular movies, these developments bring the mechanisms of membrane proteins into sharper focus and open new opportunities for understanding and modulating their function.

Supramolecular cagelike metallasilsesquioxanes: structure and catalytic activity

Bilyachenko A.N., Bachinskiy A.V.

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991, Moscow, Vavilov str. 28
Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: bilyachenko@ineos.ac.ru

Cagelike metallasilsesquioxanes is a fast-growing class of metallacomplexes with attractive (supra)molecular architectures and valuable properties [1]. Lecture will present novel approaches to Cu--silsesquioxanes and their complexes with auxiliary organic-ligands. Noncovalent mechanisms leading to intriguing aggregation of coppersilsesquioxane coordination polymers [2] will be discussed as well. Functionality of metallsilsesquioxanes in a focus of their catalytic activity will be shown.



1D coordination polymer structure of Cu_5Cs_4-phenylsilsesquioxane [3]

This work was supported by the Russian Science Foundation (grant № 25-73-20040)

References

[1] A.N. Bilyachenko, N. Reis Conceição, M.F.C. Guedes da Silva, K.T. Mahmudov, G.B. Shul'pin, A.J.L. Pombeiro, in *Synthesis and Applications in Chemistry and Materials*, *Series on Chemistry, Energy and the Environment: Metal Coordination and Nanomaterials*; World Scientific, **2024**, 11, 245

[2] A.N. Bilyachenko, A.J.L. Pombeiro, M.F.C. Guedes da Silva, E.S. Shubina, Y. Guari, J. Larionova, *Coord. Chem. Rev*. **2026**, 551, 217455

[3] A.N. Bilyachenko, I.S. Arteev, V.N. Khrustalev, L.S. Shul'pina, A.A. Korlyukov, N.S. Ikonnikov, E.S. Shubina, Y.N. Kozlov, N. Reis Conceiçao, M.F.C. Guedes da Silva, K.T. Mahmudov, A.J.L. Pombeiro, *Inorg. Chem.* **2023**, 62, 13573.

Absolute Asymmetric Supramolecular Synthesis — Engineering of Enantiomorphic Crystals

Antipin I.S.

A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, Arbuzov str., 8, Kazan, 420088
e-mail: iantipin54@yandex.ru

Homochirality is one of the signatures of life. The spontaneous generation of homochirality in an achiral environment is very important to understand the origin of life in the universe [1-3]. In this report an absolute asymmetric supramolecular synthesis by analogy with absolute asymmetric organic synthesis is introduced.

On the examples of metacyclophane and thiazolo[3,2-a]pyrimidine derivatives, a hierarchical approach to the implementation of absolute asymmetric supramolecular synthesis in the crystalline phase by tuning non-covalent intermolecular interactions leading to the formation of optically active products from achiral or racemic precursors is demonstrated,.

References

[1] D. P. Glavin, A. S. Burton, J. E. Elsila, J. C. Aponte, J. P. Dworkin, *Chem. Rev.*, **2020**, 120, 4660.
[2] A. Salam, *J. Mol. Evol.,* **1991**, 33, 105.
[3] V. Davankov, *Chirality*, **2006**, 18, 459.

Keynote Lectures

New polymer-analogous transformations in chitosan chemistry

Kritchenkov A.S.

RUDN University, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: platinist@mail.ru

Until recently, the chemistry of the biocompatible, biodegradable and non-toxic natural polymer chitosan was largely limited to the so-called classical chemical transformations (alkylation, acylation, epoxide ring opening, Schiff base formation). Expanding the range of polymer-analog reactions that can be used for chemical modification of chitosan is undoubtedly an important and urgent task of modern polymer chemistry. Selective and convenient in preparative implementation, new polymer-analogous transformations of chitin open up attractive ways to the synthesis of new polymers and systems based on them with improved physicochemical, mechanical and biological (including pharmacological) characteristics.

In our research group, research in this area is carried out in two directions: (1) ultrasound-promoted new polymer-analogous transformations of chitin and chitosan and (2) electrochemical polymer-analogous reactions of the above-mentioned polysaccharides. As a result of the development of the indicated directions, we have introduced ultrasonic thiol-in and phenol-in addition, nitrone-nitrile 1,3-dipolar cycloaddition, electrochemical direct N-arylation into the chemistry of chitin and chitosan, obtained new highly active antibacterial polymers, films and food coatings based on them, nanoparticles and drug delivery systems [1]. This report will be devoted to these and other achievements in the chemistry of saccharide polymers.

References

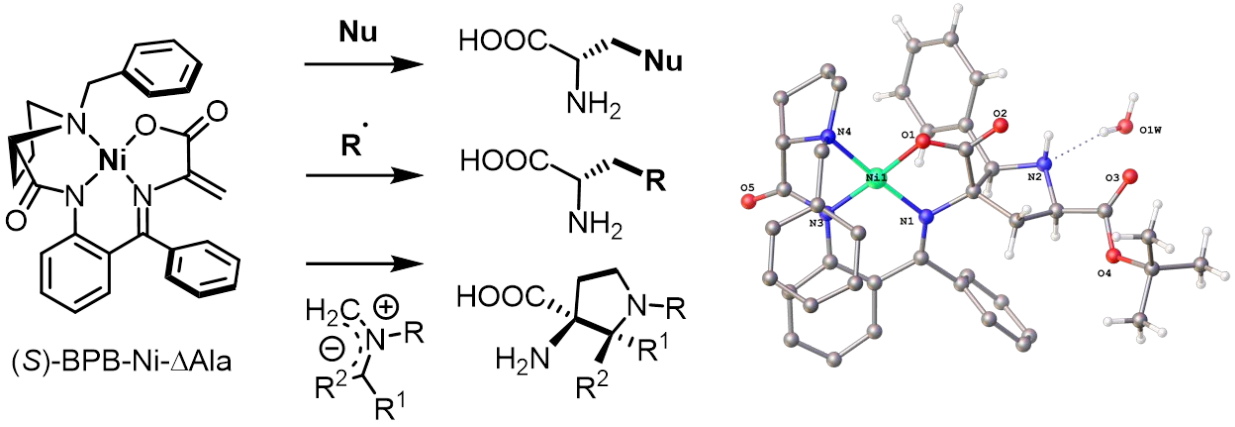
[1] Kritchenkov A. S., Zhaliazniak N. V., Egorov A. R., Lobanov N. N., Volkova O. V., Zabodalova L. A., Suchkova E. P., Kurliuk A. V., Shakola T. V., Rubanik V. V., Rubanik V. V., Yagafarov N. Z., Khomik A. S., Khrustalev V. N. *Carbohydrate Polymers*. **2020**, *242*, 116478.

Asymmetric metal-templated synthesis of non-proteinogenic α-amino acids

Larionov V.A., Stoletova N.V., Gugkaeva Z.T., Maleev V.I.

A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences,
119334, Moscow, Vavilov str. 28, bld. 1
e-mail: larionov@ineos.ac.ru

Artificial non-proteinogenic α-amino acids (α-AAs) have an attractive interest for biochemistry, medicine and pharmacy. They are intensively used in the development of new drugs and modified peptides. In most cases, such molecules can only be obtained using long synthetic transformations [1]. We have developed practically important asymmetric metal-templated methods for the synthesis of hard-to-reach α-AAs using a chiral dehydroalanine Ni(II) complex. By addition of various nucleophiles [2], radicals [3,4], and 1,3-dipoles [5,6,7] to it, we synthesized enantiopure non-proteinogenic α-AAs with quaternary carbon centers, perfluoroalkylated groups and heterocycles [2-7]. The structures and absolute configurations of the stereogenic centers in the diastereomeric Ni(II) complexes and AAs were established by X-ray diffraction analysis.



References

[1] Larionov, V.A.; Stoletova, N.V.; Maleev, V.I. *Adv. Synth. Catal.,* **2020**, 362, 4325.
[2] Gugkaeva, Z.T.; Tsaloev, A.T.; Smol'yakov, A.F.; Godovikova, M.I.; Maleev, V.I.; Larionov, V.A. *J. Org. Chem.,* **2025**, 90, 17569.
[3] Larionov, V.A.; Stoletova, N.V.; Kovalev, V.I.; Smol'yakov, A.F.; Savel'yeva, T.F.; Maleev, V.I. *Org. Chem. Front.,* **2019**, 6, 1094.
[4] Stoletova, N.V.; Smol'yakov, A.F.; Tyutyunov, A.A.; Maleev, V.I.; Larionov, V.A. *Tetrahedron Chem,* **2025**, 13, 100118.
[5] Gugkaeva, Z.T.; Panova, M.V.; Smol'yakov, A.F.; Medvedev, M.G.; Tsaloev, A.T.; Godovikov, I.A.; Maleev, V.I.; Larionov, V. A. *Adv. Synth. Catal.,* **2022**, 364, 2395.
[6] Gugkaeva, Z.T., Stukalova, M.P., Smol'yakov, A.F., Tsaloev, A.T., Maleev, V.I., Larionov, V.A. *Adv. Synth. Catal.,* **2024**, 366, 1205.
[7] Stukalova, M.P.; Gugkaeva, Z.T.; Smol'yakov, A.F.; Samorodov, A.V.; Korunas, V.I.; Krylova, I.D.; Maleev, V.I.; Larionov, V.A. *J. Org. Chem.*, **2026**, 91, doi: 10.1021/acs.joc.6c01167.

An analytical approach to modeling small-angle scattering curves for nanoparticle and hybrid systems: a case study analysis

Bakirov A.V.

National Research Centre "Kurchatov Institute", 1 Kurchatov sq., Moscow, 123098, Russia
Enikolopov Institute of Synthetic Polymer Materials RAS, 70 Profsoyuznaya str., 117393, Moscow, Russia
e-mail: bakirov.artem@gmail.com

Small-angle X-ray scattering (SAXS) is a promising technique for characterizing the nanostructure of biological and hybrid systems in solution and in the melt. The traditional *ab initio* approach (ATSAS) has proven highly valuable, as evidenced by its widespread adoption by numerous research groups worldwide (Prof. D. I. Svergun and co-workers); nevertheless, it suffers from several fundamental drawbacks, including non-uniqueness of the solution, instability of the size distribution even after 10^8 iterations, and the inability to correctly account for interparticle interference in concentrated solutions.

The alternative considered in this talk is the description of the scattering curve as a product of two model functions: the form factor P(Q), which encodes the shape, size, and polydispersity of individual particles as well as intraparticle interference, and the structure factor S(Q), which describes interparticle interference, correlation distances, and the packing and ordering of the system. The analytical approach draws upon extensive catalogs of parameterized models: spheres and shells (including bilayered and multilamellar vesicles); polymers and micelles (the Beaucage model, Gaussian and worm-like chains of Kholodenko and Koyama, block-copolymer micelles with a core and corona); locally planar and locally cylindrical objects described by cross-section form factors; core–shell structures with diffuse interfaces (fuzzy sphere, LinShell, ExpShell); star-shaped and ring polymers; as well as magnetic objects, bicontinuous structures (Teubner–Strey, DAB, Ornstein–Zernike), and fractal aggregates. The talk considers five convolution schemes for combining P(Q) and S(Q) applicable to real systems: the monodisperse approach; the locally monodisperse approximation for strongly polydisperse systems; the decoupling approximation of Kotlarchyk and Chen for weak polydispersity and anisotropy; the mixed case; and the scaling approximation of partial structure factors.

The applicability of the approach is demonstrated on a broad range of molecular systems: sol–gel-modified Nafion membranes [1–3]; thermosensitive P(D,L)LA–PEG–P(D,L)LA hydrogels for 3D printing [4]; nanodiamond hydrosols; Au and Ag nanoparticles stabilized by poly(1-vinylimidazole) [5]; cellulose nanofibrils isolated from Valonia green algae; poly(lactide-co-glycolide) nanoparticles loaded with erbium; the self-assembled palmitate–glutathione lipopeptide; as well as vesicular nanocarriers based on nonionic surfactants.

References

[1] Ruslan Mensharapov, Artem Bakirov, Darya Grineva, et al *Chimica Techno Acta* 2026 V 13 N 10047. 10.15826/chimtech.10047

[2] Ruslan M. Mensharapov, Nataliya A. Ivanova, Dmitry D. Spasov, et al *Process Safety and Environmental Protection*, V 203, 2025, 107915, 10.1016/j.psep.2025.107915.

[3] Ruslan M. Mensharapov, Nataliya A. Ivanova, Artem V. Bakirov, et al. *Polymers* **2025**, 17(11), 1542; 10.3390/polym17111542

[4] A.S. Semkina, N.M. Kuznetsov, A.V. Bakirov, et al *Chem. Eng. J.* **2026** Accepted

[5] Alexey A. Zharikov, Rodion A. Vinogradov, Artem V. Bakirov, et al. *Colloid Polym Sci* **2026** 10.1007/s00396-026-05586-w

Synthesis and crystal-chemical features of new compounds and solid solutions with the apatite structure

Bulanov E.N.

Lobachevsky University, 603022, Nizhny Novgorod, 23 Gagarin ave
e-mail: bulanoven@chem.unn.ru

Compounds with the apatite structure have the general formula $M_{10}(TO_4)_6L_2$, where M denotes large metal cations with charges from 1+ to 4+, T denotes metals, metalloids, and nonmetals forming tetrahedral groups with oxygen, and L denotes halogens and other mono- or divalent anions. In the course of this work, more than 100 phases were synthesized (more than 30 individual compounds and more than 70 solid-solution compositions). Most of the studied objects were obtained and investigated for the first time.

For most apatite series (both individual compounds with a same-type anion sublattice and solid solutions), crystal-structure refinement revealed an inverse linear correlation between the value of $r_{avg}(M)/r_{avg}(T)$ and the twist-angle of the $M^{4f}O_9$ metaprisms (φ).

It was also found that, in the case of cationic isomorphism in the systems $Ca_{10}(PO_4)_6Cl_2$–$Pb_{10}(PO_4)_6Cl_2$ and $Ca_8Bi_2(PO_4)_6O_2$–$Pb_8Bi_2(PO_4)_6O_2$, the distribution of cations among crystallographic sites is determined not only by their size but also by the coordination capabilities of the substituted ions, which leads to preferential localization of bismuth in the low-symmetry 6*h* site. In the case of defect-structure formation, cation vacancies are localized predominantly at the 4*f* sites.

We have broadened the concepts of isodimorphism and morphotropy in analyzing solid-solution formation in the systems $Pb_{10}(PO_4)_6F_2$–$Pb_{10}(PO_4)_6Cl_2$ (perfect isomorphism between end members with different structures—proper isodimorphism) and $Ca_8Bi_2(PO_4)_6O_2$–$Pb_8Bi_2(PO_4)_6O_2$ (a limited solid-solution series in a system of end members with different structural types—isodimorphism with morphotropic transformation).

According to in situ thermal X-ray diffraction data, three types of polymorphic transitions occurring in apatites upon heating were identified: a decrease in symmetry within the hexagonal system (presumably $P6_3/m \rightarrow P6_3$ or $P\bar{6}$): $Ca_{10}(PO_4)_6Cl_2$, $Ca_{10}(VO_4)_6Cl_2$, $Ca_{10}(CrO_4)_6F_2$, $Ca_{10}(CrO_4)_6Cl_2$, $Ca_{10}(PO_4)_6(OH)_2$; a decrease in symmetry from hexagonal to monoclinic (presumably $P6_3/m \rightarrow P2_1/m$ or $P2_1$): $Sr_{10}(CrO_4)_6Cl_2$, $Pb_{10}(PO_4)_6F_2$, $Pb_{10}(PO_4)_6Cl_2$, $Pb_{10}(VO_4)_6Cl_2$, $Na_6Cd_4(SO_4)_6Cl_2$; and a change in symmetry from hexagonal to orthorhombic (presumably $P6_3/m \rightarrow Pna2_1$): $Na_6Ca_4(SO_4)_6F2$. In addition, a low-temperature transition was detected for $Ca_8Bi_2(PO_4)_6O_2$, presumably leading to the formation of a superstructure.

The research was carried out with financial support via State assignment in Research scientific laboratory of "Chemistry of natural products and their synthetic analogues", grant number FSWR-2024-0002

Yuri T. Struchkov, Michail Yu. Antipin, service crystallography, and charge density

Slovokhotov Yu.L.

Institute of Control Science, Russian Acad. Sci., 65 Profsoyuznaya St., Moscow Russia;
Lomonosov Moscow State University, Leninskiye Gory, Bild. 3
e-mail: yurislovo@yandex.ru

A sort of historical essay dealing with high-precision studies of single crystals that were developed in the Laboratory for X-ray structural studies at INEOS during 1980s, will be suggested for the conference participants together with the author's personal reflections on the current state of this field. Mikhail Antipin, who initiated and powered this research direction, would have 75 this year; he worked in the laboratory headed by Yuri Struchkov whose centenary this conference is dedicated to. I am going to tell about the first high-precision X-ray studies of charge density distributions in this lab, where I was partially involved [1], their further development by Mikhail Antipin [2, 3], and the possible prospects of this direction within the recently emerged field of quantum crystallography [4].

The major obstacle for a single crystal X-ray study aimed to some unresolved academic problem is service crystallography that takes the main part of crystallographer's time. It was especially the case in Struchkov's laboratory, a driving force for the whole Russian low-molecular chemistry. In these years, prolonged data collection on a four-circle diffractometer with a point detector noticeably reduced the whole lab's information flow, being a matter of hot discussions with Prof. Struchkov. Once in the meantime, Mikhail and me had a night watching duty in INEOS during 1984 New Year's Eve: several extra days were needed to complete a dataset for chromium cluster, but it was forbidden to leave unattended the precious machinery at work. Due to absence of dedicated software, the first deformation charge density maps were hand drawings; corresponding unique codes were then written by Alexander Yanovsky and Ruben Gerr for the only Eclipse S/200 computer shared by 15 persons in the lab.

Some other not well-known historical details will be mentioned in my talk, e.g. the adventure story of a direct contact (strictly not allowed in 1984) with the famous American neutron diffraction expert Robert Bau in the attempt to launch the international X–N study of the tetrahedral $(C_5H_4Me)_4Cr_4S_4$ cluster… (By a complexity, the cluster was world record in high-precision diffraction studies that time – but, being young and not so well educated in X-ray crystallography, we have fallen into the trap of its water anti-clathrate. All but Prof. Struchkov, who provided the complete interpretation of this phenomenon explaining why our charge density maps were not so good [5]). A human dimension of R&D activity in young fearless team of the best domestic X-ray laboratory, and one of the leading structural labs in the whole world, will be presented.

Further development of high-precision diffraction studies by Mikhail Antipin included single crystals of liquids and gases [2], analysis of atomic thermal motion, perturbation crystallography, and several dozen charge-density studies. Specifically, a series of joined papers with Roland Boese, made in Germany, supported the earlier results by Jack Dunitz and co-workers on the complex, finely disordered low-temperature crystal structure of ferrocene. In a larger set of metallocenes, these papers revealed a tiny orientation disorder of □□cycloolefin ligands instead of commonly suggested internal rotation or simple libration [3]. It was a significant step towards the current feelings that positional disorder is a universal phenomenon guiding a stability among

crystal structures with the same, or almost the same, energy. Such a feeling, existing as 'folk theorem' in crystallographic community, lied a foundation for the contemporary '*alchemy'* free energy calculations [6].

In 21st century, high-precision X-ray studies had indirectly brought first to Hirshfeld surfaces of atoms in molecular crystals [7] and later to Hirshfeld non-spherical atoms in quantum crystallography calculations [4]. This emerging field will be briefly discussed; a strong achievement of 'neutron quality' bond lengths to hydrogen atoms along with the lack of improvement for other bond lengths, will be addressed. Summing up, a flow of information in structural crystallography, uniform at first glance, is actually combined by the unique results of many bright personalities like Yuri Struchkov and Michail Antipin. This material is a tribute for both of them.

References

[1] Slovokhotov Yu.L., Antipin M.Yu., Gerr R.G., Yanovskii A.I., Struchkov Yu.T. (1985) *Dokl. Akad. Nauk SSSR,* **1985**, 285 (6):1413 (in Russian).

[2] Boese R., Niederpruem N., Blaezer D., Maulitz A., Antipin M.Yu., Mallinson P.R., *J. Phys. Chem. B* **1997,** 101*,* 5794.

[3] Antipin M.Y, Boese R., Augart N., Schmid G. *Struct. Chem.* **1993**, 4, 91

[4] Grabowsky S., Genoni A., Bürgi H-B *Chem. Sci.* **2017**, 8: 4159

[5] Eremenko I.L., Shklover V.E., Struchkov Yu.T., *Metalloorganicheskaya khimiya*, **1988**, 1, 166 (in Russian)

[6[Chipot Ch., Pohorille A. (Eds.), *Free Energy Calculations: Theory and Applications in Chemistry and Biology*, Springer, **2007**, 528 p.

[7] Spackman M.A., Jayatilaka D., *CrystEngComm*, **2009**, 11, 19.

Isomeric forms, spectral behavior and biological activity of azo-compounds obtained by different methods

Kovalchukova O.V.[1,2], Polyanskaya N.A.[2,3], Tursunov I.U.[1]

[1] *A.N. Kosygin Russian State University (Technology. Design. Art), 115035, Sadovnicheskaya str. 33/1, Moscow, Russia*
[2] *Peoples Friendship University of Russia, 117198, Miklukho-Maklaya str. 6, Moscow, Russia*
[3] *Petrovsky Medical University, 117418, Tsuriupy str. 3, Moscow, Russia*
e-mail: kovalchukova-ov@rguk.ru

The structure and properties of azo and hydrazo derivatives are determined not only by the starting materials but also by the synthesis method employed. The heterocyclic component exerts a significant influence on the properties of the resulting products. The five-membered thiazolidine ring, containing nitrogen and sulfur atoms, serves as an important pharmacophore and exhibits a wide range of biological activity (antidiabetic, antioxidant, antitubercular, antimicrobial, antitumor, ets.) [1], and other types of activity, including optical and electrical properties [2].

The study demonstrates that, depending on the synthesis conditions (the condensation of 9,10-phenanthrenequinone with hydrazines (compounds of series 1) or the azo-coupling reaction of 2-cyanomethylenethiazolidin-4-one with aromatic and heterocyclic amines (compounds of series 2 and 3)), the final products are obtained in either the hydrazone or azo form; these forms can be distinguished by changes in the electronic absorption spectra of aqueous-ethanol solutions upon transition from neutral to anionic media. According to X-ray structural analysis, the structures of the series 1 compounds are stabilized by the formation of a strong intramolecular hydrogen bond. In the crystals of the series 2 compounds, an intramolecular hydrogen bond is not observed. The C=O group is in the trans-position with respect of the N-H bond of the hydrazo-fragment. The azo forms of the series 3 compounds are stabilized by hydrogen bonds involving water molecules of crystallization.

Organic ligands isolated in the hydrazone form exhibit a significant bathochromic shift of long-wavelength absorption bands in their electronic spectra upon ionization or complex formation with d-metal cations. In contrast, for compounds of the second series, virtually no shift in the long-wavelength bands is observed upon transition to alkaline solutions or upon the addition of solutions of inorganic d-metal salts.

The influence of the isomeric form of compounds on biological activity is discussed. Using a combination of *in vitro* and *in silico* methods specifically examining azo and hydrazone forms containing thiazolidine moieties, it is demonstrated that the azo isomers exhibit greater antimicrobial activity. The binding mechanisms and molecular interactions of compounds existing in azo- and hydrazone forms with microbial proteins were investigated using molecular docking. It was established that compounds existing as azo-isomers, exhibit higher binding affinities than the hydrazo-compound for all the studied enzymatic targets which is largely determined by formation of hydrogen bonds and hydrophobic interactions.

References

[1] Jehani, P., Siddique R., Gautam D., et al Advances in the Synthesis of Thiazolidinone Derivatives: Efficient and Scalable Methods for Pharmaceutical Applications. Journal of Heterocyclic Chemistry, 2026, V. 63, P. 648-669.

[2] Nazim M., Ameen S., Shaheer A.M., et al. Tuning electronic structures of thiazolo[5,4-d]thiazole-based hole-transporting materials for efficient perovskite solar cells. Solar Energy Materials and Solar Cells, 2018, V. 180, P. 334-342.

A new approach to designing molecular rotors

Islamov D.R.[1], Klochkova E.A.[1], Gerasimova D.P.[2], Usachev K.S.[1],[2]

[1] Kazan (Volga Region) Federal University, Kazan, Russia
[2] Arbuzov Institute of Organic and Physical Chemistry, Subdivision of the Federal Research Center "Kazan Scientific Center of the Russian Academy of Sciences", Kazan, Russia
e-mail: daut1989@mail.ru

Crystal engineering is one of the most rapidly developing fields at the interface of chemistry and physics. Within these disciplines, the rotational dynamics of molecules in crystal lattices has long been a subject of intensive research, particularly for the construction of molecular rotors. The fundamental importance of controlling motion at the molecular level was recognized by the 2016 Nobel Prize in Chemistry, awarded for the design and synthesis of molecular machines. It is known that control over molecular motion underlies the functioning of molecular rotors and is a key parameter in the operation of molecular machines. In this context, investigation of the correlation between the rotational mobility of molecules and the symmetry of the crystal structure is a topical task.

