

СРПСКО КРИСТАЛОГРАФСКО ДРУШТВО  
SERBIAN CRYSTALLOGRAPHIC SOCIETY

**XVII КОНФЕРЕНЦИЈА  
СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА**  
Изводи радова

**XVII CONFERENCE OF THE  
SERBIAN CRYSTALLOGRAPHIC SOCIETY**  
Abstracts

Ивањица - Ivanjica  
2010

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**PLENARY LECTURES**

**ПЛЕНАРНА ПРЕДАВАЊА**

## THE X-RAY CRYSTAL STRUCTURE DETERMINATION OF THE *MjRELB – MJRELE* PROTEIN COMPLEX

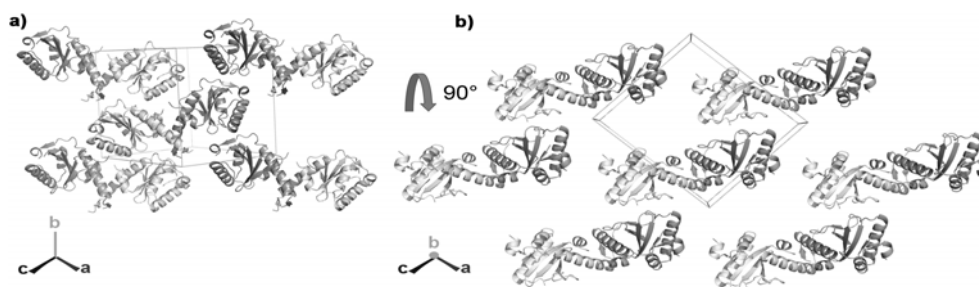
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The structure determination of macromolecules poses specific requests on crystallization, data collection, phase problem solution and structure refinement. Here we present the X-ray crystal structure determination of the *MjRelB – MjRelE* [1] protein complex with the multiple isomorphous replacement with anomalous signal (MIRAS) method for phase problem solution.

*MjRelE* protein belongs to the RelE toxin family which is spread in many bacterial species. These toxins act on translating ribosomes and have, depending on the organism, the role as a fast metabolic switch or act in conjunction with extra chromosomal DNA maintenance mechanisms [2]. The antitoxin *MjRelB* prevents the toxin from interacting with the ribosome and the mRNA by tightly binding to the toxin. The interplay between toxin production and antitoxin binding to the toxin is a sensitive equilibrium on which the survival of the bacterial cell is linked. Disrupting this equilibrium leads to bacterial cell death and is therefore a potential target for a new type of antibiotics. The three dimensional structure of this protein complex is the first step towards new antimicrobial compounds.

Three datasets from three different crystals of *MjRelB – MjRelE* protein complex were used to obtain all the necessary data: native (from the pure protein crystal); derivative with Mercury (recorded at the X-ray absorption edge of Hg); and derivative with Platinum (recorded at the X-ray absorption edge of Pt).



Crystal packing of the *MjRelB – MjRelE* protein complex in two projections

[1] D. Francuski & W. Saenger, *Journal of Molecular Biology*, 393 (2009), 898-908

[2] J. Alonso, D. Balsa, I. Cherny, S. Christensen, D. Francuski et al. In R. A. Bonomo, & M. E. Tolmasky (Eds.), *Enzyme-Mediated Resistance to Antibiotics: Mechanism, Dissemination, and Prospects for inhibition*, pp. 313-329.

## RENDGENSKA STRUKTURNA ANALIZA KRISTALNE STRUKTURE *MjRELB* – *MjRELE* PROTEINSKOG KOMPLEKSA

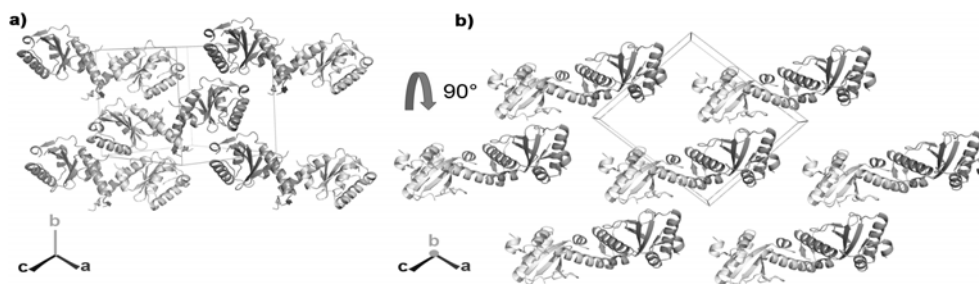
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Određivanje strukture makromolekula postavlja specifične zahteve za kristalizaciju, prikupljanje podataka, rešavanje faznog problema i utačnjavanje strukture. Ovde predstavljamo rendgensko struktorno određivanje kristalne strukture *MjRelB* – *MjRelE* [1] proteinskog kompleksa pomoću višestruke izomorfne zamene sa anomalnim signalom (MIRAS) tehnike za rešavanje faznog problema.

*MjRelE* protein pripada *RelE* proteinskoj porodici toksina koji su rašireni u mnogim bakterijskim sojevima. Oni deluju na ribosome u procesu translacije i zavisno od soja iz koga potiču, vrše funkciju brzog metaboličkog prekidača ili pak funkcionišu u sklopu mehanizama održavanja ekstra-hromozomalne DNK [2]. Njegov antitoksin *MjRelB* ga svojim vezivanjem sprečava u vezivanju sa ribozomom i iRNK te na taj način deaktivira. Održavanje osetljive ravnoteže između proizvodnje toksina i vezivanja antitoksina za njega je presudna za dalje održavanje bakterijske ćelije. Remecenje ove ravnoteže dovodi do smrti bakterijske ćelije te stoga predstavlja potencijalnu metu za nove klase antibiotika, a određivanje strukture ovog proteinskog kompleksa je prvi korak ka tom cilju.