Our studies have demonstrated the influence of the symmetry of the crystalline environment on the rotational mobility of molecules [1–3]. To explain the observed dependence, a hypothesis was proposed that considers three possible cases of molecular arrangement relative to crystallographic symmetry elements: **I**, in a general position; **II**, in a special position without symmetry-induced disorder; **III**, in a special position with symmetry-induced disorder. According to experimental data, the barriers to rotation in cases **I** and **III** are lower than in case **II**. This fact is explained, respectively, by an amplitude–phase shift of the rotational energy profiles of the two molecular moieties in case I and by an increase in the number of minima in the rotational barrier profile upon symmetry-induced disordering of molecules in case **III**. On the basis of the established regularities, an approach to reducing the activation energy of molecular rotation in crystals has been proposed, which opens prospects for the targeted design of molecular machines and rotors, including for applications in hybrid biologically active systems.

This study was supported by the Russian Science Foundation, grant no. 25-22-00239, https://rscf.ru/project/25-22-00239/

References

[1] Kataeva, O., Khrizanforov, M., Budnikova, Y., Islamov, D., Burganov, T., Vandyukov, A., Lyssenko, K., Mahns, B., Nohr, M., Hampel, S., Knupfer, M. *Cryst. Growth Des.*, **2015**, 16, 331.
[2] Islamov, D.R., Shtyrlin, V.G., Serov, N.Yu., Fedyanin, I.V., Lyssenko, K.A. *Cryst. Growth Des.*, **2017**, 17, 4703.
[3] Shekurov, R.P., Zagidullin, A.A., Khrizanforov, M.N., Islamov, D.R., Gerasimova, T.P., Akhmatkhanova, F.F., Miluykov, V.A. *Dalton Transactions*, 48, 18603.

Cyclic group 11 metal yrazolates as a rigid matrix for organic structure elucidation and photophysical tuning

Titov A.A., Smol'yakov A.F., Yakovlev G.B., Olbrykh A.P., Filippov O.A., Shubina E.S.

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova street, 28 119334, Moscow, Russia
e-mail: tit@ineos.ac.ru

Trinuclear cyclic group 11 metal pyrazolate adducts of general formula $[M(Pz)]_3$ possesses a broad class of coordination compounds, distinguished by significant structural diversity and a broad spectrum of functional properties. Of particular interest are cyclic trinuclear complexes $[M(Pz)]_3$, in which the planar geometry of the metallacycle favors the formation of metallophilic interactions in the solid state. Acting as cyclic Lewis acids, $[M(Pz)]_3$ are capable of forming supramolecular aggregates with various donor molecules, which serves as a basis for the design of new functional materials, crystal structures elucidation or catalysis [1]. The report will present the results of a study of the interaction of $[Ag((CF_3)_2Pz)]_3$ with both solid and liquid electron-density. The formation of these systems could enables the activation of triplet emission by guest molecules, which is known as the heavy-atom effect. An important feature of these systems could be the ability to achieve dual-emission luminescence, which opens up opportunities for creating functional materials that can be used as sensors, security tags, or white-light sources. [2]. On the other hand, coordination with $[Ag((CF_3)_2Pz)]$ allows for the formation of crystal structures from non-crystallizable molecules or activation of coordinated groups for further functionalization of cyclic pyrazolate.

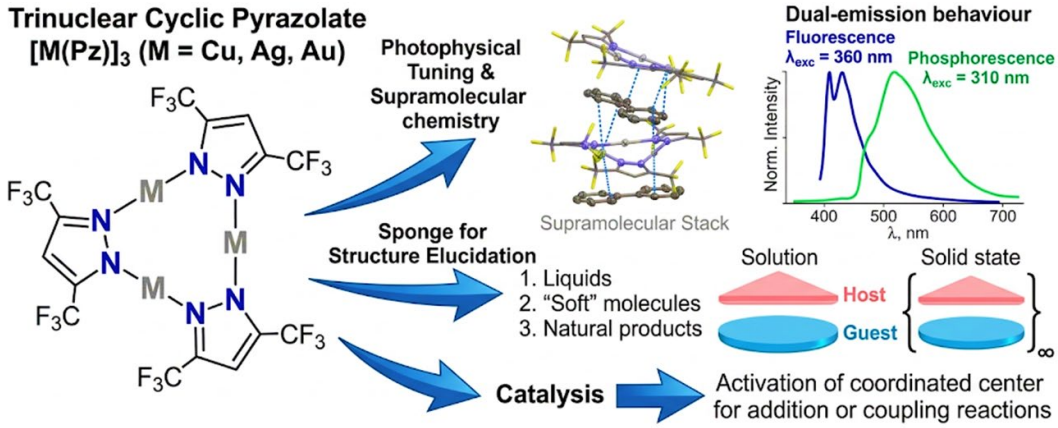


Fig. 1. Pathways of using cyclic trinuclear pyrazolate adducts in chemistry.

This work was supported by the Russian Foundation for Basic Research (grant № 25-43-02243)

References

[1] Olbrykh A.P., Yakovlev G.B., Titov A.A., Filippov O. A., Shubina E. S., *Coord. Chem. Rev.* **2026**, 552, 217477.

[2] Olbrykh A.P., Tsorieva A.V., Korshunov V.M., Smol'yakov A.F., Godovikov I.A., Korlykov A.A., Taydakov I.V., Titov A.A., Filippov O.A., Shubina E.S., *Inorg. Chem. Front.*, **2025**, 12, 81.

Control over the structure and magnetic properties of *3d*-metal clusters supported by (thia)calix[4]arenes

Ovsyannikov A.S.[1], Iova A.A.[1,2], Shutilov I.D.[1], Volodin P.A.[1], Solovieva S.E.[1], Antipin I.S.[1,2]

[1]*Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, Kazan, Russian Federation*
[2]*Kazan Federal University, Kazan, Russian Federation*
e-mail: osaalex2007@rambler.ru

Due to high modulation ability and preorganized structure, (thia)calix[4]arenes and their functional derivatives are particular suitable for binding with paramagnetic ions of *3d*-elements, leading to formation of clusters, displaying various geometries and nuclearities [1-3]. Generally, the conventional lower rim unsubstituted derivatives of calix[4]arenes (CAs) and thiacalix[4]arenes (TCAs), when coordinating with metal ions, act as O_4-tetradentate or *tetrakis*-O,S,O-tridentate ligands, affording the formation of anionic mononuclear $[CA\text{-}M^{III}]^-$ or $[TCA\text{-}M^{II}_4]$ tetranuclear sub-building units (SBU), respectively (Figure 1a). The combination of generated complex SBUs with the cationic or anionic species can result in the formation of a variety of homo- and heteronuclear cluster complexes, especially involving $Mn^{II/III}$ ions, with tunable magnetic properties (SMM behavior, ferromagnet and antiferromagnet interactions) [1,2,4,5]. Moreover, when lower rim 1.3-substituted CA derivatives, bearing the terminal chelating N,O-donor coordinating moieties, are used, the spin-state control of the formed clusters can be achieved due to guest molecule release from the macrocycle cavity (Figure 1b) [6,7].

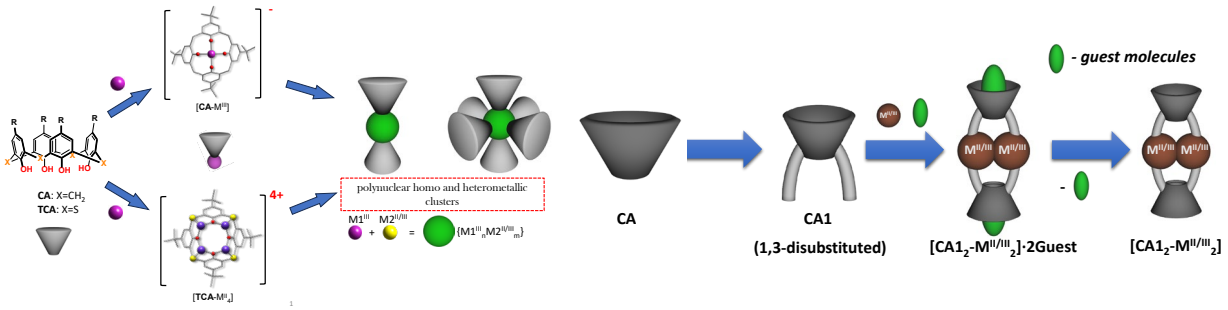


Fig. 1. a) Formation of polynuclear homo- and heteronuclear clusters built by $[CA\text{-}M^{III}]^-$ or $[TCA\text{-}M^{II}_4]$ tetranuclear SBUs. b) Formation of clusters based on 1.3-appended CA derivatives, displaying guest-induced spin-state transition.

This presentation will focus on the synthesis and rational design of various polynuclear Mn(II/III) and Fe(III) based clusters with controlled magnetic properties, supported by conventional (thia)calix[4]arenes and their 1.3-disubstituted lower-rim Schiff base derivatives. The revealed magneto-structural correlations will be discussed in details.

This work was supported by Russian Science Foundation (grant № 26-13-00454)

References

[1] Wilson, L. R. B.; Coletta, M.; Evangelisiti, M.; Piligkos, S.; Dalgarno, S. J.; Brechin, E. K. *Dalton Trans.*, **2022**, 51, 4213.

[2] Fuller, R. O.; Koutsantonis, G. A.; Ogden, M.I. *Coord. Chem. Rev.*, **2020**, 402, 213066.

[3] Khariushin, I. V.; Bulach V.; Ovsyannikov, A. S.; Solovieva, S. E.; Antipin, I. S.; Ferlay S. *Coord. Chem. Rev*., **2024**, 513, 215846.

[4] Ovsyannikov, A. S.; Strelnikova, I. V.; Samigullina, A. I.; Islamov, D. R.; Cherosov, M. A.; Batulin, R. G.; Kiiamov, A. G.; Gubaidullin, A. T.; Dorovatovskii, P.V.; Solovieva, S. E.; Antipin, I. S. *New J. Chem.*, **2024**, 48, 203.

[5] Aldoshin, S.M.; Antipin, I.S.; Kniazeva, M.V.; Korchagin, D.V.; Morgunov, R.B.; Ovsyannikov, A.S.; Palii, A.V.; Sanina, N.A.; Shilov, G.V.; Solovieva, S.E. *Isr. J. Chem.*, **2020**, 60, 600.

[6] Strelnikova, I. V.; Shutilov, I. D.; Ovsyannikov, A. S.; Islamov, D. R.; Pyataev, A. V.;. P. Gerasimova, T. P.; Khamatgalimov, A. R.; Khrizanforov, M. N.; Gubaidullin, A. T.; Burilov, V. A.; Solovieva S. E.; Antipin, I. S. *CrystEngComm*, **2024**, 26, 3973.

[7] Strelnikova, I. V.; Ovsyannikov, A. S.; Pyataev, A. V.; Islamov, D. R.; Litvinov, I. A.; Dorovatovskii, P. V.; Solovieva, S. E.; Antipin, I. S. *Eur. J. Inorg. Chem.,* **2025**, 28, e202400581.

In situ X-ray diffraction as a basic tool to study oxide and metal oxide catalysts

Bulavchenko O.A.

Boreskov Institute of Catalysis SB RAS, 630090, Novosibirsk, Lavrentiev Ave. 5
e-mail: obulavchenko@catalysis.ru

The development of the modern chemical industry is greatly influenced by the design of efficient, stable, and durable catalysts. To develop new catalysts, it is essential to have a thorough understanding of the material's structure and the processes that occur at the atomic and molecular level on the catalyst surface. X-ray diffraction is a valuable tool tocharacterize catalysts. It can distinguish between amorphous and crystalline materials, and for crystalline materials, it can determine the phase composition and structural characteristics, such as atomic arrangement, crystallite size, and strain. The development of new technologies necessitates a profound understanding of the processes involved in catalyst synthesis and operation at every stage. Modern in situ methods for analyzing materials allow us to monitor the state of a catalyst under different conditions that differ from its surroundings. This is beneficial for applied science as it allows functional materials to be studied in conditions close to their actual operation in a reactor.

In situ X-ray diffraction assists in characterizing the active catalyst, observing the behavior of the catalyst during activation and deactivation, characterizing precursor materials for the catalyst, studying some steps in catalyst preparation, and studying the catalyst in reaction media. In situ X-ray diffraction is used to track the evolution of phases and their crystal sizes, the formation of stable phases and intermediates during reactions, analyzing the presence of point and plane defects, forming nanostructural or superstructural states, and rapidly monitoring processes and chemical reaction kinetics. Due to significant progress in the development of radiation source brightness and diffraction instruments, it is now possible to characterize in detail the structural changes that occur at the atomic level under the influence of reaction conditions and temperature.

In the context of in situ X-ray diffraction studies, we discuss several examples: the study of the preparation and activation steps of Mn-Ce-Zr oxides, Mn-Al catalysts for environmental applications, and the activation process of Ni-Cu catalysts for bio-oil upgrading. We also discuss an operando study of a Mn-Zr catalyst.

The work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project FWUR-2024-0032)

References

[1] Bulavchenko, O.A.; Vinokurov Z.S., Catalysts, **2023**, 13, 1

Comparative effects of high pressure and low temperature on the crystal structure of purine nucleobase salts

Gaydamaka A.A.[1,2], Boldyreva E.V.[2], Zakharov B.A.[1,2], Rashchenko S.V.[2], Smirnova E.S.[3], Ivanova A.G.[3]

[1] –Synchrotron Radiation Facility SKIF, Boreskov Institute of Catalysis SB RAS, 630559, Koltsovo, Nikolsky Ave 1
[2] –Novosibirsk State University, 630090, Novosibirsk, Pirogova str. 1
[3] –A.V. Shubnikov Institute of Crystallography of Kurchatov Complex of Crystallography and Photonics of National Research Centre "Kurchatov Institute", 119333, Moscow, Leninsky Ave 59
e-mail: a.a.gajdamaka@srf-skif.ru

The study of crystals containing components of biologically active molecules is relevant to organic crystallography and crystal engineering, both in the design of new molecular materials for electronics and in the development of drug forms. Nucleobases and their derivatives are capable of forming crystalline salts and complexes with metals, as well as supramolecular metal-organic frameworks (porous or channel-like structures). Interest in this class of compounds is high due to their physical properties, which make them promising for use as materials, as well as because of the structural similarity of their building blocks to those found in large biomolecules and their complexes. One of the best methods for investigating intermolecular interactions in crystals is in situ analysis of the structure's response to changes in temperature and pressure (anisotropy of deformation, occurrence of structural transformations).

Comparing experimental data on crystal structures obtained under cooling and pressurization provides information on anisotropy of deformation and conformational transitions. This approach allows for quantitative characterization of thermal expansion and compressibility, as well as yields valuable insights into the characteristics of different types of intermolecular interactions and their role in forming and altering the crystal structure under external influences — both during continuous compression and in the course of polymorphic transformations.

Experimental data on the effect of temperature and pressure on the crystal structures of compounds containing nucleobases — including the mutual arrangement of nucleobases and intermolecular interactions between them, changes in the distances between nucleobase planes, molecular conformational changes, hydrogen bonding, the role of water in structure stabilization, the influence of metal cations, movement of molecular fragments, stability ranges, thermal expansion coefficients, and compressibility — are of significant interest to dynamic crystallography and crystal engineering.

Structural transformations of supramolecular complexes containing nucleic acids or their fragments play an important role in many biological processes, including contributing to the resilience of biological systems to adverse environmental factors. Therefore, the study of such systems — ranging from nucleobases to small fragments of DNA and RNA, both in the form of supramolecular associates in the liquid phase and in crystals — is of interest for understanding the biochemistry and biophysics of nucleic acids. In particular, the results can serve as starting data for computational studies, such as molecular dynamics simulations of nucleic acids.

The study aimed to investigate the response of purine nucleobase salt crystals ($Na_2Gua \cdot 7H_2O$, $KHGua \cdot H_2O$, $LiH_2Xan \cdot H_2O$, $(H_2Ade+)(2,6\text{-dhba-}) \cdot H_2O$, and $(H_2Ade+)(3,5\text{-dhba-}) \cdot H_2O$) to low temperatures and high pressures, and to analyze deformation anisotropy and structural transformations in relation to their ambient-condition structures and intermolecular interactions.

Main conclusions:

1. All studied crystalline salts of purine nucleobases undergo no phase transitions upon exposure to low temperatures (down to 100 K) and high pressures (up to 2.5 GPa).
2. $Na_2Gua·7H_2O$, $KHGua·H_2O$, and $LiH_2Xan·H2O$ undergo phase transitions (with crystal cleavage into crystallites while retaining its external shape in the first case, and with the single crystal preserved in the second and third cases); $(H_2Ade+)(3,5\text{-dhba-})·H_2O$ undergoes reversible changes with the diffraction pattern changing from one typical of a crystal to one characteristic of a highly textured polycrystal or a highly disordered single crystal while retaining the external crystal shape despite clouding; and the structure (and, accordingly, the single-crystallinity) of $(H_2Ade+)(2,6\text{-dhba-})·H_2O$ is preserved over the entire studied range.
3. The anisotropy of hydrostatic compression and thermal expansion correlates with molecular packing and is governed by different intermolecular interactions. The high resilience of the samples to deformation is attributed to the presence of metal coordination polyhedra ($Na_2Gua·7H_2O$, $KHGua·H_2O$, $LiH_2Xan·H_2O$) or stacking interactions ($(H_2Ade+)(2,6\text{-dhba-})·H_2O$ and $(H_2Ade+)(3,5\text{-dhba-})·H_2O$).
4. Isobaric expansion upon heating and isothermal compression upon pressurization follow the inverse relationship rule between the effects of temperature and pressure. The estimated correlation between the effects of cooling and pressurization is close to the average values for crystal structures deposited in the Cambridge Structural Database, as well as to the mean values for minerals.
5. The maximum pressure that the crystals of the studied compounds withstand without destruction is significantly higher than that reported for DNA crystals in the literature.
6. Upon pressure increase to 4.5 GPa, $KHGua·H_2O$ crystals undergo a transition to an incommensurately modulated high-pressure phase, whose structure was determined by single-crystal X-ray diffraction.

Further details can be found in the following works [1-5].

The work was carried out with the support of the Priority 2030 Program at NSU, the strategic project "Center for the Integration of Personalized Biomedicine, Pharmacy and Synchrotron, binary Technologies". Gaydamaka A.A. also thanks the Ministry of Science and Higher Education of the Russian Federation for financial support within the framework of the state assignment of the Synchrotron Radiation Facility — Siberian Circular Photon Source "SKIF" (FWUR-2024-0040).

References

[1] Gaydamaka A.A., Rashchenko S. V. Acta Cryst. 2024. B80, 676-681.
[2] Gaydamaka A.A., Bogdanov N.E., Zakharov B.A., Goryainov S.V. Boldyreva E.V. Acta Cryst. 2024. B80, 311–325.
[3] Gaydamaka A.A., Rashchenko S.V., Semerikova A.I., Smirnova E.S., Ivanova A.G., Arkhipov S.G., Zakharov B.A., Bogdanov N.E. and Boldyreva E.V. Acta Cryst. 2023. B79, 495–509.
[4] Gaydamaka A.A., Arkhipov S.G., Boldyreva E. V. Acta Cryst. 2021. B77, 808–818.
[5] Gaydamaka A.A., Arkhipov S.G., Zakharov B.A., Seryotkin Yu.V. Boldyreva E.V. CrystEngComm. 2019. 21(30), 4484–4492.

Synthesis of platinum, palladium and rhodium-based bimetallic complexes: structural and catalytical insights

Yakushev I.A., Sosunov E.A., Panina M.V.

Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 119071, Moscow, Leninskii prospect, 31
e-mail: ilya.yakushev@igic.ras.ru, ilya.yakushev88@gmail.com

Bimetallic compounds and catalysts are widely used in petroleum chemistry, chemical technology and fine chemical synthesis, so finding ways to control the process of formation of such functional materials is an important problem, as crucial as studies of their chemical properties, deposition on a carrier, and degradation under operating conditions. The use of modern techniques enables the combined application of diffraction analysis and spectral techniques, such as X-ray absorption fine structure spectroscopy (EXAFS, XANES) or mass spectrometry, yielding unique data on the structure of functional materials. The most crucial part of the structural investigation (both spectral and XRD) of these compounds in many cases presents some challenges because of unknown fragmentation pathways, poor crystallinity of the samples, structural disordering, etc. In some cases, the lack of experimental data leads to enormously large structural parameters (*R*-factors *etc.*) and in some cases – even to erroneous interpretations, or wrong or incomplete models. Nevertheless, in the present work, using a number of mono- and bimetallic compounds of Pt, Pd and Rh as examples [Figs. 1-3], we reveal the possibility of synthesizing bimetallic carboxylate-bridged compounds of the general formula $[M_1M_2(OOCR)_x]$, or in the case of rhodium – a chloride-bridged coordination polymer $\{[Cu(H_2O)_4RhCl_5(H_2O)]\cdot 4H_2O\}_n$, which demonstrates activity in the partial oxidation of alkanes.

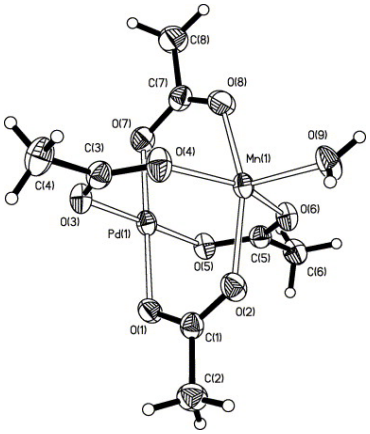


Fig. 1. $[PdMn(OOCMe)_4]$

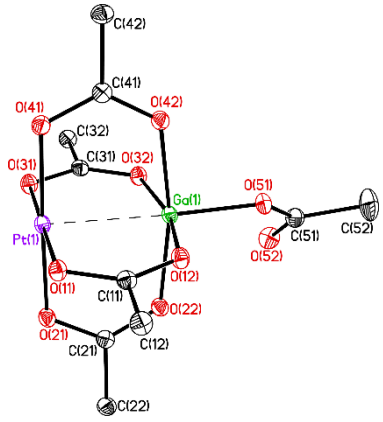


Fig. 2. $[PtGa(OOCMe)_5]$

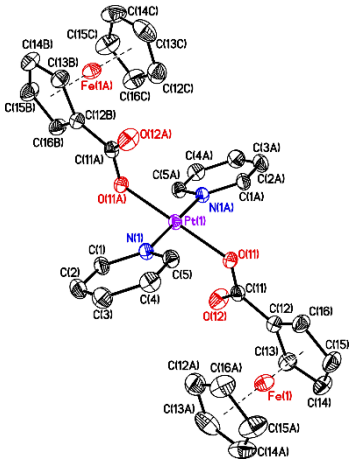


Fig. 3. $[PtPy_2(OOCFc)_2]$

This work was supported by the Ministry of Science and Higher Education of the Russian Federation as part of the State Assignment of the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences

References

[1] Ellert, O.G.; Tsodikov, M.V.; *et al. Russ. Chem. Rev.,* **2014**, 83, 718.
[2] Smirnova, N.S.; Khramov, E.V.; *et al. Intermertallics*, **2021**, 132, 107160.

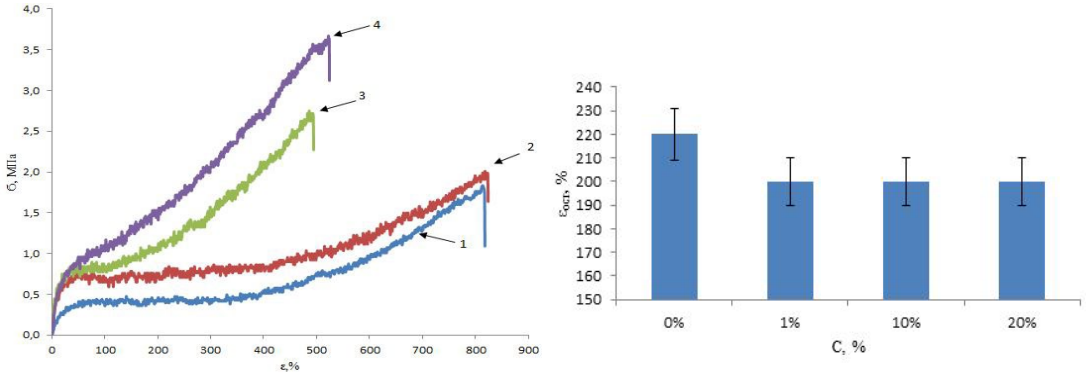
Influence of Nanocarbon Particles on the Mechanical Properties of Rubber Polymers

Rubanik V.V.[1], Savitsky V.O.[1], Rubanik V.V. jr.[1], Phuong D.T.[2], Bui H.T.[2]

[1] *Institute of Technical Acoustics, NAS of Belarus, Vitebsk, Belarus*
[2] *Institute of Materials Science, VAST, Hanoi, Vietnam*
e-mail: ita@vitebsk.by

Nanomodified rubber compounds were prepared from mill-sheeted natural rubber SVR-3L (Vietnam) with silicon dioxide (20 wt %) and nanographite particles (0, 1, 10, and 20 wt %) produced by ultrasonic-assisted liquid-phase exfoliation of graphite [1].