Tri skupa podataka, svaki sa drugog kristala *MjRelB* – *MjRelE* proteinskog kompleksa, je bilo neophodno za rešavanje faznog problema: nativni (samo proteini *MjRelB* i *MjRelE*); derivatni sa živom (prikupljeni na absorpcionoj ivici za Hg); i derivatni kristali sa platinom (prikupljeni na absorpcionoj ivici za Pt).



Kristalno pakovanje *MjRelB* – *MjRelE* proteinskog kompleksa u dve projekcije

[1] D. Francuski & W. Saenger, *Journal of Molecular Biology*, 393 (2009), 898-908.

[2] J. Alonso, D. Balsa, I. Cherny, S. Christensen, D. Francuski et al. In R. A. Bonomo, & M. E. Tolmasky (Eds.), *Enzyme-Mediated Resistance to Antibiotics: Mechanism, Dissemination, and Prospects for inhibition*, pp. 313-329.

## TITANIUM PHOSPHATE HYBRID MATERIALS

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Metal salts of phosphoric acid have been known for over a century. However, research on layered metal phosphates, and their relatives, only began in the late 1950's, when some of these salts found applications as cation exchangers for the treatment of radioactive waste streams. In 1964, was obtained the first crystalline such compound,  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, which allowed a better understanding of their layered structure and chemical reactivity. Although only two crystalline forms of layered titanium phosphates are known,  $\alpha$ -Ti(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and  $\gamma$ -Ti(H<sub>2</sub>PO<sub>4</sub>)(PO<sub>4</sub>)·2H<sub>2</sub>O, many derivatives have been reported, including partially and completely substituted ion-exchanged forms and intercalation compounds. Surprisingly, the  $\gamma$ -layered titanium phosphate is less studied than the  $\alpha$ -phase, even though the  $\gamma$ -layers are more rigid, thicker, acidic and amenable to intercalation processes. This is probably due to the fact that the structure of the  $\gamma$ -phase was only theoretically proposed. Now, we revise the structural and thermal data of the  $\gamma$ -titanium phosphate, using a combination of scientific methods that had never been applied jointly to explore and clarify the thermal decomposition behaviour of this material [1].

Although monoalkylamines are usually employed as templates for the synthesis of titanium phosphate metastable phases, the structural features of  $\gamma$ -titanium phosphate alkylamine-intercalated compounds only recently have been reported [2]. Key to the full elucidation of the structure of the materials was the combination of XRD and NMR evidence with theoretical calculations of <sup>1</sup>H NMR chemical shifts. In this way, and in particular, it was possible to: *i*) assign all <sup>1</sup>H NMR resonances; *ii*) identify an unusual strong hydrogen bond bridging between the  $\gamma$ -titanium phosphate layers; and *iii*) establish the location/orientation of the guest alkylamine molecules in the interlayer space.

Since the great success of carbon nanotubes in 1991, interest in low-dimensional nanomaterials has fuelled a spectacular and unusual activity. Nowadays the nanotubes are not only made of carbon but also of inorganic materials, many of which are related with previously well-known layered structures. Organic-inorganic hybrid nanotubes based on the  $\gamma$ -titanium phosphate structure spaced with trialkylamines have been prepared by using microemulsion-mediated solvothermal and microwave-assisted methods. The interlayer distance in the inorganic sheets of the nanotube can be controlled by both the alkyl chain length and the amount of the amine template. All nanotubes obtained are open-ended with concentric cylinders, i.e., layers that fold and close within themselves. The possible reason for having this morphology seems to be related to the combination of two factors: *i*) the interaction between the nitrogen of trialkylamine molecules and the hydrogen belonging to inorganic skeleton that seeks to be maximum, and *ii*) the pseudo-conical geometry of the trialkylamine molecules that limits the number of accessible acid centers. In this way, the number of H-N links will depend on the length of the alkyl chain [3].



In conclusion, studies using diffraction methods in tandem with high-resolution NMR spectroscopy should provide valuable information on the local environment in the inorganic-organic materials, including new  $\gamma$ -titanium phosphate based nanotubes.

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## PAIR-DISTRIBUTION FUNCTION OF AB-INITIO MOLECULAR DYNAMICS GENERATED Se-CLUSTERS IN NdY ZEOLITE

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The regular porous structure provided by an alumino-silicate structure, specifically a zeolite of the neodymium-Y (NdY) type, constitute an ideal template to tailor the nanostructures of selenium (Se) as it has been done with other species [1], yielding a structure that differs from its bulk counterpart. Pores in the NdY zeolite are spherical and in the nanometer range, 13 Angstroem. By constraining the size of the Se structures within the nanometer range it is expected to bring about different physical properties, as it is actually observed in the optical spectral response of the nanoclusters during absorbance analysis, where a shift toward longer wavelength was recorded.

Typically the crystalline structure manifests itself as a long-range feature in an X-ray diffraction profile and the intense and well-defined Bragg peaks allow its accurate analysis. The long-range order aspect of Se in NdY zeolite was studied by means of high energy X-rays, 41 keV, from a synchrotron storage ring in a setup that enabled recording an extended angular range up to 110 degrees. Rietveld analysis allowed the extraction of an initial set of atomic positions that describe the average long-range order. Such information served as starting point for pair-distribution function (PDF) analysis that is able to reveal not only the long-range but also the short-range order, particularly local distortions that may comprise cluster topological variations together with their statistical occupancy distribution [2]. The PDF technique, developed to study disordered matter, as is the case of liquids and gases, and in contrast with the Rietveld method, takes all scattered information into account, that is, including also the low intensity diffuse scattering which reflects local distortions, besides the Debye-Waller factor, also susceptible of modeling during Rietveld analysis, as is well known. Thus after all appropriate corrections, Fourier transforming the entire profile and via customary analysis of the real-space radial profile it is possible to disclose any statistical short-range order simultaneously with the long-range order, complementing the overall investigation. To shed further light into the system, we have also resorted to using ab-initio molecular dynamics to generate stable clusters bearing a ring topology as a

precursor, that tend to satisfy the spatial boundary pore conditions provided by the rigid template constituted by the zeolite. Those initial ring-like clusters are relaxed to achieve conditions of minimum energy by introducing bond-length and bond-orientation changes. It is to be noted that all available pores in the zeolite are not fully populated, but only about 30% of them, an aspect that has to be taken into consideration since it has implication of statistical occupancy that affect the diffuse scattered intensity, as indicated above. The clusters are then integrated into the zeolite and the overall structure is modeled to yield a diffraction pattern that is compared against the one experimentally obtained. Some preliminary results are shown that highlight coordination tendencies.

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## STRUCTURAL INVESTIGATIONS ON NEPHELINE-TYPE COMPOUNDS

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The crystal structure of a new synthetic  $\text{Na}_{8-r}\text{Al}_{8-r}\text{Si}_{8+r}\text{O}_{32}$  ( $r = 0.15$ ) modification [1] is monoclinic with space group symmetry  $P112_1$ ,  $a = 9.9897(6)$ ,  $b = 9.9622(6)$ ,  $c = 24.979(2)$  Å, and  $\gamma = 119.788(4)^\circ$ . The phase was named monoclinic trinepheline because the length of its  $c$  lattice parameter is  $3\times$  the length of the  $c$  parameter in nepheline, whereas the  $a$  parameter is almost the same in both structures, similarly to a previously investigated trinepheline of hexagonal symmetry [2]. The structure of monoclinic trinepheline can be described as a consecutive stacking of basic nepheline [3] like modules (containing two tetrahedral sheets) and one sheet corresponding to those observed in the hexagonal trinepheline structure [2].

When heated to 373(5) K, monoclinic trinepheline transformed to hexagonal symmetry (S. G.  $P6_1$ ,  $a = 9.969(1)$ ,  $c = 25.056(2)$  Å,  $V = 2156.4(4)$  Å<sup>3</sup>), i.e., the tripling of the  $c$  lattice constant is retained. However, the superlattice reflections responsible for the tripling were very weak resulting in a higher final  $R$  value. The average structure of this phase corresponds to that of a conventional pure sodium nepheline with  $P6_3$ -symmetry [4]. The tripling of the  $c$  lattice parameter of the high-temperature modification is due to ordering phenomena of one apical oxygen and one sodium ion situated in a ditrigonal ring close to the  $6_1$  screw axis. Upon further heating the order is averaged and at 473(5) K the crystal structure corresponds to that of conventional nepheline (S. G.  $P6_3$ ,  $a = 9.977(2)$ ,  $c = 8.354(2)$  Å,  $V = 720.2(2)$  Å<sup>3</sup>). The same structure is retained until 873(5) K where the following unit cell parameters are observed:  $a = 10.057(2)$ ,  $c = 8.380(2)$  Å,  $V = 734.0(2)$  Å<sup>3</sup>.

A new synthetic  $\text{Na}_{8-r}\text{Al}_{8-r}\text{Si}_{8+r}\text{O}_{32}$  ( $r = 0.48$ ) modification is characterized by the simultaneous occurrence of (a) incommensurate satellite reflections [5] and (b) commensurate superstructure reflections pointing to a tripling of the unit cell parameter  $c$ . Following these observations the data set was integrated with three different approaches: as a classic nepheline structure (corresponding to an average structure), as a hexagonal trinepheline, and as an incommensurately modulated nepheline. The average basic nepheline structure was refined to an  $R$ -index of 0.024 in space group symmetry  $P6_3$ . In spite of very long exposure times to X-ray radiation, only a small portion of the sharp superstructure as well as satellite reflections had statistically significant intensities [ $I > 2\sigma(I)$ ].

In a previous work [6] the product of the thermal transformation of zeolite Na-LTA has been described as a standard nepheline. TEM investigations conducted on the synthesized powder material proved the presence of a structure with tripled  $c$  unit cell

parameter compared to that in classical nepheline. Comparison of the theoretical X-ray powder diagrams of all the known trinepheline compounds to the experimental powder pattern lead to the conclusion that it is actually mixture of two phases. Rietveld refinement against XRPD data as binary mixture of classical Na-nepheline [4] and monoclinic trinepheline resulted [1] in a significantly better agreement between calculated and observed step intensities.

Ten nepheline single crystals from five different localities representing rocks from nepheline-syenite pegmatites to urtite, ijolite and cancrinite-ijolite were investigated chemically and structurally. The chemical compositions were determined by electron microprobe, whereas the crystal structures were refined against X-ray diffraction data to *R* values of 0.022-0.031. In all cases the crystal structures conformed to space group *P*6<sub>3</sub>, but at the same time all crystals produced some satellite reflections testifying to the modulation effects in their structure.