With increasing nanographite content, the tensile strength increased and the elongation at break decreased. At 1 wt % nanographite, the tensile strength increased from 1.9 to 2.0 MPa, while the elongation at break remained unchanged. At 10 wt %, the tensile strength increased sharply to 2.7 MPa, and the elongation at break decreased from 810% to 480%. At 20 wt %, the tensile strength reached 3.6 MPa, while the elongation at break remained essentially unchanged at 510% (Figure 1a). The residual elongation (tensile set) remained within experimental error at 200% (Figure 1b).



a b

Figure 1 – Dependence of tensile strength on relative elongation (a) and residual elongation (b) of natural rubber polymers with different nanographite concentrations: 1 – 0 wt%, 2 – 1 wt%, 3 – 10 wt%, 4 – 20 wt%.

Thus, incorporating nanographite particles into the rubber matrix improves the tensile properties. At 20 wt % nanocarbon particles, the tensile strength is 3.6 MPa, twice that of the nanographite-free polymer.

This work was supported by the Belarusian Republican Foundation for Fundamental Research (BRFFR), project No. T19B-009

References

[1] Rubanik V.V., Rubanik V.V. jr., Savitsky V.O. Ultrasonic dispersion of graphite in a liquid medium // Modern Methods and Technologies for Creating and Processing Materials: Collection of Scientific Papers. In 2 books. Book 1 / editorial board: V.G. Zalesky (editor-in-chief) [et al.]. – Minsk: FTI NAS of Belarus, 2025. – P. 266-282.

Oral Reports

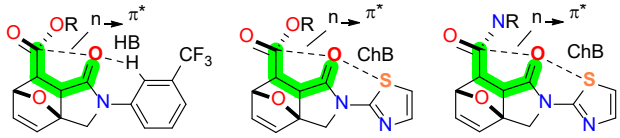
Weak interactions in directing molecular conformation and crystal packing of some azole 3a,6-epoxyisoindole-7-carboxyliates

Kolesnik I.A.[1], Potkin V.I.[1], Grigoriev M.S.[2], Frontera A.[3], Nikitina E.V.[4], Zubkov F.I.[4]

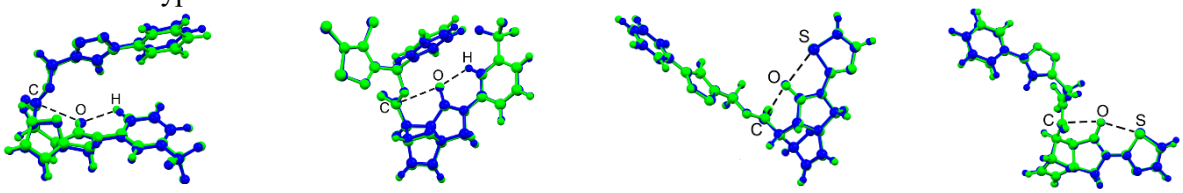
[1]*Institute of Physical Organic Chemistry, NAS of Belarus, 13 Surganov str., 220072 Minsk, Belarus;*
[2]*Frumkin Institute of Physical Chemistry and Electrochemistry, RAS, 31 Bldg 4, Leninsky prosp., Moscow, 119071, Russian Federation;*
[3]*Department of Chemistry, Universidad de les Islas Baleares, Crta. de Valldemosa km 7.5, 07122 Palma de Mallorca, Baleares, Spain;*
[4]*Faculty of Science, RUDN University, 6 Miklukho-Maklaya St., 117198 Moscow, Russian Federation*
e-mail: irynakolesnik93@gmail.com

Despite being individually subtle, weak interactions collectively determine the three-dimensional shape, stability, and solid-state properties of molecules. In turn, these characteristics directly influence the biological activity and the performance characteristics of materials obtained from them.

Isoxazole and isothiazole derivatives of 1-oxoepoxyisoindole-7-carboxylic acids present a rigid core – 1-oxotetrahydro-3a,6-epoxyisoindole frag-ment – where the C-atom of the ester or amido group is located at four bond distance from the oxo O-atom. This rigid scaffold appeared to be an ideal platform for studying how subtle structural variations can modulate the balance of weak interactions in the molecule. It was not only suitable to analyze n → π* interactions, but, due to the diversity of substituents, also allowed studying the influence of hydrogen or chalcogen bonding on this interaction.



To characterize and compare multiple non-covalent interactions within the molecules of 1-oxoepoxyisoindole-7-carboxylic acids derivatives **1**–**4**, we used the combination of experimental and computational methods. Compounds under study were synthesized by coupling the corresponding acids with heterocyclic alcohols or amine. X-ray structural analysis allowed to reveal the exact structures of the compounds obtained which became a reference point for further theoretical research. Further investigation using DFT calculations and a number of analysis tools (such as NCIplot, as well as NBO and ELF analysis) identified several types of weak interactions inside the molecules under consideration.



1 **2** **3** **4**

All four compounds exhibited characteristic charge transfer between the carbonyl oxygen lone pair and the antibonding π orbital of the adjacent carbonyl group, that is n→π* interaction which was stronger in ester derivatives **1**–**3** than in the amide analog **4**. Compounds **1** and **2** exhibited intramolecular C–H···O hydrogen bonds, while derivatives **3** and **4** displayed pronounced (stronger than n→π* interaction) S···O chalcogen bonding due sulfur atoms acting as effective σ-hole donors. The obtained results highlight the cooperative participation of weak interactions in guiding crystal packing and provide valuable information for the future design of new supramolecular systems.

This work was funded by the Belarusian Republican Foundation for Fundamental Research (Project No. X25KI-027) and Russian Science Foundation (Project No. 26-13-00201

Synthesis, crystal structure and spectroscopic properties of the cobalt(III) complex with 3,5-di-tert-butylsalicylaldehyde acetylhydrazone

Fatullayeva P.A. [1], Khrustalev V.N. [2], Alirzayev A.T. [1]

Institute of Chemistry of the Ministry of Science and Education of Azerbaijan
[b]Peoples' Friendship University of Russia (RUDN University)
e-mail: pfatullayeva43@gmail.com

Hydrazones derived from acylhydrazides and salicylaldehyde derivatives represent a promising class of polydentate ligands due to the presence of multiple donor sites and their ability to undergo keto–enol tautomerism. Their coordination with transition-metal ions may be accompanied by deprotonation of the phenolic group, formation of stable chelate rings, and changes in the oxidation state of the metal center. Cobalt complexes are of particular interest, as hydrazone ligands can stabilize both Co(II) and Co(III), while the coordination process may be accompanied by oxidation of Co(II) to Co(III). Oxidation of Co(II) to Co(III) directly during complex formation with hydrazone and N-acylhydrazone ligands is well documented. It has been shown that deprotonation of the hydrazone ligand upon coordination can be accompanied by spontaneous oxidation of Co(II) to Co(III), including under aerobic conditions and, in some cases, even under an inert atmosphere [1–3].

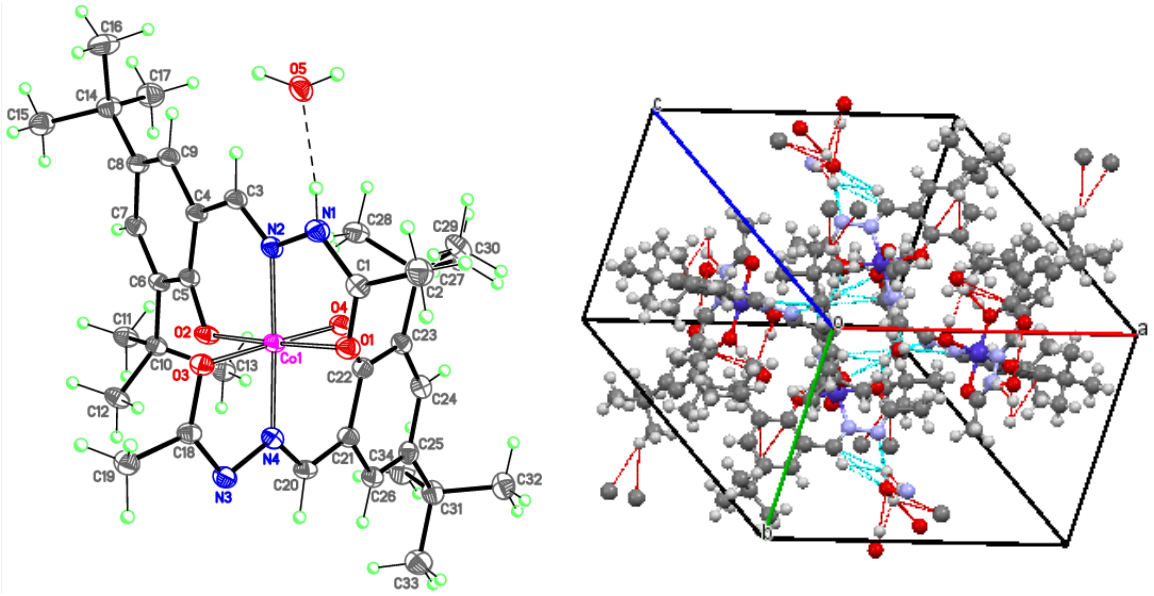
In the present work, a new cobalt complex with the acetylhydrazone of 3,5-di-tert-butylsalicylaldehyde was synthesized and structurally characterized. According to the single-crystal X-ray diffraction analysis, the central cobalt atom exhibits a six-coordinate distorted octahedral CoN_2O_4 environment and is coordinated by two tridentate O,N,O-donor hydrazone ligands. Coordination is accompanied by deprotonation of the phenolic groups and oxidation of the initial Co(II) to Co(III). The retention of the hydrazide N–H group is consistent with the
- established molecular structure.

The bulky 3,5-di-tert butyl substituents exert a pronounced steric effect on the spatial organization of the complex. They shield the aromatic surfaces, prevent close π–π stacking interactions, and promote a specific molecular packing arrangement in the crystal. In addition, the tert-butyl groups increase the hydrophobic character of the organic part of the ligand.

The spectroscopic characteristics of the complex are consistent with the formation of Co–O and Co–N bonds and with a low-spin octahedral Co(III) center having a d^6 electronic configuration. According to the single-crystal X-ray diffraction analysis, the complex is mononuclear and has the composition $[Co(L)_2]\cdot H_2O$**.** The central cobalt atom is coordinated by two tridentate hydrazone ligands. Each ligand coordinates through three donor atoms—a phenolate O atom, an azomethine N atom, and a carbonyl O atom—forming a typical O,N,O-tridentate chelate fragment**.** Thus, the coordination environment of the cobalt center is CoN_2O_4**,** corresponding to a distorted octahedral geometry.

The Co–N bond lengths are 1.8544(16) and 1.8785(16) Å, while the Co–O bond lengths range from 1.8702(14) to 1.9528(14) Å. The presence of six relatively short coordination bonds confirms the formation of a stable octahedral environment around the Co(III) center. Three pairs of donor atoms are arranged predominantly in trans positions: the O4–Co1–O3, O2–Co1–O1, and N4–Co1–N2 angles are 178.68(6), 177.22(6), and 173.73(7)°, respectively, indicating only a slight deviation from ideal octahedral geometry.

A crystallization water molecule is present in the structure and participates in an extended system of intermolecular hydrogen bonds. The hydrazide N–H group is retained after coordination, which is consistent with the persistence of the corresponding ν(N–H) band in the IR spectrum. The water molecule acts simultaneously as both a hydrogen-bond donor and acceptor, contributing to the additional stabilization of the crystal packing.



a b

Fig. a- Molecular structure and b- crystal packing of the $[Co(L)_2]\cdot H_2O$ complex

Complex formation is accompanied by systematic changes in the main characteristic bands of the hydrazone ligand. The most informative feature is the disappearance or significant weakening of the phenolic ν(O–H) band, which is consistent with deprotonation of the phenolic group and formation of a Co–O bond. Upon coordination, the ν(C=N) band of the azomethine fragment shifts to lower wavenumbers due to the involvement of the azomethine nitrogen atom in Co–N bond formation.

The electronic spectrum of the complex is characterized by intense bands in the ultraviolet region, predominantly associated with intraligand π→π* transitions of the aromatic and hydrazone systems. The longer-wavelength bands in the approximately 300–400 nm region may contain contributions from n→π* transitions and ligand-to-metal charge-transfer (LMCT) transitions.

The synthesized complex with the cobalt(III) ion is expected to be biologically active.

References

[1] W. Huang, Y. Li, J. Yong et al.Hydrazone-based cobalt complexes toward multielectron redox and spin crossover. RSC Adv. 2018. DOI: 10.1039/C8RA02963F.

[2] Esther S. Areas, Bruna Juliana da S. Bronsato, Thiago M. Pereira et al. Novel CoIII complexes containing fluorescent coumarin-N-acylhydrazone hybrid ligands: Synthesis, crystal structures, solution studies and DFT calculations. Spectrochim. Acta A Mol. Biomol. Spectrosc. 2018. https://doi.org/10.1016/j.saa.2017.06.031

[3] G.A.Gamov, M.N.Zavalishin, A.Y.Khokhlova et al. Complexation between nickel(II), cobalt(III) and hydrazones derived from pyridoxal 5′-phosphate and hydrazides of 2-,3-,4-pyridinecarboxylic acids in aqueous solution. J. Coord. Chem. 2018, 71, 3304–3314. DOI: 10.1080/00958972.2018.1512708.

Electrolyte-Dependent Crystal Chemistry of Silver-Modified Hydroxyapatite Synthesised by Reaction–Diffusion: A Powder Diffraction and Spectroscopic Study

Omiyale O.C.

Department of Infochemistry, ITMO University, St. Petersburg, Russia
e-mail: oomiiale@itmo.ru

Controllable crystalline structure of hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) is crucial in the development of smart biomaterial coatings for biomedical applications such as orthopaedic and dental implants. Herein, we utilize the reaction–diffusion phenomenon of Liesegang ring formation on an agar gel platform for the design and fabrication of silver-functionalized HA nanoparticles with well-defined crystallography, and characterize their underlying structure–function correlation associated with near-infrared (NIR) photothermal response.

Three series of HA were prepared via the slow diffusion of external solutions containing either 1 M $CaCl_2$ (HA-Cl), 1 M $Ca(NO_3)_2$ (HA-NO_3), or 1 M $Ca(NO_3)_2$ together with 1 wt.% $AgNO_3$ (HA-Ag) through a gel medium loaded with 0.2 M Na_2HPO_4 at pH 7.4. Complete Liesegang rings of HA-Cl and HA-NO_3 with p-factors of ~1.00 were formed after 12 h; the presence of Ag^+ reduced the p-factor spacing to 0.81 for HA-Ag.

Powder X-ray diffraction (XRD) (Bruker D2 Phaser; copper Kα radiation with $\lambda = 0.15406$ nm; scan from 10 to 80° of 2θ) showed that the three systems were phase pure HAp (hexagonal) with lattice parameters determined using Rietveld refinement as $a = b = 9.418$ Å, $c = 6.884$ Å (space group $P6_3/m$, JCPDS 09-0432). Most importantly, the presence of Ag doping resulted in peaks of new diffraction at $2\theta = 38.2°$ and 44.4°, corresponding to metallic silver (Ag^0, JCPDS 04-0783), indicating that Ag^+ substitution and nanoparticle formation occurred simultaneously within the lattice. Scherrer formulae analysis for crystalinity indicated a reduction from 90% (HA-Cl) to 65% (HA-NO_3) to 59% (HA-Ag), in accordance with increasing lattice disarray via growth inhibition due to nitrate ions and ionic substitution between Ag^+ and Ca^{2+}.

SEM-EDX analysis (FEI Quanta Inspect S with 20 kV) confirmed particle sizes of 55.6 ± 4 nm (HA-Cl), 86.8 ± 7 nm (HA-NO_3), and 80.8 ± 6 nm (HA-Ag), with Ca/P atomic ratios of 1.41, 1.97, and 0.97, respectively. Ca/P ratio of HA-Ag (0.97 < 1.67 stoichiometric) is diagnostic of calcium-deficient HA arising from Ag^+/Ca^{2+} isomorphous substitution, corroborated by EDX quantification of 12.4 wt.% silver, consistent with literature reports of effective Ag incorporation in the range 10–15 wt.%.

The infrared spectra collected using an FTIR spectrophotometer (Nicolet iS5, wavenumbers 500 – 4000 cm^{-1}, resolution 4 cm^{-1}) confirmed the presence of characteristic HA spectral features in all samples: 3(PO_4^{3-}) asymmetric vibration at 1089 – 1043 cm^{-1}; 1(PO_4^{3-}) symmetric vibration at 962 – 1020 cm^{-1}; 4(PO_4^{3-}) O-P-O bending vibration as a doublet at 601 – 567 cm^{-1}; structural O-H vibration at 3387 cm^{-1}; and type-B CO_3^{2-} carbonate substitution for PO_4^{3-} at 1483 – 1364 cm^{-1}. The lack of any novel bands in the region of 380 – 600 cm^{-1} and 450 – 300 cm^{-1} related to Ag-O or Ag-P stretching, respectively, confirms that there is no formation of chemical bonds between Ag particles and the host crystal. At the same time, the sharpness of the 1(PO_4^{3-}) peak indicates the preservation of the HA structure. Surface charges measured by Zetasizer (Photocor Compact Z, pH 7.4) were determined to be –15 mV (HA-Cl), –20 mV (HA-NO_3), and –11 mV (HA-Ag), where the lower surface charge value is associated with partial neutralisation by Ag^+ species.

The DFT calculations using Local Density Approximation (LDA) and Generalised Gradient Approximation (GGA) methodologies support the experimental observations concerning the NIR photosensitivity: the doped silver decreases the theoretical electronic band gap value from 5.41 eV (HA without doping) to 3.37 eV (12.4 wt.% Ag), hence allowing for light absorption by a wavelength of 808 nm and efficient photothermal conversion. These theoretical results regarding band gap reduction, which are confirmed experimentally via XRD measurements indicating the change in lattice parameters following the introduction of Ag ions, provide the quantum mechanical explanation for the NIR-to-heat transformation necessary for triggering drug release.

The current study thus reveals a causal relationship between the reaction-diffusion process under electrolyte control, crystal chemistry of the products (purity, crystallinity, lattice substitutions, Ca/P ratio), and their functional photothermal properties at the NIR region of the spectrum. The agar gel diffusion process turns out to be an effective means of synthesis for patterned biomimetic HA nanocomposites.

Aggregation-Induced Emission in Supramolecular Complexes of a Bis(styryl) Dye with Cucurbiturils

Sulimova O.V.[1,2], Ustimova M.A.[1], Chernikova E.Yu.[1], Fedorova O.A.[1]

[1] A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, Moscow, Russia
[2] D. Mendeleev University of Chemical Technology of Russia, Moscow, Russia
e-mail: olesya.sulimova.2004@mail.ru

Aggregation-induced emission (AIE) is a unique phenomenon in which compounds exhibiting weak emission in dilute solutions show an increase in fluorescence intensity in the aggregated and solid states [1]. Owing to these properties, AIE fluorophores have found broad applications in various fields of medicine, as well as in the development of optoelectronic devices and smart materials [2].

The AIE effect is generally attributed to the restriction of intramolecular motions in the aggregated state. Such restriction can result from the formation of a host–guest supramolecular complex. Among macrocyclic host molecules, cucurbit[n]urils (CB[n]) are particularly advantageous because they can bind a variety of guest molecules through their hydrophobic cavity and highly polarized carbonyl groups [3].

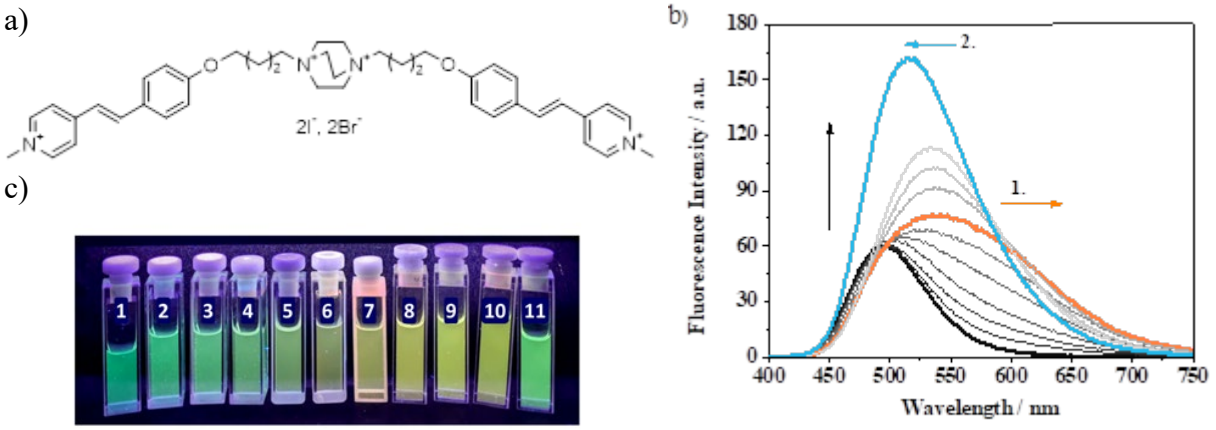


Fig. 1. a) Structure of the tetracationic bis(styryl) dye; b) fluorescence spectra of the dye in the presence of CB[8]; c) photographs of cuvettes containing solutions at different dye:CB[8] ratios.

In this work, supramolecular complexes of a tetracationic bis(styryl) dye (Fig. 1a) with cucurbiturils differing in the volume of their internal cavities (CB[7] and CB[8]) were synthesized and studied. The effect of encapsulation on the key optical properties of AIE fluorophores was also investigated (Fig. 1b,c).

This work was financially supported by the Russian Science Foundation (Project No. 25-23-20209)

References

[1] Luo J. et al. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole // Chem. Commun. 2001. Vol. 18. P. 1740–1741.
[2] Zhu C. et al. Aggregation-induced emission: a trailblazing journey to the field of biomedicine // ACS Appl. Bio Mater. 2018. Vol. 1. No. 6. P. 1768–1786.
[3] Barrow S.J. et al. Cucurbituril-Based Molecular Recognition // Chem. Rev. 2015. Vol. 115. P. 12320–12406.

Crystal Structure and Vibrational Properties of Guanidinium *trans*-Diaquabis(malonato)aluminate(III): Experimental and Periodic DFT Study

Kiryak D.V.[1], Charkin D.O.[1,2], Kireev V.E.[2], Kompanchenko A.A.[2], Gosteva A.N.[2], Aksenov S.M.[2]

[1] *Lomonosov Moscow State University, 1 Leninskie Gory, Moscow 119991, Russia*
[2] *Laboratory of Arctic Mineralogy and New Materials, Kola Science Centre RAS, 14 Fersman St., Apatity 184209, Russia*
e-mail: kiryakdv@my.msu.ru

Malonate complexes of Al(III) combine flexible chelate geometry with hydrogen-bonded crystal packing and therefore provide useful systems for relating local coordination to vibrational properties. The guanidinium salt Gua[Al(mal)$_2$)(H$_2$O)$_2$] was studied by single-crystal X-ray diffraction, FTIR spectroscopy (4000–400 cm^{-1}) and Raman spectroscopy (532 nm excitation), together with periodic density-functional calculations.

Single-crystal data were collected at 296.5 K with Mo Kα radiation (λ = 0.71073 Å). The compound crystallizes in the monoclinic space group *P2$_1$/n* with a = 6.8335(3), b = 18.7935(7), c = 9.8756(4) Å, β = 101.088(4)°, V = 1244.60(9) Å^3, Z = 4, R$_{int}$ = 0.0278 and R$_1$ = 0.0336. The discrete *trans*-[Al(mal)$_2$(H$_2$O)$_2$]$^-$ anion contains octahedral AlO$_6$ with Al–O = 1.846–1.933 Å; the two aqua ligands are nearly linear across Al [O(H$_2$O)–Al–O(H$_2$O) = 179.48(5)°]. Guanidinium cations and coordinated water molecules form N–H···O and O–H···O contacts with carboxylate oxygen atoms.