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## STRUKTURNA ISPITIVANJA JEDINJENJA TIPa NEFELINA

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Kristalna struktura nove sintetičke  $\text{Na}_{8-r}\text{Al}_{8-r}\text{Si}_{8+r}\text{O}_{32}$  ( $r = 0,15$ ) modifikacije [1] je monoklinične simetrije, prostorna grupa  $P112_1$ ,  $a = 9,9897(6)$ ,  $b = 9,9622(6)$ ,  $c = 24,979(2)$  Å i  $\gamma = 119,788(4)^\circ$ . Jedinjenje je nazvano monoklinični trinefelin zato što je  $c$ -parametar tri puta duži od  $c$ -parametra nefelina, dok je  $a$ -parametar gotovo isti u obe strukture, slično ranije ispitivanom trinefelinu heksagonalne simetrije [2]. Struktura monokliničnog trinefelina može se opisati kao uzastopno slaganje jedinične ćelije nefelina [3] (koji sadrži dva tetraedarska sloja) i sloja koji odgovara heksagonalnom trinefelinu [2].

Zagrevanjem do 373(5) K monoklinični trinefelin se transformiše u heksagonalnu simetriju (P. G.  $P6_1$ ,  $a = 9,969(1)$ ,  $c = 25,056(2)$  Å,  $V = 2156,4(4)$  Å<sup>3</sup>). Pri tome je trostruko veći parametar jedinične ćelije  $c$  očuvan. Međutim, superstrukturne refleksije su veoma slabih intenziteta što je rezultovalo višom krajnjom  $R$ -vrednošću. Srednja struktura ove faze odgovara čistom natrijumskom nefelinu simetrije  $P6_3$  [4]. Tri puta veći parametar  $c$  visokotemperaturne modifikacije je posledica uređenja jednog apikalnog kiseonika i natrijuma koji se nalazi blizu zavrtanjske ose  $6_1$  u ditrigonalnom prstenu. Pri daljem zagrevanju pomenuti atomi više nisu uređeni i na 473(5) K kristalna struktura odgovara konvencionalnom nefelinu (P. G.  $P6_3$ ,  $a = 9,977(2)$ ,  $c = 8,354(2)$  Å,  $V = 720,2(2)$  Å<sup>3</sup>). Isti tip strukture je očuvan i do 873(5) K sa sledećim parametrima jedinične ćelije:  $a = 10,057(2)$ ,  $c = 8,380(2)$  Å,  $V = 734,0(2)$  Å<sup>3</sup>.

Nova sintetička  $\text{Na}_{8-r}\text{Al}_{8-r}\text{Si}_{8+r}\text{O}_{32}$  ( $r = 0,48$ ) modifikacija istovremeno pokazuje (a) satelitske refleksije [5] neproporcionalno modulirane strukture i (b) superstrukturne refleksije koje su posledica tri puta većeg parametra  $c$ . Zbog toga su eksperimentalni podaci integrisani u tri grupe: kao klasična (srednja) struktura nefelina, kao heksagonalni trinefelin i kao neproporcionalno modulirani nefelin. Srednja osnovna struktura nefelina utaćnjena je do  $R$ -indeksa 0,024 u prostornoj grupi  $P6_3$ . Uprkos veoma dugom vremenu izlaganja rendgenskom zračenju veoma mali deo oštrih superstrukturnih i satelitskih refleksija izmeren je sa statistiki značajnim intenzitetima [ $I > 2\sigma(I)$ ].

U prethodnom radu [6] proizvod termalne transformacije zeolita Na-LTA opisan je kao standardni nefelin. TEM ispitivanja sintetisanog polikristalnog materijala pokazala su prisustvo strukture sa tri puta većim parametrom  $c$  u poređenju sa klasičnim nefelinom. Poređenjem teorijskih rendgenskih dijagrama praha svih poznatih struktura trinefelina sa izmerenim dijagramom praha zaključeno je da je sintetisani materijal mešavina faza. Podaci su utaćnjavani Ritveldovom metodom kao binarna mešavinu klasičnog Na-nefelina [4] i

monokliničnog trinefelina [1]. Dobijeno je znatno bolje slaganje između izračunatih i izmerenih intenziteta.

Deset monokristala nefelina iz pet različitih lokaliteta ispitani su hemiski i strukturno. Monokristali su izdvojeni iz stena tipa nefelin-sijenitskih pegmatita, urtita, ijolita i kankrinit-ijolita. Hemijski sastav utvrđen je elektronskom mikrosondom. Kristalne strukture su utačnjene iz podataka dobijenih rendgenskom difrakcijom do  $R$ -vrednosti 0,022-0,031. U svim slučajevima kristalne strukture imaju simetriju  $P6_3$ . U isto vreme, svi kristali pokazuju satelitske refleksije ukazujući na efekte modulacije u strukturi.

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**ORAL PRESENTATIONS**

**САОПШТЕЊА**

## CRYSTAL-CHEMICAL INVESTIGATIONS OF ALKALINE EARTH HYDROGEN ARSENATES AND THEIR POTENTIAL IMPLICATIONS FOR SOIL REMEDIATION

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Arsenic is known to be one of the most toxic elements in nature. It may occur in 4 oxidation states: -III, 0, III and V and is naturally released in the environment by weathering and volcanism. However, its most important source is industrial activity. Arsenites ( $\text{AsO}_3^{3-}$ ) and arsenates ( $\text{AsO}_4^{3-}$ ) are the most prevalent forms of arsenic in natural surface environments such as soils and waters. However, mobility and bioavailability of As depend on its speciation both in solutions and in solids. For example, arsenates are less mobile and toxic than arsenites but sorb more strongly [1 and references therein].