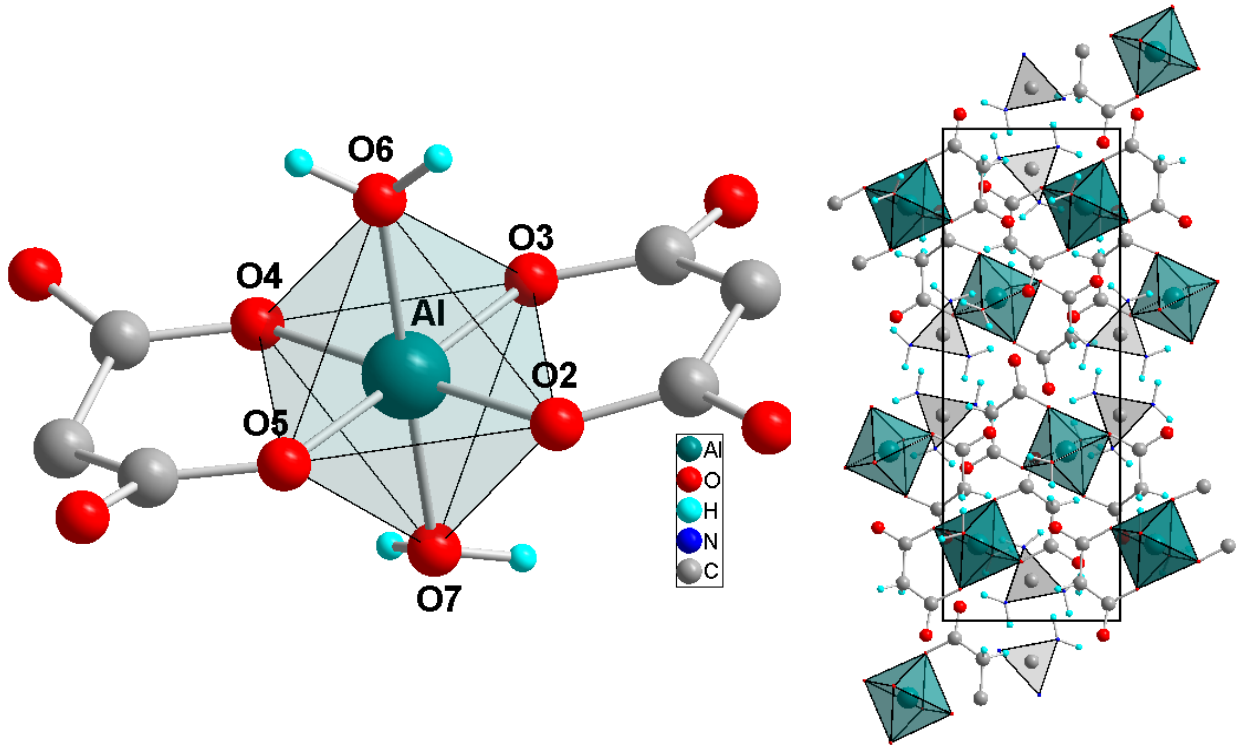


Fig. 1. Coordination environment of Al(III) in *trans*-[Al(mal)$_2$(H$_2$O)$_2$]$^-$; H atoms are shown only for the coordinated H$_2$O ligands.

Periodic DFT calculations were performed at the PBE level with norm-conserving pseudopotentials and a 2 × 1 × 2 k-point mesh; atomic positions were relaxed while the lattice parameters were fixed at the experimental values. The six Al–O distances are reproduced within 0.023

Å, and the calculated trans O(H_2O)–Al–O(H_2O) angle is 179.29°. Γ-point phonon frequencies and eigenvectors, Born effective charges, ε_∞ and infrared intensities were obtained by density-functional perturbation theory in Quantum ESPRESSO [1]. Because the analytic second-order Raman implementation in PHonon is restricted to LDA and norm-conserving pseudopotentials, Raman susceptibility derivatives were calculated within LDA at the PBE geometry without LDA re-optimization and combined with the PBE eigenvectors in post-processing following Ref. [2].

Factor-group analysis (C_{2h}, 140 atoms per cell) gives $\Gamma_{opt} = 105A_g + 105B_g + 104A_u + 103B_u$, corresponding to 210 Raman-active and 207 IR-active optical modes.

Without empirical frequency scaling, the calculated IR and Raman spectra reproduce the principal experimental band pattern in the fingerprint region. Eigenvector analysis assigns the low-frequency modes mainly to collective translations and librations of the ionic fragments, whereas the 1500–1700 cm^{-1} region contains strongly mixed carboxylate, H_2O-bending and guanidinium vibrations. The high-frequency region comprises C–H, O–H and N–H stretching modes. Deviations are most evident for X–H stretches, where the harmonic approximation and the sensitivity of hydrogen-bonded modes to the density-functional description limit quantitative agreement; close individual coincidences in this region are therefore not treated as a measure of predictive accuracy.

The combined diffraction and periodic-DFT results provide a consistent structural and vibrational description of Gua[Al(mal)$_2$(H_2O)$_2$]. In particular, the fixed-cell PBE relaxation accurately retains the experimentally observed AlO_6 coordination, while the calculated normal modes support assignment of the dense IR and Raman spectra. The remaining discrepancies in the X–H region motivate an explicit anharmonic treatment in further work.

References

[1] Giannozzi P. et al. J. Chem. Phys., 2020, 152, 154105.
[2] Lazzeri M.; Mauri F. Phys. Rev. Lett., 2003, 90, 036401.

Interpretation of X-ray Diffraction Data of Metal-Organic Framework Polymers [REBTC] (RE = La-Lu, Y; BTC - $C_6H_5(COO)_3$)

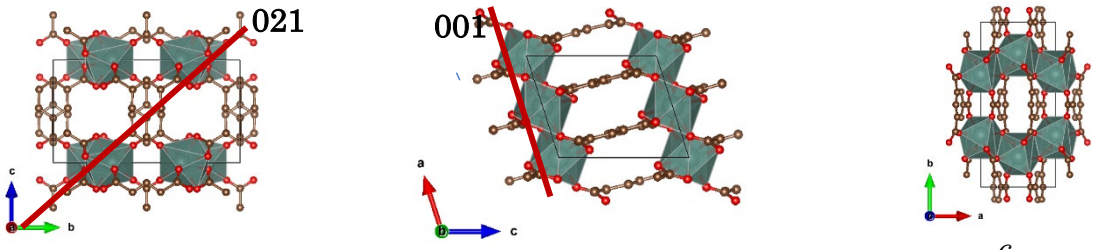
Valeshnyy D.A.[1], Mushtakov A.G.[2], Svetogorov R.D.[3], Kuz'micheva G.M.[1]

[1]MIREA – Russian Technological University, 119454, Moscow, Vernadsky av. 78
[2]Peoples' Friendship University of Russia named after Patrice Lumumba, Moscow, Russia
[3]NRC "Kurchatov Institute", Moscow, Russia
e-mail: valeshnyy96@mail.ru

Powder X-ray diffraction is the main method for phase identification and structural characterization of polycrystalline samples and determination of the geometric dimensions of the unit cell. The greatest amount of information can be obtained from complete groups of compounds with a logical change of the cation in a series, such as rare-earth elements (*RE*). The aim of this work is to establish the change in the crystal structure of polycrystalline metal-organic polymers in the *RE*-BTC system (*RE* = La-Lu, Y; BTC - $C_6H_5(COO)_3$).

Metal-organic framework polymers (MOFs) in the *RE*-BTC system (*RE* = La-Lu,Y) were synthesized by the hydrothermal method (t = 8 h, t = 140°C). Commercial samples of $RE(NO_3)_3 \cdot xH_2O$ were used as precursors. Powder Synchrotron X-ray Diffraction study of the samples (sphere with a diameter of ~ 150 μm) was carried out at the Belok/XSA beamline at the Kurchatov synchrotron radiation source (NRC "Kurchatov Institute", Moscow).

Single-phase nanosized samples [*RE*(BTC)] with *RE* = Sm-Tm, Y crystallize in the C2/m space group, Z = 8 with unit cell parameters a ~ 6.94 Å, *b* ~ 14.70 Å, *c* ~ 8.49 Å, β ~ 107º (MIL-78 type [1]) (Fig. 1, 2a). The [*RE*(BTC)] phase with *RE* = Yb, Lu (Fig. 2b) contains ~91% and ~85% of the MIL-78-type phase for Yb and Lu and ~9% and ~15% of a phase with hexagonal unit cell parameters *a* = 8.8788(5) Å, *c* = 18.653(2) Å of a new type X (peaks * in Fig. 2b), respectively.

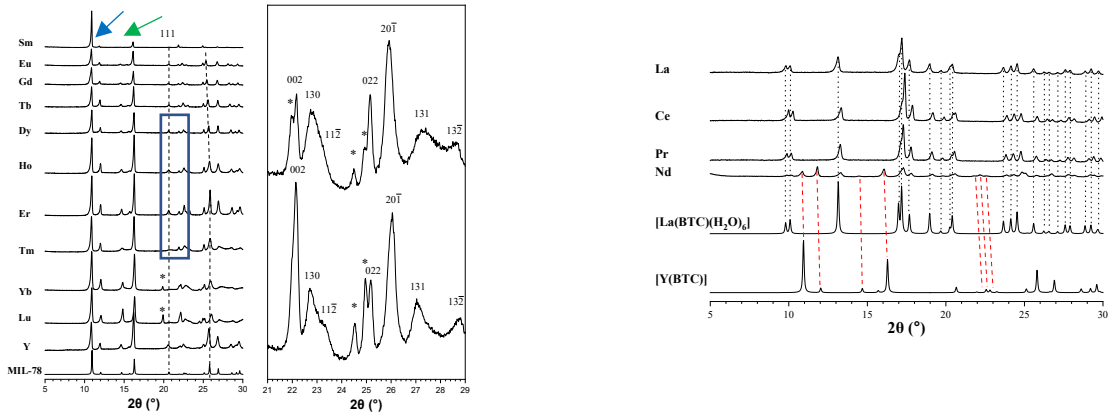


a *b* *c*

Fig. 1. Projections of the structure of [*RE*BTC] of the MIL-78 type onto the YZ (a), XZ (b), XY (c) planes.

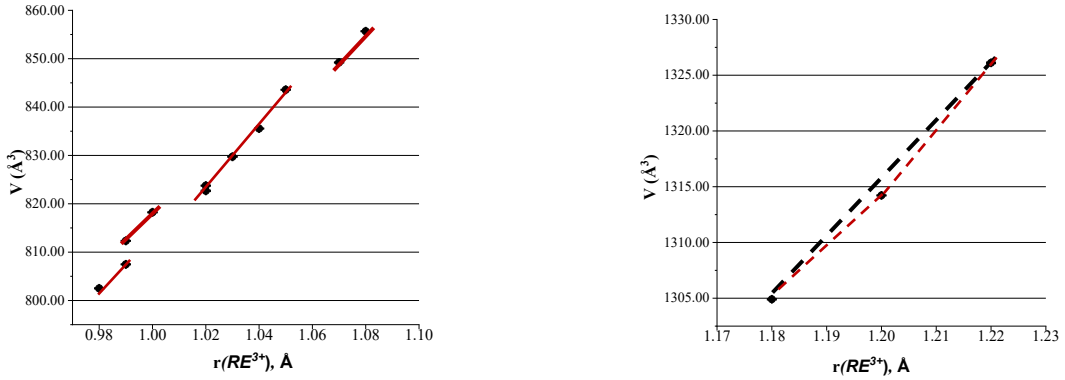
The diffraction patterns of *RE*3+(BTC) (Fig. 2a) show a redistribution of the strong-intensity reflections 001 (Fig. 1b) (green arrow in Fig. 2a) and 021 (Fig. 1a) (blue arrow in Fig. 2a), and merging of the 130, 11-2 and 13-1 peaks (blue rectangle in Fig. 2a), starting from Ho.

In the dependence of V, Å^3 of [*RE*(BTC)] (MIL-78 type) on the *RE* radius (*r(RE),* Å) according to Shannon (Fig. 3a), the tetrad effect is clearly visible: Sm÷Eu ([Xe]4f^6), Gd (**[Xe]4f^7**; **χ=2.40**)÷Ho(χ=2.11) (Y), Er (χ=2.02)÷Tm (χ=2.03), Yb ([Xe]4f^{13}; χ=1.70)÷Lu (**[Xe]4f^{14}**; **χ=2.68**), caused by the electronic structure of *RE* (stable **4f^7** and **4f^{14}**, and unstable shells near them), and the electronegativity value (c) according to Oganov.



a b c

Fig. 2. Diffraction patterns of RE^{3+}(BTC) with *RE* = Sm-Lu, Y (MIL-78 type) (a) and part of the diffraction patterns with *RE* = Yb, Lu (b) (*- type X), with *RE* = La-Nd (*RE*(BTC)(Cc) type) (c).



a *b*

Fig. 3. Unit cell volume of *RE(BTC)* (MIL-78 type) and [*RE*(BTC)(H2O)6] (*REBTC(Cc)* type) as a function of the ionic radius of *RE* [3] (*a* and *b*).

Single-phase (according to the X-ray experiment data, Fig. 2c) nanosized samples [*RE*(BTC)(H2O)6] with *RE* = La-Pr crystallize in the Cc space group, Z = 4 with unit cell parameters *a* ~ 11.52 Å, *b* ~ 18.04 Å, *c* ~ 7.35 Å, β ~ 119º (*RE*BTC(Cc) type [2]) (Fig. 3), while the sample with *RE* = Nd contains ~57% of the MIL-78-type phase and ~43% of the *RE*(BTC)(Cc) type. For them, an arc-shaped dependence of V, Å^3 on the atomic number of *RE* and on *r(RE),* Å is observed (Fig. 3b). In this case (Fig. 2c), there is no redistribution of the reflection intensities, since no special directions are observed in the projections of the *RE*(BTC)(Cc)-type structure.

Thus, the decrease in the unit cell volume caused by lanthanide contraction and the influence of the tetrad effect for *REBTC* with *RE* from La to Lu has been demonstrated.

The work was carried out with financial support from the Ministry of Science and Higher Education of the Russian Federation (Project No. FSFZ-2024-0003)

References

[1] C. Serre, F. Millange, C. Thouvenot, N. Gardant, F. J. Mater. Chem. **2004**, *14*, 1540–1543.
[2] Y.-H. Wen, J.-K. Cheng, Y.-L. Feng, J. Zhang, Z.-J. Li, Y.-G. Yao. Chinese Journal of Structural Chemistry, **2005**, *24(12)*, 1440–1444**.**
[3] Shannon, Robert. Acta Crystallographica Section A. **1976**, *32*. 751-767.

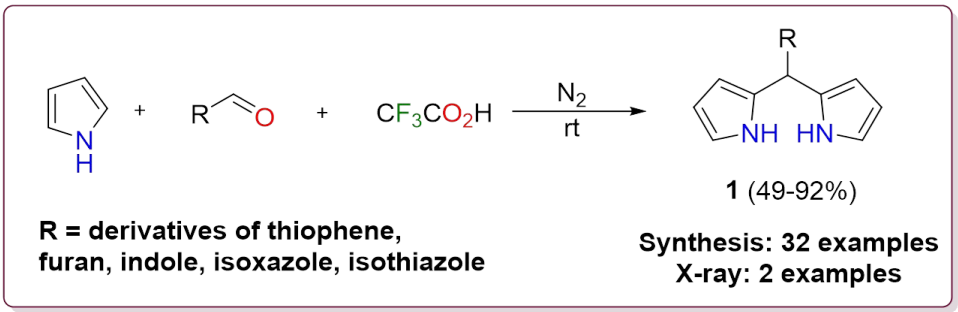
New BODIPY fluorophores with five-membered heterocycles at the *meso*-position: design, synthesis and crystal structure

Shelukho E.R., Yakovleva E.D., Polianskaia Z.A., Polyanskaya D.K., Maslova V.S., Larionov A.S., Khrustalev V.N., Zaytsev V.P.

RUDN University, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: shelukho-er@rudn.ru

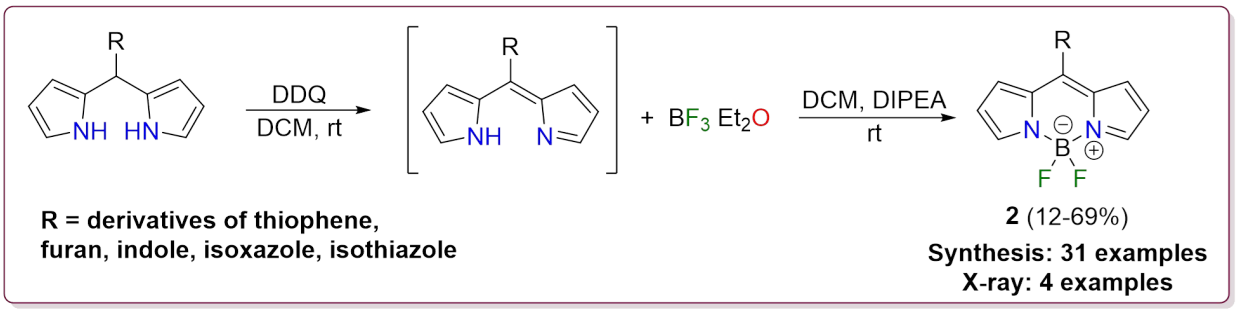
BODIPY is the acronym for 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, and is a family of complexes well-known for their properties as fluorophores. These molecules represent a prominent class of functional compounds with favorable photophysical properties, including a large molar absorption coefficient, narrow absorption and emission bands, high fluorescence quantum yield, and excellent photochemical stability [1]. Owing to these characteristics, they have found widespread applications as fluorescent probes, in cell imaging, organic light-emitting diodes (OLEDs), dye-sensitized solar cells (DSCs) and phototherapy as a promising photosensitizer for photodynamic therapy (PDT) [2-3]. Nevertheless, the structural versatility of BODIPYs, including modifications at specific positions of the core, allows for fine-tuning of their chemical and photophysical properties, including singlet oxygen generation, as well as enhancement of their photodynamic efficiency and biocompatibility, thereby improving their role in imaging and therapeutic applications in PDT [4]. Thus, the photophysical behavior of BODIPY may be governed by the substituent at the *meso*-position, yet replacing the typical six-membered aryl ring with five-membered heterocycles (e.g., furan, thiophene, pyrrole, selenophene) has received limited attention. Herein, the purpose of this study is the synthesis of a novel BODIPY derivatives functionalized with a five-membered heterocycles ring at the *meso*-position to investigate its influence on the structural, electronic, and photophysical properties of the resultant fluorophores.

Thus, a two-stage method for obtaining target BODIPY-type compounds was developed. In the first stage, various heterocyclic aldehydes were utilized as starting compounds and introduced into a condensation reaction with pyrrole under acid catalysis in inert atmosphere, which was led to the formation of wide range of intermediate dipyrromethanes (Scheme 1).



Scheme 1. Synthesis of dipyrromethanes **1**.

The resulting dipyrrolmethanes **1** was then introduced into the oxidation with DDQ in CH_2Cl_2, followed by neutralization with DIPEA and subsequent treatment with $BF_3{\times}OEt_2$, provided the corresponding BODIPY complexes **2** (Scheme 2).



Scheme 2. Synthesis of BODIPY dyes **2**.

During the experimental part of the work, both precursor compounds **1** and the target BODIPY scaffolds **2** were isolated in the form of crystalline solids. Some of them were studied using X-ray structural analysis, which resulted in a wide range of their crystal structures. (Figure 1).

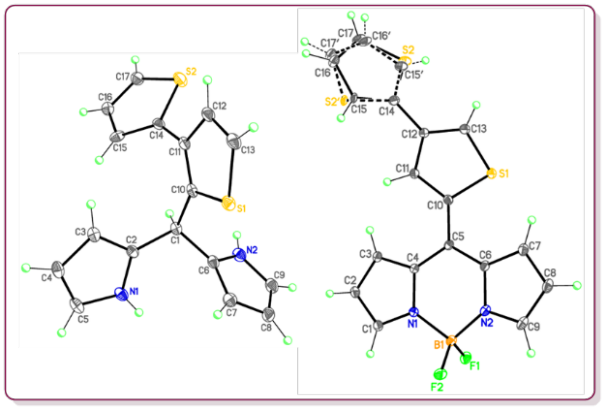


Fig. 1. The example of dipyrromethane **1** and BODIPY **2** crystal structures

Currently, a systematic analysis of the photophysical parameters of the obtained target fluorophores is being carried out, and subsequent determination of their biological activity is planned. Moreover, in collaboration with colleagues from the Department of Physical and Colloid Chemistry (Faculty of Science, RUDN University) studies to investigate the synergy of the physical properties of the obtained fluorophores and MOF structures with different compositions are being conducted.

The work was supported by RUDN University: project № 021422-2-000 "Systems of Grant Support for Scientific Projects of RUDN University" and grant funding for young scientists "Joint Start: Let's Make Science Together".

References

[1] Yadav, I. S. & Misra, R. *J. Mater. Chem.* **2023**, C 11, 8688–8723.
[2] Gawale, Y., Palanisamy, P., Lee, H. S., Chandra, A., Kim, H. U., Ansari, R., Mi, Y. C. & Kwon, J. H. *ACS Appl. Mater. Interfaces.* **2024**, 16, 22274–22281.
[3] Prieto-Montero, R., Prieto-Castañeda, A., Sola-Llano, R., Agarrabeitia, A. R., García-Fresnadillo, D., López-Arbeloa, I., Villanueva, M. A., Ortiz, M. J., de la Moya, S. & Martínez-Martínez, V. *Photochem. Photobiol.* **2020**, 96, 458–477.
[4] Malacarne, M. C., Gariboldi, M. B. & Caruso, E. *Int. J. Mol. Sci.* **2022**, 23, 10198.

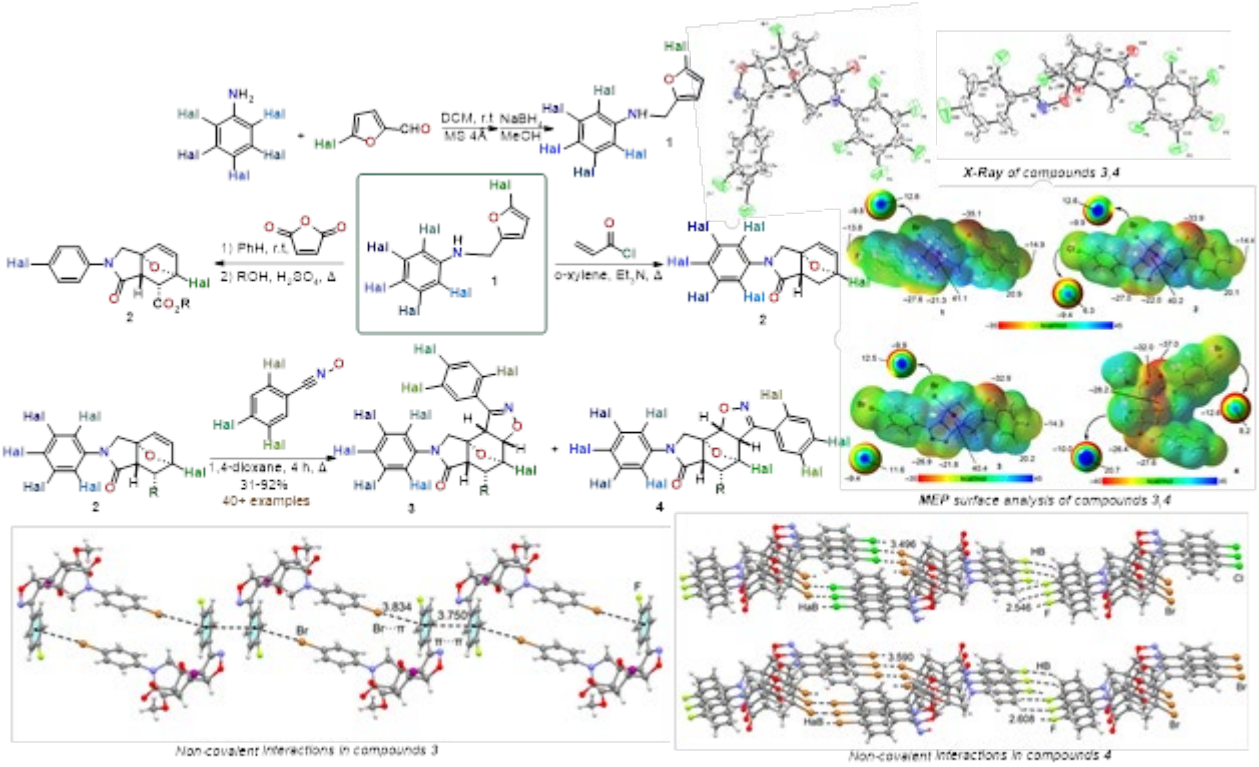
Non-covalent interactions in epoxyisoxazoloisoindol derivatives

Maslova V.S., Khrustalev V.N., Frontera A., Zubkov F.I., Zaytsev V.P.

RUDN University, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: ver.maslova2000@gmail.com

Non-covalent interactions (NCIs) play an important role in defining the structures and properties of molecules and materials. Among them, σ-hole interactions, particularly halogen bonding (HaB), are important due to their strong directionality and tunability. The combination of X-ray crystallography and computational methods provides an effective approach for characterizing these interactions and their contribution to crystal packing [1].

An approach to the synthesis of polyhalogen-substituted 4,8a-epoxyisoxazoloisoindoles was developed. The method involves reductive amination, an intramolecular Diels–Alder reaction (IMDAF) [2], and a subsequent (3+2)-cycloaddition of aromatic nitrile oxides to 3a,6-epoxyisoindoles [3]. A broad range of novel polyhalogenated heterocycles was obtained, some of which were characterized by X-ray crystallography and DFT calculations. MEP, QTAIM, NCIplot, and NBO analyses were used to characterize the observed halogen bonds.



This work was supported by the RUDN University Scientific Projects Grant System (grant No. 021422-2-000)

References

[1] Zheng, J., et al. *Bioorg. Nanoscale Adv.*, **2021**, 3, 6342.
[2] Maslova, V. S., et al. *Acta Cryst.*, **2026**, E82, 1052-1056.
[3] Maslova V. S., et al. J. Mol. Struct., 2026, 1361, 145700.

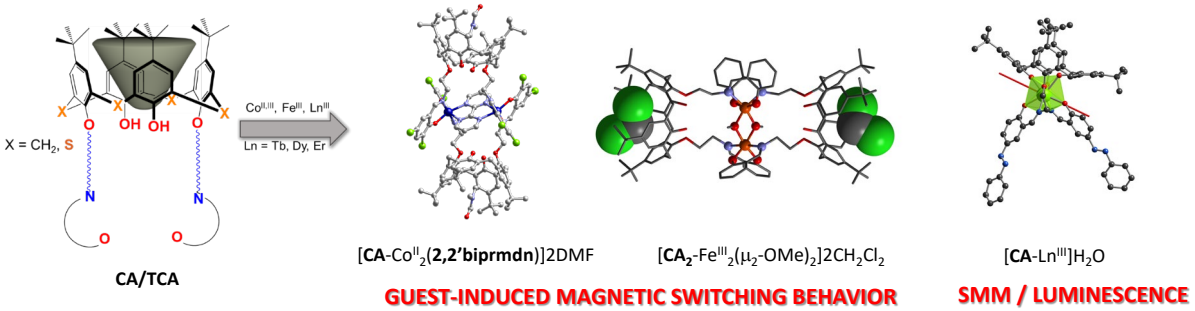
Rational approach to the design of molecular magnets and luminescent thermometers based on complexes of 1,3-disubstituted derivatives of (thia)calix[4]arenes with *3d*-/*4f*-metal cations

Iova A.A.,[1,2] Ovsyannikov A.S.,[1] Solovieva S.E.[1], Antipin I.S.[1,2]

[1] *A.E. Arbuzov Institute of Organic and Physical Chemistry of FRC Kazan Scientific Center of RAS, 420088, Kazan, Arbuzov str. 8*
[2] *Kazan Federal University, 420111, Kazan, Kremlevskaya str., 29*
e-mail: aa.iova@mail.ru

Due to the rapid development of quantum technologies in the field of information processing and storage, there is a growing need to create new quantum computer memory cells (Qbits). These cells can be formed by magnetoactive complexes of *3d*- and *4f*-cations, which exhibit spin-crossover properties, or by molecular magnets (SMMs) [1,2]. Due to their ability to undergo f-f transitions, Ln(III) ion complexes are attractive research targets for the production of new luminescent materials that can be used in molecular thermometry, OLED technology, bioimaging, and other applications [3].

(Thia)calix[4]arenes are attractive macrocyclic ligands for the preparation of new complexes with tunable magnetic and luminescent properties due to the possibility of fine-tuning the conformational flexibility, pre-organization of the arrangement of coordinating centers, the nature of the substituents of the upper/lower rims, which allows for the preparation of functional complexes, including luminescent nanomagnets [4]. In this work, the synthesis and structure of new $Co^{II,III}$, Fe^{III}, Ln^{III} (Ln = Dy, Tb, Er) complexes based on 1,3-disubstituted derivatives of (thia)calix[4]arenes (CA, TCA) functionalized with salicylideneamine coordinating centers are presented. The influence of the ligand structure on the magnetic and luminescent properties of the obtained complexes is shown.



This work was supported by grants from the Russian Science Foundation (№ 22-73-10139-P)

References

[1] Atzori, M.; Sessoli, R. *J. Am. Chem. Soc*. **2019**, 141, 29.
[2] Darawsheh, M.; Barrios, L.A.; Roubeau, O. *Angew. Chem.* **2018**, 130, 41.
[3] Kitagawa, Y.; Ferreira da Rosa, P.P.; Hasegawa, Y. *Dalton Trans.* **2021**, 50, 42.
[4] Ovsyannikov, A.S.; Khariushin, I.V.; Solovieva, S.E.; Antipin, I.S. *RSC adv*. **2020**, 10, 20.

Specifics of evaluating the real composition of single-crystal solid solutions $[Co_{1-x}Ni_x)_3(C_6H_5(COO)_3)_2(H_2O)_{12}]$ based XRD data

Mushtakov A.G.[1,2], Lazarenko V.A.[3], Svetogorov R.D.[3], Kuz'micheva G.M.[2], Markova E.B.[1,2]

[1]*Peoples' Friendship University of Russia named after Patrice Lumumba, 6 Miklukho-Maklaya St, Moscow, 117198, Russian Federation*
[2]*MIREA – Russian Technological University, 78 Vernadsky Ave., Moscow 119454, Russian Federation*
[3]*National Research Center «Kurchatov Institute», 1 Akademika Kurchatova pl., Moscow 123182, Russian Federation*
e-mail: 1142220147@rudn.ru

Traditional X-ray structural analysis of crystals allows for determining atomic coordinates, atomic displacement parameters, and the occupancy of each crystallographic position, i.e. the real (crystallochemical) composition. The site occupancy (p) is proportional to the atomic form factor, which, at a zero diffraction vector, equals the atomic number of the element (N). In the case of compounds containing atoms with close N values that occupy the same structural position, determining the content of each element requires a specific approach, particularly, calculations based on mid- and high-angle reflections. However, the number of such reflections may be too low to perform a complete structural analysis. The aim of this work is to perform X-ray structural analysis of single-crystals metal-organic frameworks with the framework composition $[(Co_{1-x}Ni_x)_3(C_6H_5(COO)_3)_2(H_2O)_{12}]$, and to determinate of cation site composition.

The single-crystals with initial composition $[(Co_{1-x}Ni_x)^{2+}{}_3(BTC)^{3-}{}_2(H_2O)_{12}]$, where is $(BTC)^{3-}$ – $C_6H_3(COO^-)_3$, with size up to ~3÷4 mm were grown by a solvothermal method (t = 130 °C, τ = 8 h) in solvent mixture of $(CH_3)_2NCHO:C_2H_5OH:H_2O$ = 1:1:1 (fig. 1).

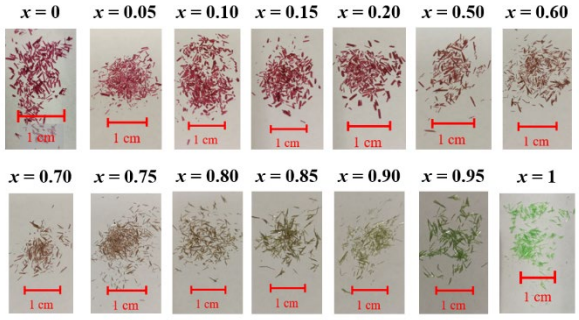
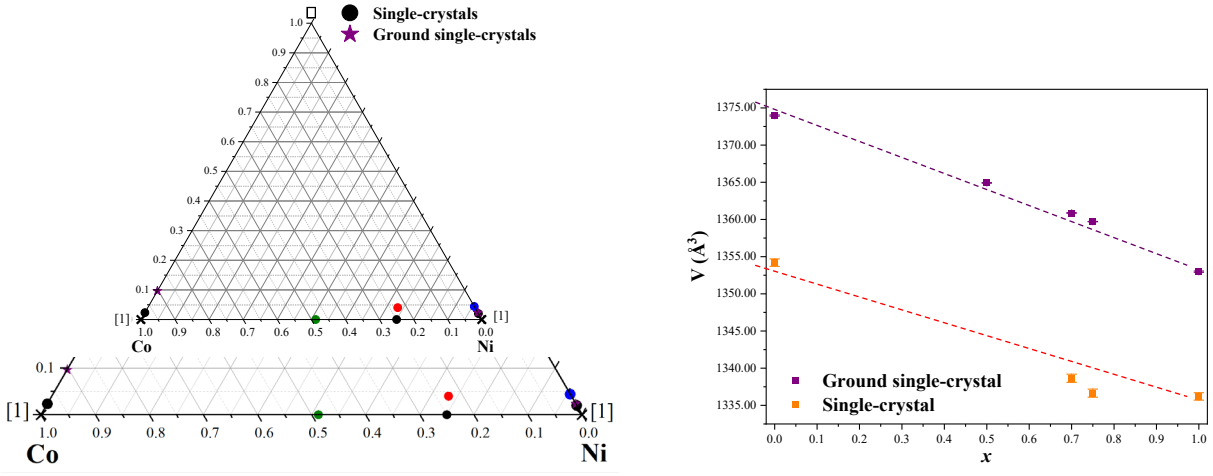


Fig. 1. Appearance of the $[Co_{1-x}Ni_x)^{2+}{}_3(BTC)^{3-}{}_2(H_2O)_{12}]$ single crystals.

X-ray diffraction data collection for single crystals of $[(Co_{1-x}Ni_x)^{2+}{}_3(BTC)^{3-}{}_2(H_2O)_{12}]$ ([*x*(Co,Ni)(BTC)]) c *x* = 0 (marked as Co(BTC)), 0.50, 0.70, 0.75, 1.00 (Ni(BTC)) was performed at the "Belok/XSA" beamline at the Kurchatov Synchrotron Radiation Source (NRC "Kurchatov Institute", Moscow). The [*x*(Co,Ni)(BTC)] solid solutions crystallize in sp. gr. C2 (*Z* = 4) (*M*BTC(C2) type) with *a*~17 Å, *b*~13 Å, *c*~6.5 Å, β~112° [1]. The *M*BTC(C2) type structure has two cation sites *M*1 and *M*2.

Determination and structure refinement CoBTC and NiBTC single-crystals (λ = 0.7527 Å at 100 K; SHELXT and OLEX2 software) and structure refinement of ground single-crystals (λ = 0.75 Å; GSAS-II software, Rietveld refinement) yielded the compositions $[(Co^{2+}{}_{2.71(2)}\square_{0.29})(BTC)^{3-}{}_{1.81}(H_2O)_{11.14(4)}]$ and $[(Ni^{2+}{}_{2.93(4)}\square_{0.07})(BTC)^{3-}{}_{1.95}(H_2O)_{11.12(6)}]$, which differ from $[(Co^{2+}{}_{2.93(1)}\square_{0.07})(BTC)^{3-}{}_2(H_2O)_{11.94(4)}]$ and match $[(Ni^{2+}{}_{2.94(2)}\square_{0.06})(BTC)^{3-}{}_2(H_2O)_{11.96(4)}]$ respectively [2] (fig. 2).



a *b*

Fig. 2. Real composition diagram of $[(Co_{1-x}Ni_x)_3(C_6H_5(COO)_3)_2(H_2O)_{12}]$ (a): blue circle – composition (1), green circle – composition (2), red circle – composition (3), black circle – composition according to [2], cross – composition according to [1]; unit cell volume (V,Å^3) of single crystals (orange squares) and ground single-crystals (purple squares) of the initial compositions (b)

Refinement of the site occupancies for Ni(1) (pNi1) и Ni(2) (pNi2) in structure with initial composition [0.75(Co,Ni)(BTC)] (nominally $[Co_{0.25}Ni_{0.75})_3(C_6H_5(COO)_3)_2(H_2O)_{12}]$) led to decrease pNi after traditional steps of refinement (lattice constants, atoms coordinates, atomic displacement in isotropic and anisotropic approximations). This indicates either high vacancy content – $[(Ni_{2.868(8)}\square_{0.132})(BTC)^{3-}{}_2(H_2O_w)_{12}]$ (1) or substitution of Ni (N(Ni) = 28) on Co (N(Co) = 27) – $[(Ni^{2+}{}_{1.538(34)}Co^{2+}{}_{1.462})](BTC)^{3-}{}_2(H_2O_w)_{12}]$ (2). However, both scenarios are unrealistic. This implies that vacancies (□) are present along with Co in the Ni(1) and Ni(2) sites, as previously found for the compositions with x = 0 and 1 [2]. Since the simultaneous presence of Ni, Co, and vacancies cannot be refined within this experiment, we utilized unit cell volume analysis (V, Å^3) of the initial samples (Fig. 2b) and the real composition diagram (Fig. 2a) to determine composition. The value V,Å^3 (fig. 2b) exhibits a virtually linear relationship with the compositions of the ground single-crystals for [*x*(Co,Ni)(BTC)] with *x* = 0.50, 0.70, 0.75. Meanwhile, a negative deviation from the straight line indicates a higher real Ni content in the crystals: *x* = 0.70 (Ni/Co>2.33) and 0.75 (Ni/Co>3). Considering the vacancies in the crystal structure (fig. 2), the calculated composition of $[(Co_{0.23}Ni_{0.73}\square_{0.04})_3(BTC)_2(H_2O_w)_{12}]$ (3) (fig 2a, red dot) for the initial $[(Co_{0.30}Ni_{0.70})_3(C_6H_5(COO)_3)_2(H_2O)_{12}]$ proved to be entirely realistic, thereby demonstrating the efficiency of the applied approach.

The work was supported by Ministry of Science and Higher Education of the Russian Federation (grant № FSFZ-2024-0003)

References

[1] O. M. Yaghi, Hailian Li, T. L. Groy. *Journal of the American Chemical Society*, 1996, 118 (38), 9096–9101

[2] A. G. Mushtakov, G. M. Kuz'micheva, A. V. Savchenkov, I. A. Kaurova, E. B. Markova, R. D. Svetogorov, V. A. Lazarenko, E. V. Khramov, R. G. Chumakov, N. A. Anistratov, R. P. Terekhova, I. G. Bratchikova, A. A. Kholodkova, A. A. Strekalova. *Inorganic Chemistry Communications*, 2026, 189, 116775.

Influence of molecular and crystal structure on photophysical properties in cyclometalled platinum complexes with carboxylate and pyridine ligands

Sosunov E.A., Yakushev I.A.

Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninsky pr. 31, Moscow, 119991 Russia
e-mail: boulderax159@gmail.com

Nowadays, various cyclometaled complexes of platinum metals are promising materials in modern inorganic chemistry due to their rich photophysical properties. These complexes find application as photocatalysts [1] and precursors for OLED displays [2]. One of the goals of coordination chemistry is to produce complexes with predictable photophysical properties that can be regulated in several ways: by changing crystal and/or electronic structure. This work is attributed to cyclometaled platinum complexes with carboxylate and pyridine ligands with the common formula view (ppy)Pt(Py)(OOCR), where R = Me, t-Bu, Ph, $CH(Ph)_2$, $C(Ph)_3$, C_6F_5, (o-C_6H_4F), (m-C_6H_4F), (p-C_6H_4F). While the molecular structures of the complexes are similar, their crystal structures are quite different from each other. Complexes can be systematized by the presence and type of π-staking interaction in their crystal packing (**Figure 1**). Formation of dimer stacks linked via π-staking interaction between aromatic systems of 2-phenylpyridine ligands and C-H…O contacts observed in all series except the diphenyl acetate complex, $CH(Ph)_2$. Absence of π-stacking observed only for the polymorph modification of the acetate complex, while the infinite π-stacking observed for complexes with R = Me, C_6F_5 and p-C_6H_4F. Emission spectra of complexes are very sensitive to the presence of stacking interactions. An increase in the convergence of aromatic systems results in an increase in the intensity of low energy emission band. We assume that this happens due to changes of 2-phenypyridine vibronic progression.

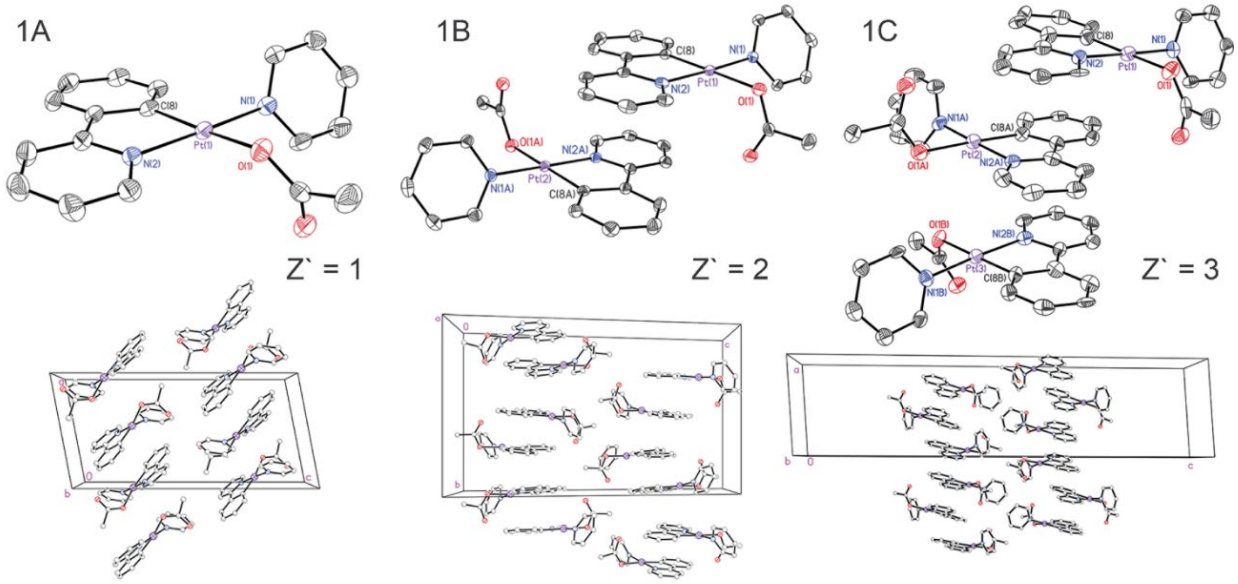


Fig. 1. Crystal structures and packs of various polymorphs of the acetate complex

References

[1] Gomez de Segura D. *et. al. Inorganic Chemistry*, **2024**, 63, 3, 1589-1606.
[2] Williams J. A. G. *et. al. Coordination Chemistry Reviews*, **2008**, 252, 23-24, 2596-2611.

Lanthanide 1D coordination polymers with bulky cyclohexanecarboxylate ligands: synthesis, structure and properties

Sabitova I.A., Grebenyuk D.I., Tsymbarenko D.M., Lyssenko K.A.

Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Russia
email: i_sabitova@yahoo.com

The lanthanide carboxylate complexes are a large and developing class of coordination compounds with various structural dimensions. The coordination polymers based on α-aliphatic carboxylates with bulky substituents can reveal specific structural features, which affect their functional properties [1–3]. Moreover, remaining the polymeric pattern, it is possible to demonstrate the effect of new neutral ligands on the crystal structure and compound's characteristic. The cyclohexanecarboxylate (chc^-) is a promising ligand for studying structural features due to it is bulky ligand, but at the same time its cyclic fragment is devoid of excessive branching and is not prone to specific stacking interactions [4].

In this work [5], we developed two experimental procedures to obtain 1D coordination polymers with the compositions of $[Ln_3(chc)_9(Hchc)_{0.5}]_n$ (**Ln_3**) and $[Ln_5(chc)_{15}]_n$ (**Ln_5**). The reaction of $Ln(NO_3)_3$ with a Nachc/Hchc buffer in an aqueous solution leads to different products depending on Ln: **Ln_3** for Dy–Tm and **Ln_5** for Yb, Lu. It is worth noting, that the resulting complexes do not coordinate a large number of additional neutral ligands, neither water nor carboxylic acid, since **Ln_3** only contain 1/6 Hchc per one Ln atom. This feature originates from sterical hindrances caused by bulky cyclohexanyl substituents of chc^- ligands. The elimination of Hchc molecules at 100 ºC occurs easily and is accompanied by a solid-state transformation of **Ln_3** to **Ln_5**. The resulting **Ln_5** are stable up to 250 ºC and decompose to Ln_2O_3 at higher temperatures.

$[Ln_3(chc)_9(Hchc)_{0.5}]_n$ have helix-like polymeric structures formed by the chc^- ligand with coordination modes of two types, bridging and chelate-bridging, and terminal Hchc molecules. The solid-state transformation of **Ln_3** to **Ln_5** leads to a decrease of Ln coordination number, while the helix-like motif of 1D polymer remains, although its period increases (**Fig. 1**). The H···H interchain contacts dominate in both **Ln_3** and **Ln_5** structures.

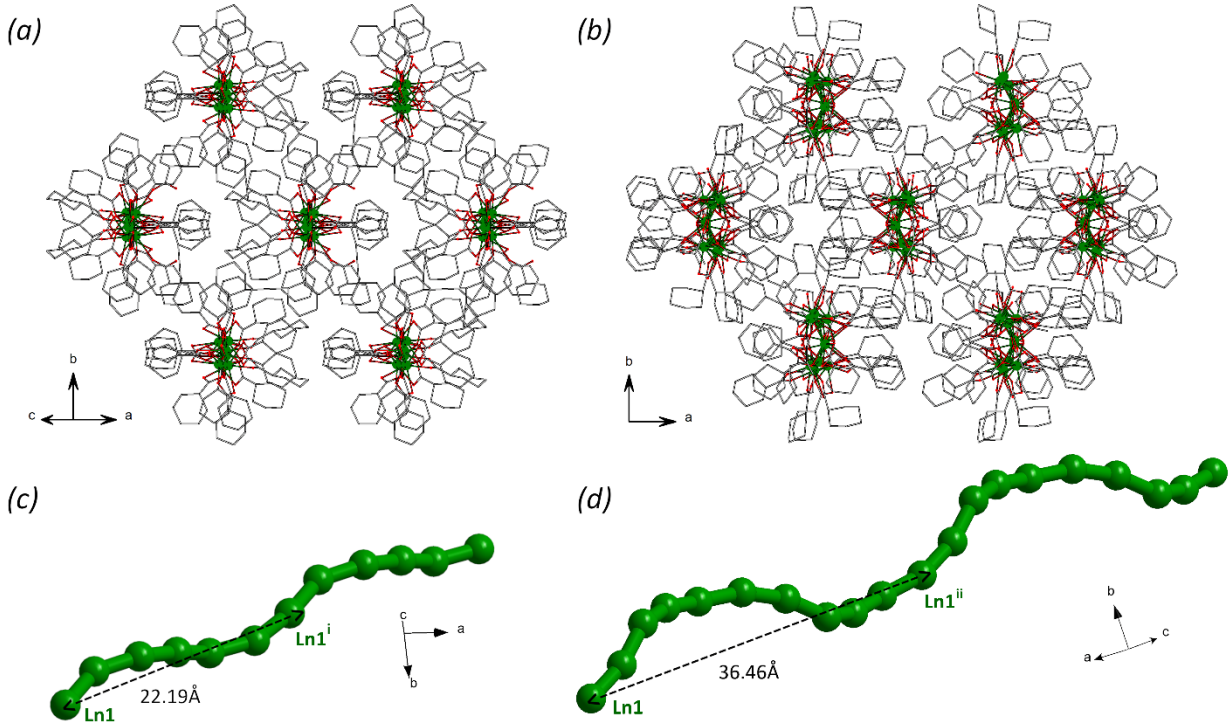


Fig. 1. Packing manner of polymeric chains in the crystal structure of **Ho$_3$** *(a)* and **Lu$_5$** *(b)*. The view on the separate Ln backbone within the polymeric chain in the crystal structure of **Ho$_3$** *(c)* and **Lu$_5$** *(d)*. Symmetry codes: (i) 1+x, y, 1+z; (ii) x, y, 1+z.

The study of the magnetic behavior of **Ln$_3$** and **Ln$_5$** in both dc and ac regimes revealed slow magnetic relaxation of **Dy$_3$** and **Dy$_5$** analogs. The out-of-phase component of magnetic susceptibility $\chi''(T)$ of both compounds shows frequency dependence below 7.5 K in zero external field, although without the appearance of maxima. Transformation from **Dy$_3$** to **Dy$_5$** is accompanied by the elimination of Hchc molecules and a change of Dy local environment, which leads to the enhancement of SMM properties, with **Dy$_5$** showing slower magnetic relaxation with a higher U_{eff} barrier.

This work was supported by the Russian Science Foundation (project No. 25-13-00131)

References

[1] Tsymbarenko D., Martynova I., Grebenyuk D., Shegolev V., Kuzmina N. *J. Solid State Chem.,* **2018**, 258, 876.
[2] Grebenyuk D., Zobel M., Polentarutti M., Ungur L., Kendin M., Zakharov K., Degtyarenko P., Vasiliev A., Tsymbarenko D., *Inorg. Chem.*, **2021**, 60, 8042.
[3] Anureeva M., Kendin M., Gamzatov A., Tsymbarenko D., *JACS*, **2025**, 147, 46348.
[4] Grebenyuk D., Tsymbarenko D., *J. Struct. Chem*., **2022**, 63, 432.
[5] Grebenyuk D., Sabitova I., Long H., Gavrilkin S., Tsvetkov A., Lyssenko K., Tsymbarenko D., *J. Solid State Chem.,* **2026**, 360, 126085.

X-ray structural analysis of α-$NiSO_4 \cdot 6H_2O$ single crystals doped with low concentrations of Y^{3+} and Ti^{4+} ions

Arbanas L.A.[1,2], Khrustalev V.N.[2], Lazarenko V.A.[3], Kaurova I.A.[1], Kuz'micheva G.M.[1], Manomenova V.L.[3]

[1] MIREA – Russian Technological University, Moscow 119454, Russia

[2] Peoples' Friendship University of Russia named after Patrice Lumumba (RUDN University), Moscow, Russia

[3] National Research Center "Kurchatov Institute", Moscow, Russia

e-mail: arbanas@mirea.ru

Conventional single-crystal X-ray diffraction (SCXRD) analysis makes it possible to determine atomic coordinates, atomic displacement parameters, and occupancies of crystallographic sites, i.e., the real (crystal-chemical) composition. The site occupancy (p) is proportional to the atomic form factor, which at zero scattering vector equals the atomic number (N). A decrease in p(N) upon occupancy refinement corresponds to vacancies or ions with a smaller N, and an increase corresponds to ions with a larger N.

SCXRD of doped crystals with activator ions introduced into the crystal matrix in small amounts (< 4 wt%) requires solving a number of problems:

- identification of the minimum concentration of impurity ions detectable in a given structural experiment;
- determination of the structural location of dopants (substitutional or interstitial) and their content in specific crystallographic sites depending on the studied region of a large-sized crystal;
- identification of additional point defects compensating for the change in electroneutrality of the system upon doping;
- modeling the distribution of impurity ions over the crystal volume (length and cross-section) or over growth sectors;
- formulation of the reasons for discrepancies between the refined (crystal-chemical, real) compositions of doped crystals measured on different instruments.