A better knowledge of As immobilization mechanism in natural and experimental systems, is necessary to develop remediation process. Due to the difference in sorption efficiency, and in toxicity between arsenite and arsenate remediation processes often suggest immobilizing As in its highest oxidation state. However, arsenates are insufficiently studied, and their crystal-chemical behaviour and stability fields are often unknown. No matter what the origin of the arsenates in the soils, the identification of its presence is essential. Secondary minerals, which may form in soils, are usually dependent upon the availability of cations in the soils. Often the cations of iron, calcium and magnesium are the available cations. It is important, therefore, to study potential arsenates of these and related metals.

The comprehensive crystal-chemical study on synthetic arsenate compounds in the system  $M^{2+}\text{-As-O-H}$  ( $M^{2+} = \text{Sr, Ba}$ ) yielded four compounds with unknown structural features: three new structure types,  $\text{Sr}_5(\text{As}_2\text{O}_7)_2(\text{AsO}_3\text{OH})$  [2],  $\gamma\text{-Ba}(\text{AsO}_3\text{OH})$ , (in preparation), and  $\text{Sr}(\text{AsO}_3\text{OH})$  [3] and one already known structure type  $\alpha\text{-Ba}(\text{AsO}_3\text{OH})$  [3]. The arsenate compounds were synthesized under hydrothermal conditions in Teflon-lined stainless steel autoclaves at 493 K under autogeneous pressure (2 - 3 days, pH = 5.5 - 6.5). The compounds were analyzed using scanning electron microscopy with EDX analysis, single-crystal X-ray diffraction, and partly by infrared and Raman spectroscopy.

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- [1] F. Juillot, Ph. Ildefonse, G. Morin, G. Calas, A. M. de Karsabies, M. Benedetti, *Appl. Geochem.*, 14 (1999), 1031-1048.
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- [3] T. Mihajlović, H. Effenberger, *Z. Kristallogr.*, 221 (2006), 770-781.

## КРИСТАЛОХЕМИЈСКА ИСПИТИВАЊА ХИДРОГЕНАРСЕНАТА ЗЕМНОАЛКАЛНИХ МЕТАЛА И МОГУЋНОСТ ЊИХОВЕ ПРИМЕНЕ ЗА РЕМЕДИЈАЦИЈУ ЗЕМЉИШТА

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Арсен, један од најпознатијих отрова, јавља се у четири оксидациона стања: -III, 0, III и V. У природи се ослобађа вулканизмом и површинским распадањем. Ипак, највеће количине арсена потичу од његове широке индустријске примене. У земљишту и води најраспрострањеније су соли арсена, арсенити ( $\text{AsO}_3^{3-}$ ) и арсенати ( $\text{AsO}_4^{3-}$ ). Присуство и покретљивост арсена зависе од формирања његових секундарних једињења у растворима и земљишту. Арсенати су нпр. мање мобилни и мање отровни него арсенити, али су зато много бољи сорбенти [1 и цитирана литература].

Ради успешне ремедијације арсена, неопходно је константно радити на његовој имобилизацији како из природних тако и из вештачких система. Због већ наглашене разлике у својствима и токсичности између арсенита и арсената, за имобилизацију арсена углавном се користе арсенати. Упркос томе кристалохемија арсената и њихове области стабилности су недовољно проучавани. Без обзира на њихово порекло у земљишту неопходна је тачна идентификација појединачних арсената. Који ће се од секундарних минерала арсена формирати зависи пре свега од доступности различитих катјона у земљишту. Најраспрострањенији катјони у земљиштима су гвожђе, калцијум и магнезијум. Због тога је неопходно проучавање арсената ових и њима хемијски сличних елемената.

У току кристалохемијских испитивања система  $M^{2+}\text{-As-O-H}$  ( $M^{2+} = \text{Sr, Ba}$ ) добијене су четири супстанце:  $\text{Sr}_5(\text{As}_2\text{O}_7)_2(\text{AsO}_3\text{OH})$  [2],  $\gamma\text{-Ba}(\text{AsO}_3\text{OH})$  (рукопис у припреми) и  $\text{Sr}(\text{AsO}_3\text{OH})$  [3] који кристалишу као нови типови структура и  $\alpha\text{-Ba}(\text{AsO}_3\text{OH})$  [3] који има већ познати тип структуре. Све четири супстанце добијене су методом хидротермалне синтезе (тефлонски суд, челични аутоклав, 493 K, 2 - 3 дана, почетни pH = 5,5 - 6,5) и испитане методом рендгенске дифракције на монокристалу и делимично инфрацрвеном и Раман спектроскопијом. Квалитативна хемијска анализа рађена је на сканирајућем електронском микроскопу са EDX-ом.

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[1] F. Juillot, Ph. Ildefonse, G. Morin, G. Calas, A. M. de Karsabies, M. Benedetti, *Appl. Geochem.*, 14 (1999), 1031-1048.

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[3] T. Mihajlović, H. Effenberger, *Z. Kristallogr.*, 221 (2006), 770-781

## AIR POLLUTION EFFECTS ON THE BLACK CRUST ON THE STONE MONUMENTS SURFACE IN THE URBAN ENVIROMENT

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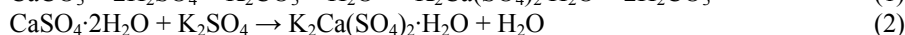
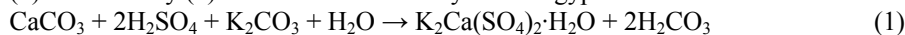
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All stone monuments are showing evidence of some form of decay under the influence of various physical, chemical and biological factors through time. The intensity and the form of decay depend on the type of stone substrate and on the surrounding environment. For the construction of cultural monuments in Belgrade, most frequently were used soft, highly porous limestone and sandstone with carbonate cement – *i.e.* the most vulnerable and the most susceptible rocks to effects of an urban atmosphere. One of the fairly common degradation forms in urban areas is the development of black crusts.

The main pollutants are products of combustion of solid, liquid and gaseous fuels, whereas the main broadcasters are power plants and traffic. The increasing combustion of fossil fuels along with diesel engines during the last few decades decreased the amount of sulfur dioxide (SO<sub>2</sub>), while nitrogen compounds (NO<sub>x</sub>), elemental carbon and carbon compounds (carbonates, alkanes and alkenes), common components in the air, became more significant accelerating and taking place in black crusts over the monument facades.

Interaction between urban aerosol and limestone/sandstone built in monuments in Belgrade is shown through mineralogical-morphological properties and mechanism of black crust formation on the cultural monuments of Belgrade Fortress, on Bajrakli mosque façade and on the monument of "Belgrade liberators in 1944".

Effects of black crusts formed in limestone or sandstone built in monuments are dual: a) aesthetic, represented with complete stone discoloration and b) physicochemical, expressed through destruction of stone substrate. In initial stage, black crust developed through accumulation of pollutants and dusts over stone facade that is sheltered from the natural rain-wash. Accumulated deposit enforced by moisture from the air is hardening and stronger grasping for the stone through time. Results of SEM-EDS and X-ray powder diffraction analysis revealed that black crusts almost regularly contain gypsum – CaSO<sub>4</sub>·2H<sub>2</sub>O, beside products of fuel burning, calcite and glassy globules. Gypsum was formed through interaction between substrate and airborne sulfur compounds. As the formed crust has a higher porosity than the stone substrate it permits larger incorporation of fly ash, soot and some other particles increasing simultaneously active surfaces for deposition of carbon compounds. Of special importance is syngenite – K<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, observed inside the investigated black crust beside regular and expected gypsum. The source of required potassium for syngenite formation could be linked to transformation of feldspar – KAlSi<sub>3</sub>O<sub>8</sub> grains present from mortar, while its crystallization should be directly (1) or indirectly (2) on account the already formed gypsum.



Despite the type of black crust constituents, the above mentioned salts entering into the pore system cause aesthetic degradation along with physicochemical destruction

## ZAGAĐENJE VAZDUHA KAO UZROK OBRAZOVANJA CRNIH KORA NA SPOMENICIMA U URBANOJ SREDINI

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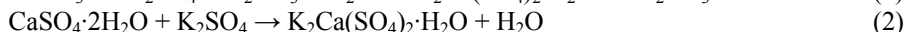
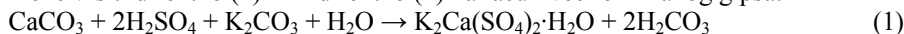
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Kamen ugrađen u kulturno istorijske spomenike vremenom podleže različitim vidovima raspadanja, pod uticajem fizičkih, hemijskih i bioloških faktora. Forme i intenzitet raspadanja zavise kako od tipa kamenog substrata tako i od sredine koja ga okružuje. U izgradnji kulturne baštine Beograda najčešće su korišćeni mekani, veoma porozni krečnjaci i peščari sa karbonatnim cementom – litotipovi najosetljiviji i najpodložniji agresivnom dejstvu urbane atmosfere. Jedan od vidova degradacije pod uticajem urbane atmosfere ovih litotipova je formiranje crnih kora.

Glavni zagađivači urbane atmosfere su produkti sagorevanja čvrstih, tečnih i gasovitih goriva, a osnovni emiteri su termoelektrane i saobraćaj. Poslednjih decenija sve veća upotreba tečnih i gasovitih goriva i dizel motora, inicirala je trend opadanja SO<sub>2</sub>, ali azotna jedinjenja (NO<sub>x</sub>), elementarni ugljenik i jedinjenja ugljenika (karbonati, alkani i alkeni), redovni sastojci atmosfere, dobijaju sve veći značaj kao katalizatori i konstituenti crnih kora na fasadama spomenika.

Interakcija urbanih aerosoli i krečnjaka/peščara ugrađenih u spomenike Beograda prikazana je kroz mineraloško-morfološka svojstva i mehanizam nastajanja crnih kora na kulturnim spomenicima Beogradske tvrđave, fasade Bajrakli džamije i spomenika „Oslobodiocima Beograda 1944“.

Alteraciono dejstvo crnih kora na ugrađene krečnjake i peščare Beogradskih spomenika je dvojako: a) estetsko, jer u potpunosti vrši dekoloraciju spomenika i b) fizičko-hemijsko, jer izaziva destrukciju supstrata. Kore se u početnom stadijumu obrazuju akumuliranjem zagađivača i prašine na fasadni kamen, koji je zaklonjen od prirodnog pranja kišnicom. Deponovani talog uz sadejstvo atmosferske vlage vremenom otvrdnjava i sve čvršće prijanja za površinu kamena. Rezultati SEM-EDS i rendgenske difrakcione analize polikristalnih uzoraka pokazuju da je u crnim korama, osim produkata sagorevanja goriva, kalcita i staklastih globula, redovan konstituent gips – CaSO<sub>4</sub>·2H<sub>2</sub>O, koji je proizvod interakcije supstrata i sumpornih jedinjenja iz atmosfere. Formirana kora ima veću poroznost od podloge tako da u većoj meri inkorporira pepeo, čađ i druge čestice istovremeno povećavajući aktivnu površinu za dalje deponovanje ugljenikovih jedinjenja. Osim gipsa u ispitivanim crnim korama konstatovano je i prisustvo singenita – K<sub>2</sub>Ca(SO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. Izvor kalijuma za formiranje singenita u crnim korama može se vezati za transformaciju feldspata – KAlSi<sub>3</sub>O<sub>8</sub> poreklom iz maltera, dok se kristalizacija singenita može vršiti direktno (1) ili indirektno (2) na račun već formiranog gipsa:



Bez obzira na vrstu konstituenta crnih kora, ove soli osim estetske degradacije, svojim ulaskom u porni sistem kamena vrše i fizičko-hemijsku destrukciju kamena.