The aim of this work is to determine the real compositions of α-NSH crystals doped with small amounts of Y^{3+} and Ti^{4+} ions from diffractometer and synchrotron data.

α-NSH:Y and α-NSH:Ti crystals were grown from aqueous solutions by the temperature reduction method [1]. Y^{3+} ions were introduced into the solution as yttrium sulfate octahydrate ($Y_2(SO_4)_3 \cdot 8H_2O$ 0.42 wt%) α-NSH:Y(1) and α-NSH:Y(2) were grown on α-NSH seeds with the (001) top face in crystallizers with volumes of 5 L (α-NSH:Y(1)) and 0.5 L (α-NSH:Y(2)). Ti^{4+} ions were introduced into the solution as titanium(IV) oxide sols with hydrodynamic particle diameters of 20.30 Å (α-NSH:Ti(1)) and 21.97 Å (α-NSH:Ti(2)) (Ti^{4+} content in the solution 0.1 wt%) [2].

Macrocrystals (~0.24 × 0.24 × 0.24 mm^3) and microcrystals (~0.02 × 0.02 × 0.02 mm^3) were measured on diffractometers (D) (Bruker D8 QUEST PHOTON-III, λ = 0.71073 Å, and Stoe STADI-VARI Pilatus-100K, λ = 0.7093 Å [2]) and at a synchrotron (S) (Belok/XSA beamline, Kurchatov Synchrotron Radiation Source, λ = 0.7527 Å) (Table).

The structures were solved by direct methods (SHELXT) and refined with SHELXL in the following stages:

(1) Refinement of the unit cell parameters, atomic coordinates, and atomic displacement parameters in the isotropic and then anisotropic approximation with p(Ni) = 1, as for the other atoms S^{6+}, O^{2-}, and H^+.

(2) Analysis of the Ni site occupancy showed: p(Ni) < 1 – vacancies in the Ni^{2+} site (N(Ni) = 28, N(Y) = 39), or vacancies or Ti^{4+} (N(Ti) = 22) in the Ni^{2+} site; p(Ni) > 1 – Y^{3+} ions in the Ni^{2+} site; p(Ni) = 1 – insufficient sensitivity of the method.

(3) Refinement of p(Ni) with the point defects found (Table). Unrealistic p(Ni) values upon occupancy refinement indicate that substitution of Ni^{2+} by Ti^{4+} in α-NSH:Ti, as well as of Ni^{2+} by Y^{3+} in α-NSH:Y, is impossible at small amounts according to the theory of isomorphism (Table) [3], but not at ultra-small amounts.

(4) Analysis of the residual electron density revealed interstitial dopant ions Y^{3+}_i and Ti^{4+}_i, except for the compositions marked **** in the Table.

(5) A series of crystal structure refinements until the R-factors stabilized. The unit cell parameters and volume are consistent with the compositions found (Table).

Table. Conditions and results of the SCXRD analysis of α-NSH:Y and α-NSH:Ti

Sample	Inst	T, K	Growth sector	N / N_{obs}***	R_1/wR_2	Refined composition
α-NSH:Y(1)	D	100	(101)	20298/1477	0.0149/0.0382	$[Ni_{1.001(2)}]$****
			(102)	20293/1507	0.0134/0.0355	$[(Ni_{0.999(2)}\square_{0.001})Y_{0.003(i)}]$
			(001)	20512/1481	0.0136/0.0351	$[(Ni_{0.990(5)}\square_{0.010})Y_{0.010(i)}]$
	S		(101)	7628/1049	0.0479/0.1280	$[Ni_{1.007(5)}]$****
			(102)	6759/945	0.0942/0.2721	$[(Ni_{0.989(5)}\square_{0.011})Y_{0.004(5)(i)}]$
			(001)	6413/1046	0.0396/0.1030	$[(Ni_{0.997(3)}\square_{0.003})Y_{0.003(3)(i)}]$
α-NSH:Y(2)	D		(101)	25387/1498	0.0165/0.0487	$[Ni_{0.985(3)}\square_{0.015}]$**
			(102)	18680/1500	0.0149/0.0404	$[Ni_{0.997(2)}\square_{0.003}]$**
			(001)*	11770/907	0.0185/0.0498	$[Ni_{0.990(3)}\square_{0.010}]$**
	S		(101)	1952/909	0.0695/0.2242	$[(Ni_{0.990(4)}\square_{0.010})Y_{0.010(4)(i)}]$
			(102)	3934/991	0.0688/0.2037	$[(Ni_{0.995(4)}\square_{0.005})Y_{0.005(4)(i)}]$
			(001)	6987/1064	0.0414/0.1190	$[Ni_{1.004(5)}]$****
α-NSH:Ti(1)	D	295	*****	22141/1630	0.0226/0.0475	$[(Ni_{0.994(2)}\square_{0.006})Ti_{0.005(1)(i)}]$
	S	100		8034/1101	0.0474/0.1170	$[Ni_{1.00(1)}]$****
α-NSH:Ti(2)	D	295		15843/1155	0.0239/0.0543	$[(Ni_{0.990(2)}\square_{0.010})Ti_{0.010(4)(i)}]$
	S	100		7756/1104	0.0420/0.1166	$[(Ni_{0.99(2)}\square_{0.012})Ti_{0.006(8)(i)}]$

* D: Rigaku XtaLAB Synergy-S (λ = 1.54184 Å); ** no residual electron density peaks; *** N / Nobs with I > 2σ(I) (D), $F_o > 4\sigma(F_o)$ (S); **** dopant ions are absent or present in ultra-small amounts; ***** growth sectors were not distinguished.

Thus, the unit cell parameters (volume) are sensitive to small dopant contents, which makes it possible to use SCXRD to establish the real composition of crystals; the differences in compositions (Table) may be caused by growth defects (zonal inhomogeneity) or methodical reasons (experimental parameters and conditions).

The work was carried out in accordance with the Project of MIREA – Russian Technological University No. 230-MKM

References

[1] Manomenova, V.L.; Rudneva, E.B.; Voloshin, A.E. Russ. Chem. Rev., 2016, 85, 585.

[2] Kuz'micheva, G.M.; Arbanas, L.A.; Manomenova, V.L.; Kaurova, I.A.; Rybakov, V.B.; Khramov, E.V.; Lobanova, N.A.; Stefanovich, S.Yu.; Dorokhov, A.V. J. Alloys Compd., 2023, 965, 171369.

[3] Urusov, V.S. Theory of isomorphous miscibility. Moscow: Nauka, 1977 (in Russian).

Metal-Induced Halogen Bonding in Platinum-Group Isocyanide Complexes

Kinzhalov M.A.

St Petersburg State University, Russia, 199034 St Petersburg, Universitetskaya Nab. 7–9
e-mail: m.kinzhalov@spbu.ru

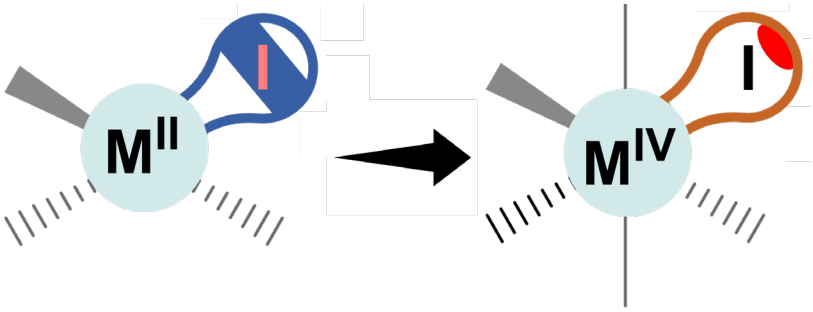
Coordination compounds of platinum-group metals are promising for the design of functional materials owing to the combination of their electronic and stereochemical characteristics. The fundamental properties of such complexes are determined by the nature of the metal center and by the electronic, donor–acceptor, and steric properties of the ligands. In the crystalline phase, the functional response is largely governed by crystal packing, which is formed by an ensemble of noncovalent interactions—hydrogen and halogen bonds, π–π stacking, and others. Despite the relatively low energy of individual contacts, their cooperative action defines the supramolecular organization and, consequently, the macroscopic properties of the material.

This report presents the results of our research group on the crystal-chemical regularities of complex self-assembly. Special attention is paid to metal-induced effects that enhance directional noncovalent contacts. It is shown that coordination of a metal ion, depending on its oxidation state, allows the electrophilic or nucleophilic properties of ligands to be tuned deliberately, which is a key factor in the rational design of supramolecular architectures. For activated halogens, electrophilic–nucleophilic dualism is realized: along with a positively charged σ-hole, a negatively charged electron belt is retained.

The starting point of these studies, as in the works of Chugaev, was isocyanide complexes of palladium and platinum dihalides. Among these classical compounds, complexes with halogen-substituted aryl isocyanides proved unexpectedly interesting: the substituent halogen atoms in the isocyanide ligands have an anisotropic electron-density distribution with a positive σ-hole, while the coordinated halide ligands exhibit a negative potential over the entire surface and act as nucleophilic centers. Such compounds are supramolecular synthons combining two σ-hole electrophilic centers and two nucleophilic centers in one molecule [1]. The resulting halogen bonds organize the molecules into layered structures; in some cases, cyclic four-center nodes including complementary C–X···X–M halogen bonds and a central M–X···X–M contact have been characterized [2]. Such nodes are characterized by positive cooperativity: the formation of each halogen bond increases the polarization of neighboring atoms and strengthens subsequent interactions.

The addition of halogen-bond donor molecules allows the system to switch from self-association to the formation of supramolecular adducts. In particular, upon addition of dihalomethanes, which also have an anisotropic electron-density distribution on the halogen atoms, adducts are formed in which the dihalomethane molecule acts as a bifunctional halogen-bond donor and the metal complex acts as an acceptor through the coordinated halide ligands [3]. The system permits isostructural replacement of both halogen atoms at different positions and the central metal atom while retaining the overall architecture, which is convincing evidence of controlled assembly based on halogen bonds. It was also found that the solubility of the complexes increases in parallel with the ability of the haloalkane to form halogen bonds; diiodomethane proved to be the leading solvent, which is of practical importance for the study of organometallic compounds by NMR spectroscopy. When shorter bifunctional donors, such as molecular iodine, are used, the system becomes more labile and adapts to the amount of added iodine, forming adducts of 1:1 composition (supramolecular chains) and 1:2 composition (layered structures) [4].

The situation changes dramatically on going from iodide complexes of Pt^{II} to iodide complexes of Pt^{IV}. Oxidation of the metal induces strong polarization of the coordinated iodide ligand: despite the overall negative charge, a positive σ-hole develops on the iodine atom [5]. As a result, the anionic iodide ligand acquires an electrophilic function unusual for it and acts as a halogen-bond donor toward the electron belt of the halogen atom of a neighboring molecule. In the crystal of *trans*-$[PtI_4(CNR)_2]$, two iodide groups act as donors and the other two as halogen-bond acceptors, which leads to the formation of two-dimensional supramolecular sheets.



The obtained results provide a scientific basis for the targeted design of hybrid materials with tailored properties. Understanding crystal-chemical factors and the role of intermolecular interactions in solid-state organization is a necessary condition for the creation of new generations of energy-efficient optoelectronic devices, sensors, and catalysts operating under mild conditions.

This work was supported by a grant from the Russian Science Foundation and the St. Petersburg Science Foundation (project number 25-13-20028, https://rscf.ru/project/25-13-20028/)

References

[1] *Angew. Chem. Int. Ed.*, **2018**, 57, 12785
[2] *Chem. Eur. J.*, **2019**, 25, 13671
[3] *Chem. Asian J.*, **2019**, 14, 3915
[4] *Cryst. Growth Des.*, **2020**, 20, 1975; *Inorg. Chem.*, **2021**, 60, 13200
[5] *Inorg. Chem.*, **2025**, 64, 25161

Correlation between the structure and scintillation properties of materials

Molokeev M.S.[a,b,c]

[a] *Siberian Federal University, Svobodny str. 79, 660041, Krasnoyarsk, Russia*
[b] *RUDN University, Miklukho-Maklaya str. 6, 117198 Moscow, Russia*
[c] *Kirensky Institute of Physics, SB RAS, Akademgorodok str. 50-38, 660036, Krasnoyarsk, Russia*
e-mail: msmolokeev@mail.ru

Random Forest and Decision Tree algorithms were used to establish correlations between the structure and scintillation properties of hybrid organic–inorganic metal halides (OIMH). Based on the analysis of 371 samples, a predictive model was constructed that enables prediction of the distance between metal centers, d(M…M) (Figure 1), with an error of ~0.5 Å; this distance correlates with the photoluminescence quantum yield (PLQY) [1]. The model operates on DeepSMILES representations in combination with metal (M) and halide (X) types. Key structural features were identified: terminal $–NH_3$ and N–H groups restrict the increase in d(M…M), whereas [N^+] moieties and aliphatic chains promote its growth.

The resulting correlations provided the basis for the targeted synthesis of five new compounds. Among them, $[DMe]MnBr_4$ exhibited the highest light output and considerable application potential (Figure 1).

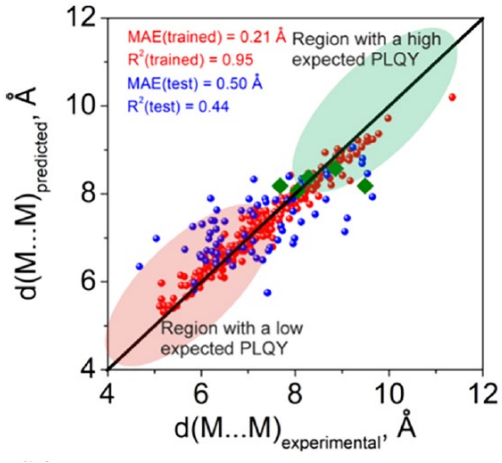




Fig. 1. Left: correlation plot of predicted versus experimental M…M distances, which determine the photoluminescence quantum yield (PLQY). Green diamonds indicate the newly synthesized compounds. Right: photograph of an operating detector based on the new scintillator, imaging a connector.

This work was supported by the Russian Science Foundation (grant № 24-43-00006)

References

[1] Molokeev, M.S.; Su, B.; Aleksandrovsky, A.S.; Golovnev, N.N.; Plyaskin, M.E.; Xia, Z. *Chem. Mater.*, **2022**, 34, 537-546.

σ-Hole interactions in phosphine selenides: structural, spectroscopic and computational insights

Mulloyarova V.V., Galiakhmetov S.A., Shitov D.A., Antonov A.S.

Saint Petersburg State University, 199034, Saint Petersburg, Universitetskaya Emb. 7/9
e-mail: vmulloyarova@gmail.com

Halogen and chalcogen bonds are directional noncovalent interactions that play an important role in determining the structure and properties of molecular systems [1–3]. Their formation is associated with a donor–acceptor interaction between the electron density of one molecule and a σ-hole of another. Phosphine selenides R_3PSe represent a convenient model system for studying such interactions because the selenium atom can act both as an electron donor and as an electron acceptor. The high polarizability and lone electron pairs of Se contribute to its electron-donor properties, while the σ-hole located along the extension of the P=Se bond in phosphine selenides allows selenium to act as an electron-density acceptor.

In this work the interactions of phosphine selenides with halogen- and chalcogen-bond acceptors and donors were investigated. In halogen-bonding systems with perfluorinated iodobenzenes, single-crystal X-ray diffraction demonstrated that Et_3PSe can form multiple Se···I halogen bonds with *o*-$C_6F_4I_2$. Two crystalline complexes were obtained, featuring three and two Se···I halogen bonds, respectively (Figure 1). Solid-state MAS NMR spectroscopy provided complementary evidence for these structural differences. The two crystalline complexes were distinguished by their NMR signals, with two signals observed in the ^{31}P spectrum and three signals in the ^{77}Se spectrum, consistent with the presence of nonequivalent P=Se units and different Se···I halogen-bonding environments. QTAIM analysis provided further insight into the nature of these interactions.

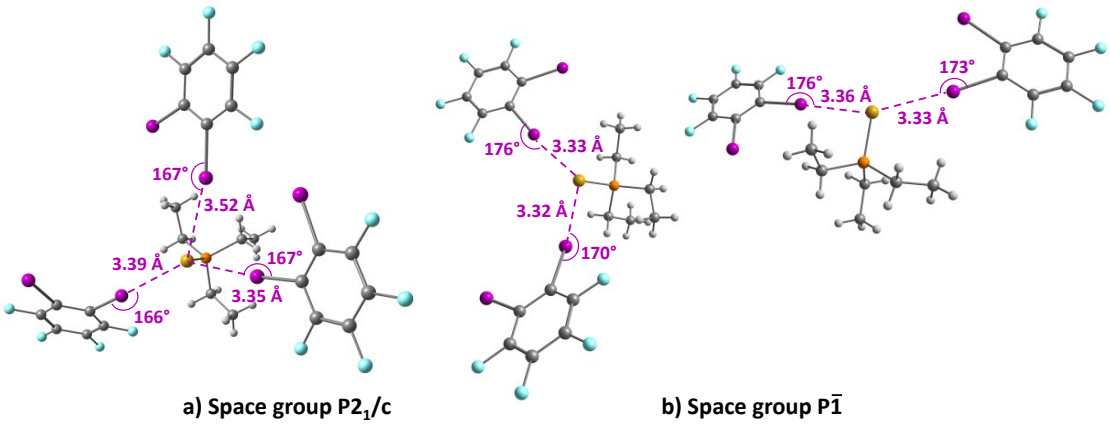


Fig. 1. Crystal structures of Et_3PSe with *o*-$C_6F_4I_2$ complexes featuring three (a) and two (b) Se···I halogen bonds.

In contrast, the parent phosphine selenides exhibit a low ability to act as electron-density acceptors in chalcogen bonds. To enhance this ability, a simple structural modification was proposed based on alkylation of the selenium atom. Quantum-chemical calculations of $[Et_3PSeMe]^+$ complexes with four pyridine N-oxide derivatives were performed at the PW6B95-DKH-D3/jorge-TZP-DKH level of theory and showed the formation of Se···O chalcogen-bonding interactions (Figure 2). The calculated structures demonstrate the formation of chalcogen-bonded complexes with different pyridine N-oxide derivatives.

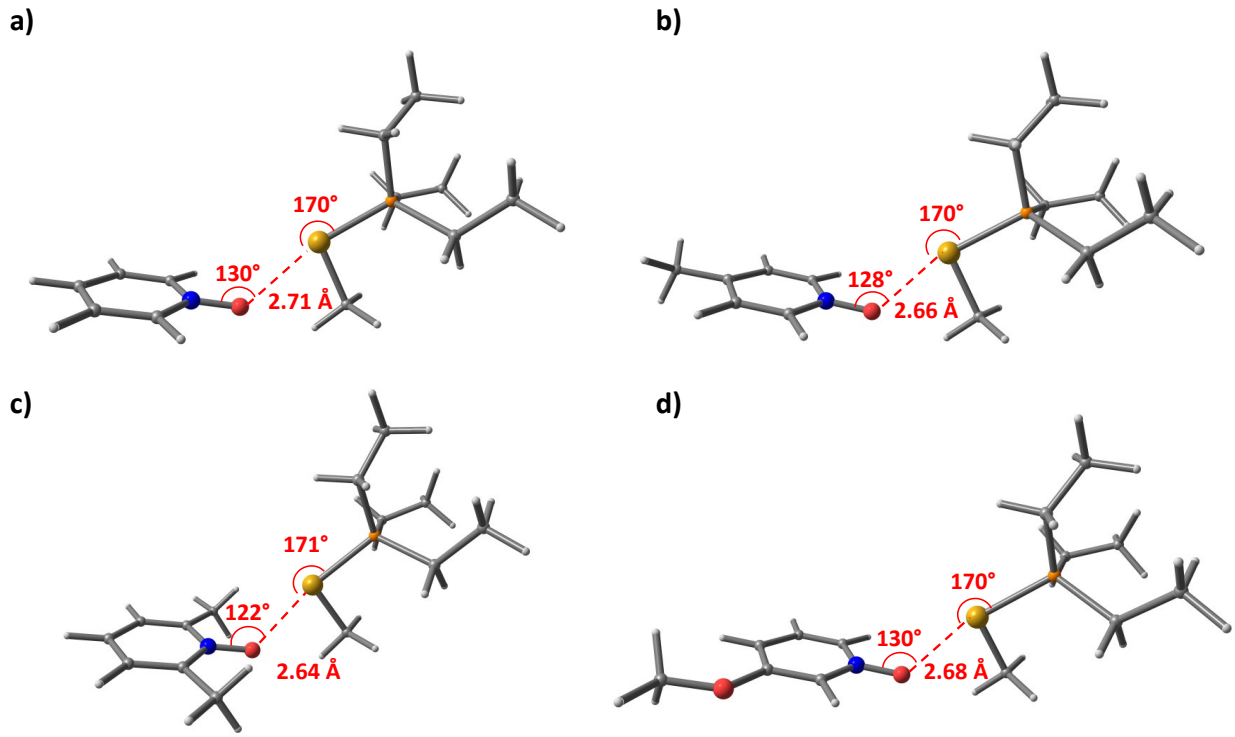


Fig. 2. Calculated structures of the chalcogen-bonded complexes of $[Et_3PSeMe]^+$ with pyridine N-oxide derivatives: (a) pyridine N-oxide, (b) 4-methylpyridine N-oxide, (c) 2,6-dimethylpyridine N-oxide, and (d) 3-methoxypyridine N-oxide.

Thus, phosphine selenides demonstrate the ability of selenium to perform opposite donor–acceptor functions in halogen and chalcogen bonding. Alkylation of the selenium atom provides a means of tuning its acceptor properties and enhancing the ability of phosphine selenides to form chalcogen bonds.

This work was supported by the Russian Science Foundation (grant № 26-23-20099), and the St. Petersburg Science Foundation (grant № 26-23-20099)

References

[1] Wang, H.; Bisoyi, H.K.; Urbas, A.M.; Bunning, T.J.; Li, Q. *Chem. – Eur. J.*, **2019**, 25, 1369–1378.
[2] Ho, P.C.; Wang, J.Z.; Meloni, F.; Vargas-Baca, I. *Coord. Chem. Rev.*, **2020**, 422, 213464.
[3] Haque, A.; Wong, W.-Y.; Alenezi, K.M.; Khan, M.S.; Raithby, P.R. *Chem. Soc. Rev.*, **2023**, 52, 454–472.

Sorption of Congo red by chitosan composites with Mg/Fe and Mg/Al layered double hydroxides synthesized under ultrasonic treatment

Golubev R.A., Semenkova D.I., Nguyen L.V., Kirichuk A.A., Kritchenkov A.S.

Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: golubev-ra@rudn.ru

Synthetic dyes are among the most persistent and toxic pollutants of industrial wastewaters, and their removal remains an important problem of environmental chemistry. Congo Red (CR) is a widely used anionic azo dye that is difficult to biodegrade and is therefore often employed as a model adsorbate. Layered double hydroxides (LDH) possess a high anion-exchange capacity and a large surface area, while chitosan (CS) provides amino and hydroxyl groups capable of electrostatic and hydrogen-bonding interaction with dye anions. Combination of LDH with chitosan gives a composite whose sorption properties can be tuned by the conditions of synthesis, and such CS-LDH composites have proved to be efficient sorbents of Congo Red [1, 2]. In the present work the effect of the ultrasonic treatment (frequency) used in the synthesis on the sorption of CR by the CS-LDH composites was studied.

The sorbents (CS-LDH composites) were prepared on the basis of Mg/Fe and Mg/Al layered double hydroxides with different molecular mass of the chitosan matrix (250, 890 and 1500 kDa). Two methods were used to obtain the LDH phase: traditional co-precipitation and ultrasound-assisted synthesis at 28 kHz, 40 kHz and 1.7 MHz.

The CR concentration in solution was determined photometrically at 505 nm in 1 cm cells. A calibration plot was constructed from standard solutions containing 70-700 mg/L of the dye; it is linear over the whole range studied ($R^2 > 0.999$).

Sorption experiments were carried out in the batch mode at room temperature. A portion of the dye solution (9.00 g, C = 0.700 g/L) was diluted with water to 10.00 g, and ca. 0.030 g of the sorbent was added. The suspensions were kept in the dark for 24 h; then an aliquot (1.00 g) of the equilibrium solution was diluted to 25.00 g and analyzed photometrically. The equilibrium sorption capacity qe (mg/g) and the degree of extraction R (%) were calculated as

$$q_e = (C_0 - C_e)*V/m;$$
$$R = (C_0 - C_e)/C_0*100\%,$$

where C0 and Ce are the initial and equilibrium dye concentrations (mg/L), V is the volume of the solution (L) and m is the mass of the sorbent (g).

The initial CR concentration in the working solutions was 577-638 mg/L (mean 612 mg/L). The equilibrium sorption capacities found for both series of composites are summarized in the figure 1 below.

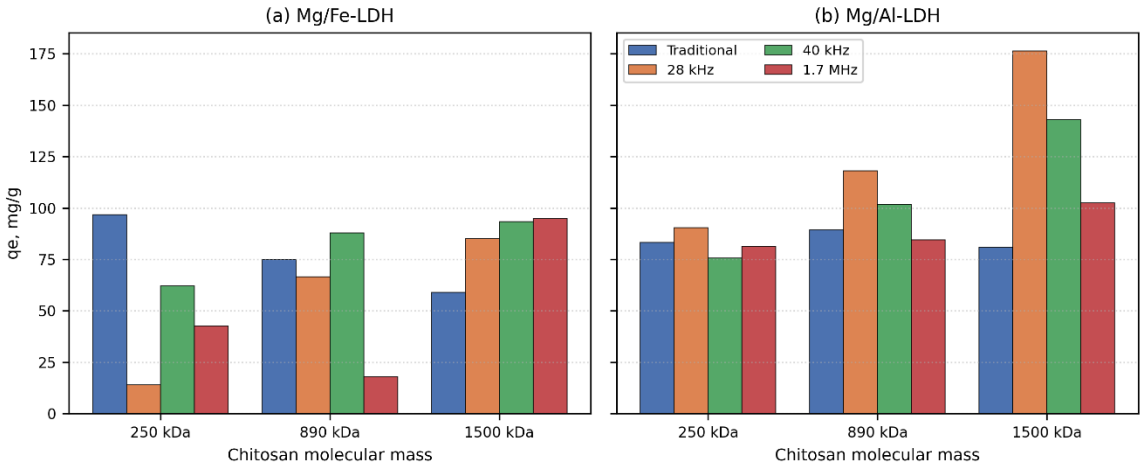


Figure 1. Equilibrium sorption capacity (qe) of the CS-LDH composites towards Congo Red as a function of the chitosan molecular mass and the method of synthesis: (a) Mg/Fe-LDH; (b) Mg/Al-LDH.

For the Mg/Fe series the sorption capacity lies in the range 14-97 mg/g and depends non-monotonically on the synthesis conditions: the best results were obtained for the Mg/Fe-250 sample prepared by the traditional method and for Mg/Fe-1500 obtained under ultrasonic treatment. The lowest capacities were found for the samples treated at 28 kHz (250 kDa) and 1.7 MHz (890 kDa).

The Mg/Al composites sorb CR noticeably better. The maximum value, q_e = 176.4 mg/g (R = 85.8%), was achieved for the Mg/Al-1500 sample synthesized at 28 kHz; this is about 1.8 times higher than for the corresponding Mg/Fe composite. For the Mg/Al series the sorption capacity also increases with increasing molecular mass of chitosan, the sequence 250 < 890 < 1500 kDa being observed for all methods of synthesis.

Thus, ultrasonic treatment of the reaction mixture in the course of the synthesis is an efficient tool for controlling the sorption properties of CS-LDH composites, and the nature of the trivalent cation (Al vs. Fe) is the key factor determining the affinity of the composite to the anionic dye.

This work was supported by Belarusian Republican Foundation for Fundamental Research (grant № Т25УЗБ-121)

References

[1] Fei, C.; Chen, C.; Zhang, H.; Liu, A.; Ju, D.; Yang, X.; Wang, F.; Xia, M.; Huang, P. The effective removal of Congo red dye via chitosan-layered double hydroxide composite and the deep insight into mechanism. J. Ind. Eng. Chem. 2024, 135, 143-153.

[2] Mohadi, R.; Siregar, P.M.S.B.N.; Palapa, N.R.; Taher, T.; Lesbani, A. Layered Double Hydroxide/Chitosan Composite (Mg-Al/CT) as a Selective Adsorbent in Congo Red Adsorption from Aqueous Solution. Ecol. Eng. Environ. Technol. 2022, 23 (2), 144-152.

Regularities of changes in the crystal structures of $ALnCuSe_3$ (A = Sr, Eu) compounds

Habibullayev N.N., Andreev O.V.

Tyumen State University, 625003, Volodarskogo St., 6, Tyumen, Russia
e-mail: n.n.khabibullaev@utmn.ru

Quaternary selenides $ALnCuSe_3$ (A = Sr, Eu; Ln = lanthanide) are promising semiconductor and thermoelectric materials. In this work, using our experimental data obtained by X-ray powder diffraction (XRPD) with Rietveld refinement, we present the regularities of changes in structural types and unit cell parameters in the $EuLnCuSe_3$ and $SrLnCuSe_3$ series. In particular, the figure shows the dependences of the unit cell parameters (a, b, c) and the unit cell volume V on the lanthanide ionic radius (rLn^{3+}) for the $SrLnCuSe_3$ series (Fig. a, b). Similar dependences are observed for $EuLnCuSe_3$. $ALnCuSe_3$ compounds crystallize in the orthorhombic system, space group *Pnma* for Ln = La, Ce, Pr, Nd, Sm, Gd−Ho, and space group *Cmcm* for Ln = Er, Tm, Yb, Lu. The crystal structures belong to three structural types: Ba_2MnS_3 (Ln = La, Ce), Eu_2CuS_3 (Ln = Pr, Nd, Sm, Gd−Ho), and $KCuZrS_3$ (Ln = Er−Lu) [1, 2].

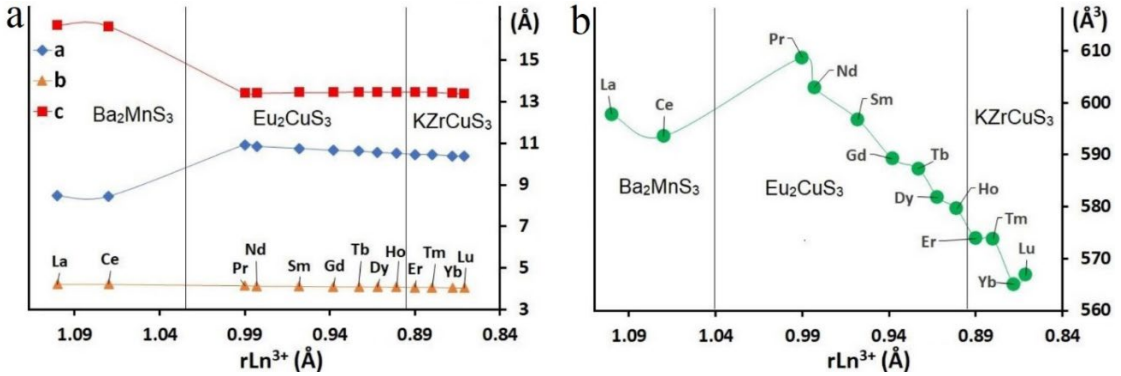


Fig. − a) Regularity of changes in the parameters (a, b, c) and b) unit cell volumes as a function of the lanthanide ionic radius (rLn^{3+}) in the $SrLnCuSe_3$ series.

The unit cell volume of $ALnCuSe_3$ compounds decreases in a correlated manner with the change in the ionic radius of trivalent rare-earth elements due to 4f contraction. Overall, the tetrad effect is manifested in the changes of the unit cell parameters and volumes. The first change in structural type occurs between cerium and praseodymium, which is close to the neodymium–samarium instability zone. The second change in structural type occurs between holmium and erbium, which almost coincides with the crystal-chemical instability zone for rare-earth compounds of the yttrium subgroup. The obtained regularities demonstrate the capabilities of powder diffraction for establishing structural types and subtle effects in quaternary selenide series and can be used for the targeted search for new materials with desired properties.

This work was carried out within the framework of state assignment № FEWZ-2024-0052

References

[1] Strobel, S.; Schleid, T. J. Alloys Compd., **2006**, 418, 80–85.
[2] Habibullayev, N.N.; Burkov, A.T.; Novikov, S.V.; Yurev, I.O.; Aleksandrovskiy, A.S.; Zakharova, A.D.; Shulaev, N.A.; Denisenko, Y.G.; Andreev, O.V. Eur. Phys. J. Plus, **2024**, 139, 412.

Biologically Significant Fragments of O-Alkylsulfonyl-β-(benzimidazol-1-yl)-propioamidoximes as a Pathway to the Antimicrobial, Antifungal, Antidiabetic Drugs

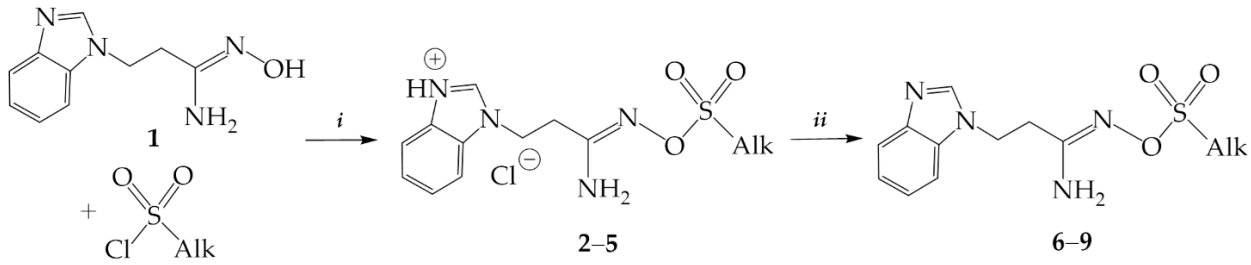
Kayukova L.A.[1], Vologzhanina A.V.[2], Seidakhmetova R.B.[3], Yerlanuly A.[1], Sartoyeva A.B.[1]

[1] JSC A.B. Bekturov Institute of Chemical Sciences, 106 Shokan Ualikhanov Str., 050010, Almaty, Kazakhstan; [2] A.N. Nesmeyanov Institute of Organoelement Compounds, 119334, Moscow, Russia; [3] NAO Medical University of Karaganda, 100012, Karaganda Medical University, Karaganda, Kazakhstan

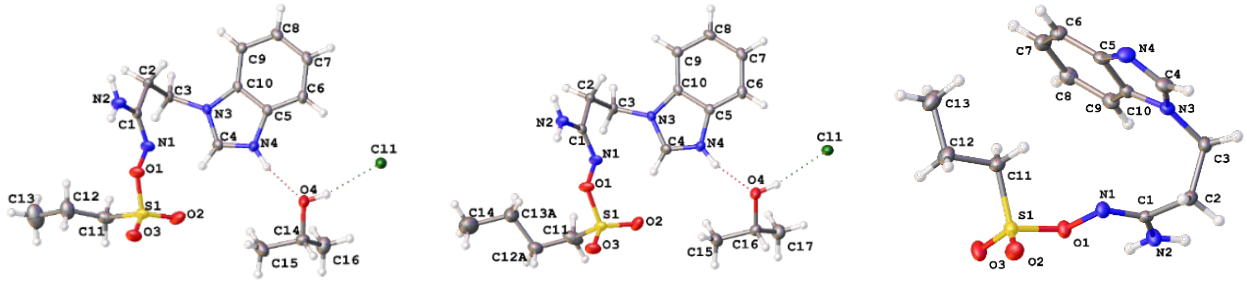
e-mail: lkayukova@mail.ru

The integration of benzimidazole, amidoxime, and sulfonyl pharmacophores into a single molecular framework embodies the hybridization strategy in medicinal chemistry for discovering promising bioactive compounds.

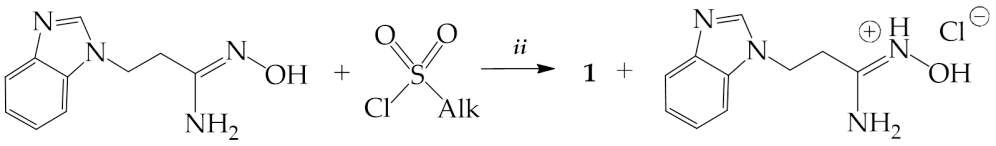
This work aimed to synthesize novel O-alkylsulfonyl-β-(benzimidazol-1-yl)propioamidoximes and evaluate their *in vitro* antimicrobial, antifungal, and antidiabetic activities to identify potential therapeutic agents. The target O-alkylsulfonylamidoximes were synthesized via the reaction of β-(benzimidazol-1-yl)propioamidoxime with alkylsulfonyl chlorides in a water-acetone mixture. The structures of the synthesized compounds were confirmed by physicochemical and spectral methods (FT-IR, NMR, X-ray diffraction).



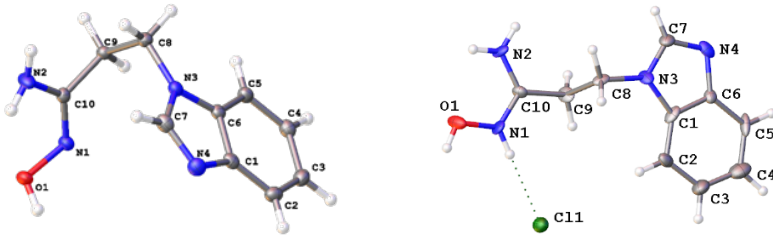
2–5: Alk = Me (**2**), *n*-Pr (**3**), *i*-Pr (**4**), *n*-Bu (**5**); **6–9:** Alk = Me (**6**), *n*-Pr (**7**), *i*-Pr (**8**), *n*-Bu (**9**);
***i*:** H_2O : acetone (1:6), r.t.; ***ii*:** H_2O, K_2CO_3



Crucially, the substrate's internal basicity precluded the need for an external base, which was found to produce a mixture of the substrate (**1**) and its hydrochloride (**10**) [1].



Alk = Me, *n*-Pr, *i*-Pr, *n*-Bu; ***ii***: $CHCl_3$, Bu_3N, r.t.



A plausible mechanism for the formation of the observed products (**1**, **10**) during the attempted alkylsulfochlorination of amidoxime **1** in the presence of Bu_3N involves the disproportionation of alkylsulfonyl chlorides. In this case, reaction products (1, 10) are formed by removing of alkylsulfonyl chlorides from the reaction with β-(benzimidazol-1-yl)propioamidoxime to form sulfene intermediates [2] and alkylsulfonyltributylammonium chlorides.

Biological screening of the resulting O-alkylsulfonyl derivatives (**2**–**9**) for antimicrobial, antifungal, and antidiabetic activity found effective samples of amidoximes with antimicrobial and antifungal activities that were near or exceeded the activity of the reference drugs gentamicin and nystatin; in addition, two samples with antidiabetic activity higher than acarbose were found. This establishes hybrid O-alkylsulfonyl-β-(benzimidazol-1-yl)propioamidoximes as a highly promising scaffold for the development of novel antimicrobial, antifungal, and antidiabetic drugs [3].

This study has been supported by the Committee of Science of the Ministry of Science &High Education of the Republic of Kazakhstan (Grant number BR27101179)

References

[1] Kayukova, L.A.; Yerlanuly, A.; Duisenali, A.M.; Vologzhanina, A.V.; Belyankova, Y.O. Chem. J. Kaz., 2024, 2, 36–41. (In Russ.).

[2] King, J.F.; King, J.A.J.; Harding, D.R.K.; Harding, D.J. Can. J. Chem., 1976, 54, 2652-2657.

[3] Kayukova, L.; Vologzhanina, A.; Dubasova, E.; Seidakhmetova, R.; Yerlanuly, A.; Sartoyeva, A.; Malmakova, A. Int. J. Mol. Sci., 2026, 27, 6224.

Aspects of the biochemical engineering of inulinase preparations from Aspergillus awamori and Kluyveromyces marxianus

Kozhokina O.M., Kupriyanovskaya D.E.

Voronezh State Medical University N.N. Burdenko, Russia,
394036, Voronezh, Studencheskaya str.10
e-mail: kde-35@mail.ru

In today's context, nutrition science is becoming increasingly important, contributing to the growing popularity of fructose as a sugar substitute. The key advantages of this product are that it can be consumed by people with diabetes mellitus and that it has a reduced cariogenic effect. In addition to its dietary properties, fructose is widely used in the food industry: its ability to prevent crystallisation in mixtures with glucose helps improve the texture of ice cream and confectionery products [1].

During the study, highly active immobilised inulinase preparations were synthesised from strains of Kluyveromyces marxianus and Aspergillus awamori. Their catalytic properties were comparatively analysed under batch and continuous fermentation conditions using inulin.

The enzyme was immobilised on a pre-treated support by covalent binding and adsorption, in accordance with standard protocols [2]. The concentration of free protein was determined using the Lowry method, while its modified version was applied to the immobilised inulinase. Catalytic activity was assessed spectrophotometrically using Seliwanoff's reaction to quantify fructose [1].

The study identified two biocatalysts as the most effective: Kluyveromyces marxianus inulinase immobilised on the VION KN-1 ion-exchange fibre by adsorption, and Aspergillus awamori inulinase immobilised on AV-26 resin using a glutaraldehyde cross-linking method to bind the enzyme to the support [3].

It was established that the immobilised preparations retained their initial levels of catalytic activity and protein concentration for two years when stored dry at room temperature.

A comparative analysis was carried out of the stability of the two enzyme preparations in batch and continuous-flow reactors. The data obtained demonstrated the high stability of the immobilised biocatalysts: repeated use did not result in any significant reduction in their catalytic activity, which remained at its initial level.

It is well established that continuous-flow reactors are preferable for industrial applications, as they enable the technological process to be automated. We therefore investigated the characteristics of the inulin hydrolysis reaction in a column-type reactor [4].

It was found that, in order to achieve maximum efficiency of inulin hydrolysis, the optimal hydrodynamic parameters of the process depend on the biocatalytic system used. For inulinase from Kluyveromyces marxianus immobilised on the fibrous ion-exchange material VION KN-1, the optimal upward feed rate was 3 ml/min, whereas for the enzyme from Aspergillus awamori, attached to the AB-26 carrier by glutaraldehyde cross-linking, the corresponding rate was 0.25 ml/min.

The study resulted in the production of immobilised inulinase preparations of different origins, characterised by substantial activity and retention of their functional properties during prolonged storage and repeated use [5].

References

[1] Kovaleva, T.A.; Holyavka, M.G. *Bulletin of Voronezh State University. Series: Chemistry. Biology. Pharmacy*, **2008,** 2, 102–105.

[2] Kovaleva, T.A.; Holyavka, M.G.; Artyukhov, V.G.; Kayumov, A.R. *Problems of Biological, Medical and Pharmaceutical Chemistry,* **2012,** 11, 39–42.

[3] Holyavka, M.G.; Evstigneev, M.P.; Artyukhov, V.G.; Savin, V.V. *Journal of Molecular Catalysis B: Enzymatic*, **2016**, 129, 1–5.

[4] Rawat, H.K.; Soni, H.; Kango, N.; Kumar, C.G. *Biocatalysis and Agricultural Biotechnology*, **2017**, 9, 134–140.

[5] Robescu, M.S.; Bavaro, T. A, *Molecules*, **2025,** 30 (4), 939.

Biochemical engineering aspects of the regulation of amylolytic enzyme activity

Kozhokina O.M., Goryagina V.M.

Voronezh State Medical University N.N. Burdenko, Russia,
394036, Voronezh, Studencheskaya str.10
e-mail: goryagina97@bk.ru

In recent years, interest in the study of amylolytic enzymes, which are widely distributed in natural ecosystems, has increased. The importance of studying amylases is due to their high demand in modern medicine. Inhibitors of amylolytic enzymes serve as a key mechanism of cellular regulation, providing universal and highly effective control of metabolic processes. The study of substances that suppress or enhance enzyme activity is important both for practical applications and for theoretical research. Investigating this issue makes it possible to elucidate the mechanisms of enzyme function and determine the structure of their active centers and the surrounding microenvironment. This has significant practical value and contributes to the development of synthetic catalysts [1].

The study of enzyme inhibitors and activators is important both for practical applications and for theoretical research. Analysis of these aspects makes it possible to elucidate the mechanisms of enzyme function, as well as to determine the structure of their active centers and the characteristics of their microenvironment [2].

To identify the functional groups of an enzyme's active site responsible for catalysis, the enzyme is exposed to a chemical reagent that selectively interacts with the group in question, forming a stable compound. This inhibitory reaction must be specific and reduce the enzyme's catalytic activity without denaturing the protein molecule.

Two types of inhibitors are used in medical practice: reversible and irreversible. These substances are continuously being studied and refined. Irreversible inhibitors alter the chemical structure of the region of the enzyme responsible for its activity. Reversible inhibition can occur through various mechanisms: competitive, noncompetitive, uncompetitive, and mixed [3].

A competitive inhibitor competes with the substrate for the enzyme's active site and has a chemical structure similar to that of the substrate, but it does not undergo catalytic conversion.

The molecular structure of a noncompetitive inhibitor differs substantially from that of the substrate. Such inhibitors can bind reversibly both to the native enzyme and to the enzyme–substrate complex.

In uncompetitive inhibition, the inhibitor molecule does not bind to the free enzyme; instead, it interacts exclusively with the enzyme–substrate complex.

In mixed inhibition, the inhibitor molecule interacts with both the catalytic site and the enzyme's binding region, exerting a multifaceted effect on its activity.

The reactive site of the inhibitor interacts with the enzyme's active site in a manner analogous to that of the substrate. As a result, van der Waals forces, hydrophobic interactions, and ionic bonds form between them, leading to the formation of a stable complex.

Amylase activity is reduced by manganese, copper, and zinc ions, as well as by chemical compounds such as dinitrofluorobenzene, N-bromosuccinimide, trinitrobenzene, and sulfonic acid.

Most proteinaceous α-amylase inhibitors have been isolated from plants belonging to the grass, legume, and nightshade families. Protein inhibitors are characterized by bifunctionality because they contain two independent active sites. In plants, in addition to serine protease inhibitors, inhibitors of proteases and amylases belonging to other classes have also been identified. Modern biochemistry places considerable emphasis on studying the molecular basis of interactions between enzymes and protein inhibitors. It has been established that the mechanism by which an inhibitor binds to an enzyme's active site is structurally and functionally similar to the interaction between an enzyme and its substrate in limited proteolysis reactions.

The study of this issue helps elucidate the mechanisms underlying enzyme function and determine the structure of their active sites and the surrounding microenvironment. This has significant practical value and contributes to the development of synthetic catalysts.

References

[1] Kovaleva, T.A.; Makarova, E.L. *Medico-Biological and Pedagogical Foundations of Adaptation, Sports Activity and a Healthy Lifestyle,* **2012**, 258–261.

[2] Kovaleva, T.A.; Makarova, E.L.; Gladneva, A.V. *Sorption and Chromatographic Processes* **2009**, 9 (4), 537–544.

[3] Makarova, E.L. *Notes of a Scientist,* **2016**, 9 (15), 91–93.

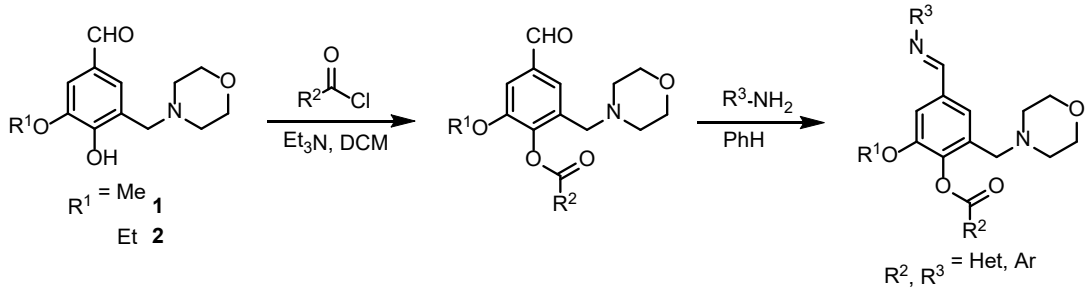
Vanillin and ethylvanillin based poly-N-heterocyclic derivatives: synthesis, structure and antimicrobial activity

Margun E.N., Adamovich D.S., Duboiskaya A.V., Berezyuk M.D., Dikusar E.A.

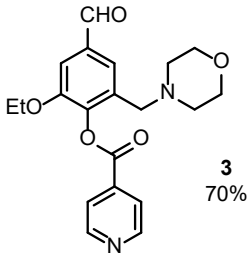
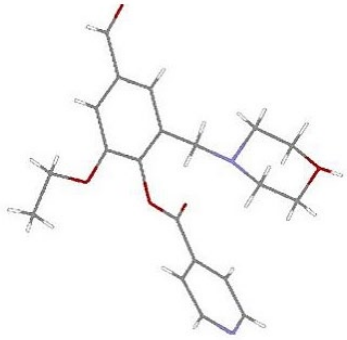
The Institute of Physical Organic Chemistry, 220072, Belarus, Minsk, Surganova str. 13
e-mail: margunen0555@gmail.com

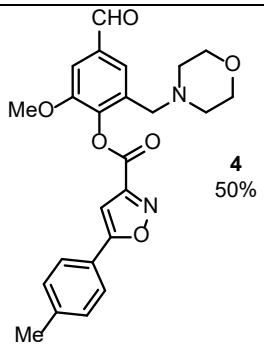
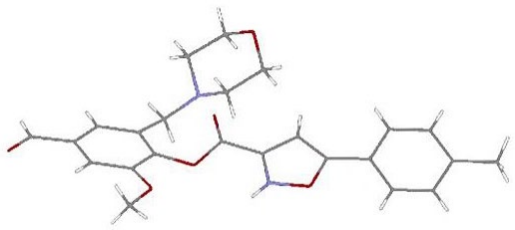
An important task in pharmaceutical chemistry is the search for new drugs with improved properties. Heterocyclic compounds are of great pharmaceutical importance, for example, they are often found in drug-like natural compounds. Nitrogen heterocycles are key structural elements of many biologically active molecules, because they act as pharmacophores, affecting the drug's spectrum and efficacy, pharmacokinetics, toxicology, and metabolic stability [1].