## STRUCTURAL ANALYSIS, ANTIOXIDANT AND CYTOTOXIC ACTIVITY OF NEWLY SYNTHESIZED STEROIDAL SALICYLIC ACID DERIVATIVES

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Because of the damaging effects of reactive oxygen species (ROS) such as hydrogen peroxide, hydroxyl radical and superoxide anion, all cells maintain an antioxidant defense system that includes antioxidant enzymes, as well as non-enzyme antioxidants (glutathione, vitamins, etc). When there is an imbalance between ROS production and the antioxidant system, a situation of oxidative stress is established [1]. Many investigators have proposed that estrogens are important brain protectors, because of their antioxidant activity in neurons. Studies *in vitro* [2] and *in vivo* [3] have shown that high, non-physiological doses of estradiol are neuroprotective. Possible antioxidant properties of the novel derivatives of estradiol, testosterone, dehydroepi-androsterone and androstenedione were examined [4]. On the other hand, many steroidal compounds and salicylic acid derivatives exhibit cytotoxicity against PC-3 (prostate cancer cells), MCF-7 (human breast adenocarcinoma ER+cells), MDA-MB 231 (human breast adenocarcinoma ER-cells) and other tumor cell lines [5, 6].

In order to investigate their antioxidant and cytotoxic activities of steroidal salicylic acid derivatives we synthesized mono-, and bis-salicyloyl derivatives of different estrone and androstene series. Structures of four of these compounds: 3-methoxy-17 $\beta$ -salicyloyloxy-estra-1,3,5(10)-triene (1), 17 $\beta$ -salicyloyloxy-19-nor-4-androstene-3-one (2), 17 $\beta$ -(2-methoxybensoxy)-5 $\alpha$ -androstane-3-one (3) and 3 $\beta$ -salicyloyloxy-24 $\beta$ -ethylcholesta-5,22-diene (4) were confirmed by X-ray structural analysis.

The antioxidant activity and cytotoxicity of the synthesized derivatives were evaluated in a series of *in vitro* tests. The newly synthesized compounds exhibited mostly cytotoxic activity against the MDA-MB 231 cells.

- [1] I. Fridovich, *J. Exp. Biol.* 201 (1998), 1203-1209.
- [2] H. Vedder, N. Anthes, G. Stumm, C. Würz, C. Behl, J-C Krieg, *J. Neurochem.* 72 (1999), 2531-2538.
- [3] R. Rontu, T. Solakivi, K. Teisala, T. L. Ki, R. Punnonen, H. Jokela, *Free Radic. Res.* 38 (2004), 129-173.
- [4] W. Klinger et al, *Toxicology Letters.* 128 (2002), 129-144.
- [5] M. Ali, N. Ahmed, G. Tessiler, J. van Lier, *Bioorg. Med. Chem. Lett.* 16 (2006), 317.
- [6] M. Valko, D. Leibfritz, J. Moncol, M. T. D. Cronin, M. Mazur, J. Telser, *The International Journal of Biochemistry & Cell Biology* 39 (2007), 44-84.

## STRUKTURNA ANALIZA, ANTIOKSIDANTNA I CITOTOKSIČNA AKTIVNOST NOVOSINTETISANIH STEROIDNIH DERIVATA SALICILNE KISELINE

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Zbog destruktivnog efekta reaktivnih kiseoničnih radikala kao što su, vodonik-peroksid, hidroksilni radikali i superkiseonični anjon, ćelije teže da održe svoje antioksidantne sisteme što uključuje antioksidantne enzime kao i neenzimske antioksidante. Kada postoji neravnoteža između produkcije reaktivnih kiseoničnih radikala i aktivnosti antioksidantnog ćeliskog sistema, dolazi do situacije koju zovemo oksidantni stres [1]. Mnoga dosadašnja istraživanja su pokazala da estrogini imaju antioksidantnu aktivnost posebno kada su u pitanju neuronske ćelije. Studije *in vitro* [2] i *in vivo* [3] su pokazale da su visoke, nefiziološke doze estradiola neuroprotektivne. Antioksidantne osobine novosintetisanih derivata estradiola, testosterona, dehidroepiandrosterona i androstendiona su takođe ispitivane [4]. Sa druge strane mnoga steroidna jedinjenja kao i neki derivati salicilne kiseline pokazuju citotoksičnu aktivnost u odnosu na PC-3 (ćelije raka prostate), MCF-7 (ćelije humanog adeno karcinoma dojke ER+ćelije), MDA-MB 231 (ćelije humanog adeno karcinoma dojke ER-ćelije) i druge tumorozne ćelije [5, 6].