In this work new biologically active polyheterocyclic compounds containing pyridine and 1,2-azoles were synthesized.



Vanillin and ethylvanillin derivatives **1** and **2** were obtained using Mannich reaction. Phenolic Mannich bases were then acylated with isonicotinic, 4,5-dichloroisothiazole- and 5-arylisoxazole-3-carboxylic acid chlorides to form esters (e.g., substances **3** and **4**) in good to high yields. The structures of compounds **3** and **4** were confirmed by X-ray diffraction analysis data for monocrystals grown from hexane. These esters were used to synthesize Schiff bases by condensation with various amines. For example, azomethine derivatives of 4-aminoantipyrine were obtained in high yields.

Name	Structure	Structure according to XRD analysis
2-Ethoxy-4-formyl-6-(morpholinomethyl)phenyl isonicotinate	 **3** 70%	

4-Formyl-2-methoxy-6-(morpholinomethyl)phenyl 5-(*p*-tolyl)isoxazole-3-carboxylate	 **4** 50%	

The antimicrobial activity of the synthesized esters was examined. The test samples were shown to exhibit antimicrobial activity comparable to a reference antibiotic ceftriaxone against *Staphylococcus aureus ATCC 6538* and *Escherichia coli ATCC 25922*. Their MICs ranged from 6.3 to 12.5 μg/ml.

A series of vanillin and ethylvanillin derivatives modified with morpholine, pyridine, and azoles (isothiazole, isoxazole, and pyrazole) were obtained. Hydroxybenzaldehydes proved to be a convenient scaffold for constructing bioactive molecules. The structures of the synthesized compounds are enriched with N-heterocycles, making them promising candidates for bioassays. Antimicrobial activity testing confirms the feasibility of expanding the range of derivatives and studying the biological activity of these compounds.

This work was supported by the Belarusian Foundation for Basic Research (grant № X25MP-011)

References

[1] Jadala, Ch.; Mishra, Sh.; Potuganti, G.R.; Cardoza, S.; Velma, G.R. *RSC Advances*, **2026**, 16, 21967.

Effect of Mg Molar Ratio and Aging Method on Congo Red Adsorption by Mg–Fe Layered Double Hydroxides

Nguyen L.V., Golubev R.A., Semenkova D.I.

Department of Human Ecology and Bioelementology & Department of General and Inorganic Chemistry, Peoples' Friendship University of Russia named after Patrice Lumumba, 6 Miklukho-Maklaya St, Moscow 117198, Russia
e-mail: linhno2109@gmail.com

Abstract: Mg–Fe layered double hydroxides (LDHs) with Mg molar ratios of 1:1, 2:1, and 3:1 were synthesized by co-precipitation and aged either thermally (70 °C, 24 h) or ultrasonically (30 W, 28 ± 2.1 kHz, 10 min). Congo red adsorption was investigated at initial concentrations of 70–630 mg/L using an adsorbent dose of 1 g/L. The 3:1 LDHs exhibited the highest adsorption capacities, reaching 176 mg/g after ultrasonic aging and 171 mg/g after thermal aging. Their adsorption isotherms showed a sigmoidal shape and were described by the Sips model ($n_S \approx 2$). Ultrasonic aging resulted in a higher adsorption capacity for the 1:1 LDH (120 vs. 100 mg/g), whereas thermal aging provided higher uptake for the 2:1 LDH at elevated Congo red concentrations (147 vs. 136 mg/g). Ultrasonic treatment reduced the aging time by approximately 144-fold while providing comparable or improved adsorption performance for the 1:1 and 3:1 compositions. Overall, the effect of aging method on Congo red adsorption was dependent on the Mg molar ratio and initial dye concentration.

Keywords: layered double hydroxides, Mg–Fe LDH, Mg molar ratio, ultrasonic aging, thermal aging, Congo red, adsorption isotherm

The ability of MgAl layered double hydroxides to adsorb sodium salicylate

Semenkova D.I., Golubev R.A., Nguyen L.V., Egorov A.R., Kritchenkov A.S.

Peoples' Friendship University of Russia, 117198, Moscow, Miklukho-Maklaya str. 6
e-mail:darya.semenkova02@mail.ru

Layered double hydroxides (LDHs) are a class of anionic clays with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, and A^{n-} is an interlayer anion. Due to their high anion-exchange capacity and tunable interlayer chemistry, LDHs are promising sorbents for the removal of organic pollutants from aqueous solutions [1]. Sodium salicylate a common pharmaceutical and industrial compound, serves as a model anionic organic pollutant. Ultrasound-assisted synthesis has been reported to modify the morphology and textural properties of LDHs, potentially enhancing their sorption performance [2]. In this work, we investigated the effect of ultrasound frequency (28 and 40 kHz) on the sorption capacity of MgAl-LDHs toward sodium salicylate.

MgAl-LDH samples were synthesized by three methods: (i) conventional coprecipitation (standard LDH), (ii) ultrasound-assisted coprecipitation at 28 kHz (US-28), and (iii) ultrasound-assisted coprecipitation at 40 kHz (US-40). Ultrasonic treatment was carried out in two ways: 1 - first, add alkali to the salt solution, then carry out ultrasonic treatment for 15 minutes; 2 - add alkali to the salt solution and simultaneously carry out ultrasonic treatment. The samples were characterized using a suite of physicochemical techniques, including X-ray diffraction (XRD), infrared (IR) spectroscopy, and thermogravimetric analysis coupled with differential scanning calorimetry (TGA–DSC). The XRD patterns showed the characteristic reflections of layered double hydroxides, indicating that the synthesized materials exhibit the typical LDH structure.

Sorption experiments were carried out under static conditions at room temperature. In each experiment, 0.050 g of LDH was placed into a solution of NaSal (total mass 10 g) with initial concentrations (C_0) ranging from 200 to 20 000 mg/L. After 24 h of contact without agitation, the supernatant was analyzed by photometry at λ = 530 nm using the colored complex of salicylate with Fe^{3+} ions. The equilibrium concentration (C_e) was determined from a calibration curve, and the sorption capacity (q_e, mg/g) was calculated from the mass balance.

For the standard LDH, the sorption capacity increased with the initial NaSal concentration over the range of C_0 = 200–10 000 mg/L, reaching a maximum q_e value of approximately 182 mg/g. To evaluate the effect of ultrasound treatment, paired sorption experiments were performed, in which US-treated and standard LDH samples were exposed to identical NaSal solutions, and the difference in equilibrium absorbance (ΔA) was used to calculate the additional sorption capacity. At C_0 = 10 000 mg/L, US-28 samples exhibited an average additional q_e of approximately 66 mg/g, while US-40 samples showed a comparable increase of roughly 67 mg/g relative to the standard LDH. Direct sorption isotherms measured for the US-28 samples over an extended concentration range (up to 40 000 mg/L) confirmed an absolute sorption capacity of approximately 199 mg/g at C_0 = 10 000 mg/L, which exceeds the value obtained for the standard LDH under the same conditions. At higher initial concentrations the sorption efficiency declined, suggesting saturation of the available exchange sites.

The results indicate that ultrasound-assisted synthesis at both 28 and 40 kHz enhances the sorption performance of MgAl-LDHs toward sodium salicylate, particularly at elevated initial concentrations. The improvement can be attributed to changes in particle size distribution,

crystallinity, and specific surface area induced by acoustic cavitation during synthesis [2, 3]. Both ultrasound frequencies provided a comparable enhancement, suggesting that the cavitation effect within this frequency range is not strongly frequency-dependent under the conditions studied.

The work was supported by RSF 25-73-00229

References

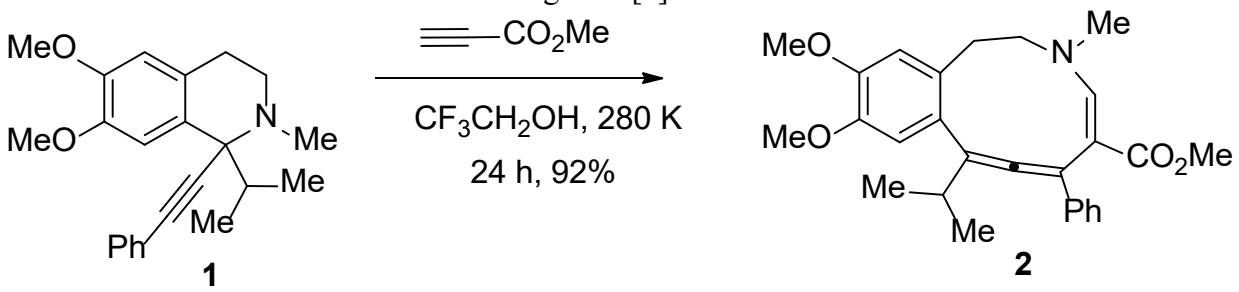
[1] Goh, K.-H.; Lim, T.-T.; Dong, Z. Water Res., 2008, 42, 1343.
[2] Benito, P.; Labajos, F.M.; Rives, V. J. Solid State Chem., 2006, 179, 3784.
[3] Xu, Z.P.; Stevenson, G.; Lu, C.-Q.; Lu, G.Q. J. Phys. Chem. B, 2006, 110, 16923.

Crystal structure and features of Methyl 8–isopropyl–10,11–dimethoxy–3–methyl–6–phenyl–3–azabenzo[*d*]cyclodeca–4,6,7–triene–5–carboxylate

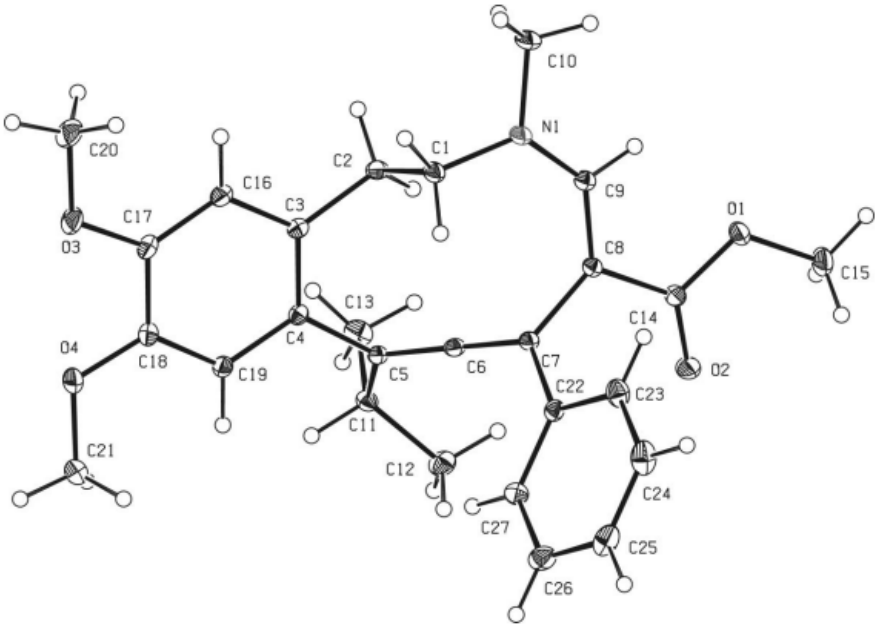
Kharchenko D.S., Zhukov G.A., Rybakov V.B., Titov A.A., Varlamov A.V.

Peoples' Friendship University of Russia (RUDN University), 117198, Moscow, Miklukho-Maklaya str. 6
e-mail: dimaharcenko513@gmail.com

The domino reaction of 1-isopropyl-6,7-dimethoxy-2-methyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline **1** with methyl propiolate in CF_3CH_2OH at 280 K leads to formation of a title compound $C_{27}H_{31}NO_4$ **2**. The azabenzo[*d*]cyclodecatriene **2** under consideration is the first example with a branched substituent on the allene fragment [1].



In the crystal of title compound $C_{27}H_{31}NO_4$ **2** molecules are bound to form a three–dimensional network by means of weak non–classical C—H···O intermolecular hydrogen bonds. These interactions (H···O) lie in interval 2.21–2.96 Å. The shortest contact is observed for C9—H9···O1 [H···O = 2.21 Å, C···O = 2.675(1) Å, C—H···O = 109°]. Remaining interactions involve the methoxy oxygen atoms O3 and O4, the carbonyl oxygen O2 and the ester oxygen O1, with H···O distances of 2.66 — 2.96 Å and C—H···O angles of 122 — 145°.



The structure of the titled compound with names of non–hydrogen atoms is shown above. According to X–ray diffraction data, the bond angle –C5═C6═C7– = 175.64 (9)°. Two methoxy–

groups: —O4—C21 and —O3—C20 lie in the plane of benzene C3/C4/C16/C17/C18/C19 ring with deviations 0.0310 (13) Å for O3 and 0.0184 (13) Å for O4. The corresponding C atoms of methyl groups (C20 and C21) have these deviations 0.0476 (19) Å and 0.2146 (17) Å respectively, so that the methyl group C20 lies within the aromatic plane, as the methyl group C21 is noticeably displaced from it. The molecule as a whole adopts the conformation of a ten-membered azabenzo[]dcyclodecatriene, and the crystal packing is further stabilized by the C—H···O.

References

[1] Voskressensky, L.G.; Titov, A.A.; Dzhankaziev, M.S.; Borisova, T.N.; Kobzev, M.S.; Dorovatovskii, P.V.; Khrustalev, V.N.; Aksenov, A.V.; Varlamov, A.V. New J. Chem., **2017**, 41, 1902–1904.

Author Index

A

Adamovich D.S. 92
Aksenov S.M. 63
Alirzayev A.T. 58
Andreev O.V. 85
Antipin I.S. 36, 48, 70
Antipov E.V. 32
Antonov A.S. 81
Arbanas L.A. 76

B

Bachinskiy A.V. 35
Bakirov A.V. 41
Berezyuk M.D. 92
Bilyachenko A.N. 35
Boldyreva E.V. 51
Borshchevskiy V.I. 34
Bui H.T. 54
Bulanov E.N. 42
Bulavchenko O.A. 50
Bumagin N.A. 15

C

Charkin D.O. 63
Chernikova E.Yu. 62
Chernyshev V.V. 33

D

Dikusar E.A. 92
Duboiskaya A.V. 92

E

Egorov A.R. 95

F

Fatullayeva P.A. 58
Fedin V.P. 31
Fedorova O.A. 62
Filippov O.A. 47
Frontera A. 57, 69

G

Galiakhmetov S.A. 81
Gaydamaka A.A. 51
Gerasimchuk N. 30
Gerasimova D.P. 46
Golubev R.A. 83, 94, 95
Goryagina V.M. 90
Gosteva A.N. 63
Grebenyuk D.I. 74
Grigoriev M.S. 57
Gugkaeva Z.T. 40

H

Habibullayev N.N. 85

I

Iova A.A. 48, 70
Islamov D.R. 46
Ismayilov R.H. 24
Ismayilova S.Z. 24
Ivanova A.G. 51

K

Kaurova I.A. 76
Kayukova L.A. 86
Kharchenko D.S. 97
Khrustalev V.N. 58, 67, 69, 76
Kinzhalov M.A. 78
Kireev V.E. 63
Kirichuk A.A. 83
Kiryak D.V. 63
Klochkova E.A. 46
Kolesnik I.A. 15, 57
Kompanchenko A.A. 63
Kovalchukova O.V. 45
Kozhokina O.M. 88, 90
Kritchenkov A.S. 39, 83, 95
Kupriyanovskaya D.E. 88
Kuz'micheva G.M. 65, 71, 76
Kuznetsov A.N. 17

L

Larionov A.S. 67
Larionov V.A. 40
Lazarenko V.A. 71, 76
Lider E.V. 15
Litvinov I.A. 13
Liu Y. 21
Lyssenko K.A. 17, 74

M
Maleev V.I. 40
Manomenova V.L. 76
Margun E.N. 92
Markova E.B. 71
Maslova V.S. 67, 69
Mohan B.B. 28
Molokeev M.S. 80
Mulloyarova V.V. 81
Mushtakov A.G. 65, 71
N
Nesterenko S.N. 17
Nguyen L.V. 83, 94, 95
Nikitina E.V. 57
O
Olbrykh A.P. 47
Omiyale O.C. 60
Ovsyannikov A.S. 48, 70
P
Panina M.V. 53
Peng S.M. 24
Petrukhina M.A. 29
Phuong D.T. 54
Polevik A.Yu. 17
Polianskaia Z.A. 67
Polyanskaya D.K. 67
Polyanskaya N.A. 45
Pombeiro A.J.L. 27
Potkin V.I. 15, 57
R
Rashchenko S.V. 51
Rubanik V.V. 54
Rubanik V.V. jr. 54
Rybakov V.B. 97
S
Sabitova I.A. 74
Sartoyeva A.B. 86
Savitsky V.O. 54
Seidakhmetova R.B. 86
Semenkova D.I. 83, 94, 95
Shelukho E.R. 67
Shevelkov A.V. 14
Shitov D.A. 81
Shubina E.S. 47
Shutilov I.D. 48
Slovokhotov Yu.L. 43
Smirnova E.S. 51
Smol'yakov A.F. 47
Solovieva S.E. 48, 70
Sosunov E.A. 53, 73
Stoletova N.V. 40
Sulimova O.V. 62
Sun D. 23
Svetogorov R.D. 65, 71
T
Takeda N. 21
Titov A.A. 47, 97
Tsymbarenko D.M. 74
Tursunov I.U. 45
U
Unno M. 21
Usachev K.S. 46
Ustimova M.A. 62
V
Valeshnyy D.A. 65
Varlamov A.V. 97
Vinokurov Z.S. 19
Virovets A.V. 26
Volodin P.A. 48
Vologzhanina A.V. 86
W
Wang Z. 23
Y
Yakovlev G.B. 47
Yakovleva E.D. 67
Yakushev I.A. 53, 73
Yerlanuly A. 86
Z
Zakharov B.A. 51
Zakharova E.Yu. 17
Zaytsev V.P. 67, 69
Zhukov G.A. 97
Zubavichus Y.V. 19
Zubkov F.I. 57, 69

Contents

Plenary Lectures ----------11

Yuri Timofeevich Struchkov. On the centenary of his birth---------- 13

Crystal and electronic structure of polar intermetallic compounds – achievements and challenges on the way to functional materials ---------- 14

Synthesis, structural features, catalytic properties and biological activity of some transition metals complexes with isoxazole and isothiazole ligands---------- 15

Structural Bonanza of Intermetallic Phosphide Platinides ---------- 17

Synchrotron radiation facility SKIF: new capabilities for chemical crystallography in Russia ---------- 19

Unusual structures of oligosilanes and siloxanes ~crystallographic work --------- 21

Synthesis and Assembly Mechanism of Silver Nanoclusters Protected by Thiacalix[4]arene ---------- 23

Structural and physicochemical studies of pyrimidine-modulated tripyridyldiamine ligand and its metal complexes ---------- 24

How can we trust our crystal structure solutions? *Pseudo*-homometry and chemical reliability in single-crystal X-ray diffraction---------- 26

MOFs and Selected Catalytic Applications towards Sustainability ---------- 27

Confinement Effects in Metal-Organic Frameworks: From Crystal Structure to Advanced Functional Materials---------- 28

Charging carbon bowls, hoops, and graphene fragments with multiple electrons through the lens of crystallography---------- 29

Current status of Pt-based 1D solids ---------- 30

Structure and functional properties of metal-organic frameworks ---------- 31

New Electrode Materials for Metal-ion Batteries ---------- 32

New materials and X-rays: what to expect when they meet? ---------- 33

Obtaining high-quality X-ray crystallographic and functional states on the membrane protein bacteriorhodopsin — 10 years later. ---------- 34

Supramolecular cagelike metallasilsesquioxanes: structure and catalytic activity 35

Absolute Asymmetric Supramolecular Synthesis — Engineering of Enantiomorphic Crystals---------- 36

Keynote Lectures ---------- 37

New polymer-analogous transformations in chitosan chemistry ---------- 39

Asymmetric metal-templated synthesis of non-proteinogenic α-amino acids ----- 40

An analytical approach to modeling small-angle scattering curves for nanoparticle and hybrid systems: a case study analysis ---------- 41

Synthesis and crystal-chemical features of new compounds and solid solutions with the apatite structure ---------- 42

Yuri T. Struchkov, Michail Yu. Antipin, service crystallography, and charge density - 43

Isomeric forms, spectral behavior and biological activity of azo-compounds obtained by different methods---------- 45

A new approach to designing molecular rotors ---------- 46

Cyclic group 11 metal yrazolates as a rigid matrix for organic structure elucidation and photophysical tuning ---------- 47

Control over the structure and magnetic properties of *3d*-metal clusters supported by (thia)calix[4]arenes ---------- 48

In situ X-ray diffraction as a basic tool to study oxide and metal oxide catalysts 50

Comparative effects of high pressure and low temperature on the crystal structure of purine nucleobase salts---------- 51

Synthesis of platinum, palladium and rhodium-based bimetallic complexes: structural and catalytical insights ---------- 53

Influence of Nanocarbon Particles on the Mechanical Properties of Rubber Polymers ---------- 54

Oral Reports ---------- 55

Weak interactions in directing molecular conformation and crystal packing of some azole 3a,6-epoxyisoindole-7-carboxyliates---------- 57

Synthesis, crystal structure and spectroscopic properties of the cobalt(III) complex with 3,5-di-tert-butylsalicylaldehyde acetylhydrazone ---------- 58

Electrolyte-Dependent Crystal Chemistry of Silver-Modified Hydroxyapatite Synthesised by Reaction–Diffusion: A Powder Diffraction and Spectroscopic Study ---------- 60

Aggregation-Induced Emission in Supramolecular Complexes of a Bis(styryl) Dye with Cucurbiturils---------- 62

Crystal Structure and Vibrational Properties of Guanidinium *trans*-Diaquabis(malonato)aluminate(III): Experimental and Periodic DFT Study ------ 63

Interpretation of X-ray Diffraction Data of Metal-Organic Framework Polymers [REBTC] (RE = La-Lu, Y; BTC - $C_6H_5(COO)_3$) ---------- 65

New BODIPY fluorophores with five-membered heterocycles at the *meso*-position: design, synthesis and crystal structure ---------- 67

Non-covalent interactions in epoxyisoxazoloisoindol derivatives ---------- 69

Rational approach to the design of molecular magnets and luminescent thermometers based on complexes of 1,3-disubstituted derivatives of (thia)calix[4]arenes with *3d-*/*4f*-metal cations---------- 70

Specifics of evaluating the real composition of single-crystal solid solutions [$Co_{1-x}Ni_x)_3(C_6H_5(COO)_3)_2(H_2O)_{12}$] based XRD data---------- 71

Influence of molecular and crystal structure on photophysical properties in cyclometalled platinum complexes with carboxylate and pyridine ligands-------- 73

Lanthanide 1D coordination polymers with bulky cyclohexanecarboxylate ligands: synthesis, structure and properties---------- 74

X-ray structural analysis of α-$NiSO_4 \cdot 6H_2O$ single crystals doped with low concentrations of Y^{3+} and Ti^{4+} ions ---------- 76

Metal-Induced Halogen Bonding in Platinum-Group Isocyanide Complexes----- 78

Correlation between the structure and scintillation properties of materials-------- 80

σ-Hole interactions in phosphine selenides: structural, spectroscopic and computational insights ---------- 81

Sorption of Congo red by chitosan composites with Mg/Fe and Mg/Al layered double hydroxides synthesized under ultrasonic treatment ---------- 83

Regularities of changes in the crystal structures of $ALnCuSe_3$ (A = Sr, Eu) compounds---------- 85

Biologically Significant Fragments of O-Alkylsulfonyl-β-(benzimidazol-1-yl)-propioamidoximes as a Pathway to the Antimicrobial, Antifungal, Antidiabetic Drugs---------- 86

Aspects of the biochemical engineering of inulinase preparations from Aspergillus awamori and Kluyveromyces marxianus ---------- 88

Biochemical engineering aspects of the regulation of amylolytic enzyme activity ---------- 90

Vanillin and ethylvanillin based poly-N-heterocyclic derivatives: synthesis, structure and antimicrobial activity---------- 92

Effect of Mg Molar Ratio and Aging Method on Congo Red Adsorption by Mg–Fe Layered Double Hydroxides ---------- 94

The ability of MgAl layered double hydroxides to adsorb sodium salicylate ----- 95

Crystal structure and features of Methyl 8–isopropyl–10,11–dimethoxy–3–methyl–6–phenyl–3–azabenzo[*d*]cyclodeca–4,6,7–triene–5–carboxylate ---------- 97

Научное издание

IV СТРУЧКОВСКИЕ ЧТЕНИЯ

На английском языке

Издание подготовлено в авторской редакции

Технический редактор *Д.Р. Попова*

Подписано в печать 10.11.2026 г. Формат 60×84/8.
Усл. печ. л. 12,09. Тираж 100 экз. Заказ 1814

Российский университет дружбы народов им. Патриса Лумумбы
117198, г. Москва, ул. Миклухо-Маклая, д. 6

Отпечатано в издательско-полиграфическом комплексе РУДН
115419, г. Москва, ул. Орджоникидзе, д. 3
Тел.: +7 (495) 955 08 61. E-mail: publishing@rudn.ru