Da bismo ispitali antioksidantnu i citotoksičnu aktivnost nekih steroidnih derivata salicilne kiseline, sintetisano je više mono- i bis-derivata salicilne kiseline iz različitih estranskih i androstanskih serija. Strukture četiri novosintetisana jedinjenja: 3-metoksi-17 $\beta$ -saliciloloksi-estra-1,3,5(10)-trien (1), 17 $\beta$ -saliciloloksi-19-nor-4-androsten-3-on (2), 17 $\beta$ -(2-metoksibenzoiloksi)-5 $\alpha$ -androstan-3-on (3) i 3 $\beta$ -saliciloloksi-24 $\beta$ -etilholesta-5,22-dien (4) su potvrđene strukturnom rendgenskom analizom. Antioksidantna i citotoksična aktivnost novosintetisanih derivata je određena u nizu *in vitro* testova. Ova jedinjenja su pokazala uglavnom blagu citotoksičnu aktivnost prema MDA-MB 231 ćelijama.

- [1] I. Fridovich, *J. Exp. Biol.* 201 (1998), 1203-1209.
- [2] H. Vedder, N. Anthes, G. Stumm, C. Würz, C. Behl, J-C Krieg, *J. Neurochem.* 72 (1999), 2531-2538.
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- [5] M. Ali, N. Ahmed, G. Tessiler, J. van Lier, *Bioorg. Med. Chem. Lett.* 16 (2006), 317.
- [6] M. Valko, D. Leibfritz, J. Moncol, M. T. D. Cronin, M. Mazur, J. Telser, *The International Journal of Biochemistry & Cell Biology* 39 (2007), 44-84.

## THERMAL DECOMPOSITION OF BRUSHITE $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ TO MONETITE $\text{CaHPO}_4$ AND THE FORMATION OF AN AMORPHOUS PHASE

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Brushite,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , is a layered structure in which the layers are held together by water molecules via hydrogen bonds. Brushite loses its water molecules in two steps when heated to form monetite  $\text{CaHPO}_4$ . The loss of water results in the formation of an amorphous phase along with monetite. The main goal of our research was to quantify the amount of an amorphous phase that forms during transformation of brushite to monetite during heating, and to describe the processes that drive its formation. We investigated the dehydration process primarily by means of X-ray diffraction, and quantified the amount of monetite and the amorphous phase as a function of heating rate and temperature via Rietveld refinements. We heated synthetic brushite powder (Aldrich Chemical Company, 98% pure) at different rates and to different temperatures. We used three different types of heating methods: thermal X-ray powder diffraction, thermogravimetric analysis (TGA), and a muffle furnace with an adjustable heating rate. Water loss was recorded by TGA and the nature of the products was investigated by Fourier transform infrared spectroscopy. Recrystallization, water loss, and the formation of the amorphous phase depend on the heating rate and/or time of exposure at temperature. The conversion temperature is about  $220^\circ\text{C}$ , although brushite can convert to monetite at lower temperatures during prolonged exposure to heat. We found that more amorphous phase forms during slower dehydration at slower heating rates. Total water loss during dehydration is less than the water content in brushite, therefore the amorphous phase is hydrated, or some water stayed trapped in the monetite structure. FTIR showed residual free water vibrations in the thermally treated sample. Amorphous phase forms due to uneven dehydration process and a structural tilt which cause some water molecules to stay trapped in the structure. Also the amorphous phase may exhibit short range order, and this amorphous material can be regarded as highly disordered monetite with some free water in the structure.



## TERMALNI RASPAD BRUŠITA $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ U MONETIT $\text{CaHPO}_4$ I STVARANJE AMORFNE FAZE

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Brušit,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , je mineral slojevite strukture u kojoj molekuli vode vezuju slojeve vodoničnim vezama. Brušit gubi vodu u dva stupnja prilikom zagrevanja i formira monetit  $\text{CaHPO}_4$ . Tokom gubitka vode pored monetita dolazi i do formiranja amorfne faze. Glavni cilj našeg istraživanja je kvantifikacija amorfne faze koja se formira tokom transformacije brušita u monetit tokom zagrevanja i procesi koji uslovljavaju njen nastanak. Dehidracija je analizirana primarno rendgenskom difrakcijom, a zastupljenost monetita i amorfne faze u funkciji stope zagrevanja i temperature određena je Ritvildovom analizom. Brušit (Aldrich Chemical Company, 98%) je zagrevan različitom brzinom do nekoliko različitih temperatura. Koristili smo tri načina zagrevanja: visokotemperaturnu difrakciju praha, termogravimetrijsku analizu (TGA) i peč sa promenljivim režimom zagrevanja. Gubitak vode registrovan je pomoću TGA, a proizvodi su analizirani FTIR spektroskopijom. Rekrystalizacija, gubitak vode, i stvaranje amorfne faze zavise od brzine zagrevanja ili dužine izlaganja povišenoj temperaturi. Temperatura faznog prelaza je oko  $220^\circ\text{C}$ , iako brušit može da pređe u monetit na nižim temperaturama tokom produženog izlaganja toploti. Našli smo da se više amorfne faze stvara tokom sporijeg zagrevanja. Ukupni gubitak vode tokom dehidracije je manji nego ukupni sadržaj vode u brušitu, tako da zaključujemo da je amorfna faza hidratizovana ili da je izvesna količina vode zarobljena u strukturi monetita. FTIR rezultati pokazuju vibracije vode u uzorcima koji su prošli termalnim tretmanom. Amorfna faza se formira zbog nejednake dehidracije i strukturnih osobina brušita, koje uzorkuju da neki molekuli vode ostanu zarobljeni u strukturi. Amorfna faza potencijalno pokazuje nedovoljan stepen uredenosti na kratkim rastojanjima, te se ovakav amorfni material može smatrati monetitiom sa visokim stepenom neuredenosti i određenim procentom nekoordinovane vode u strukturi.

## POLYSOMATIC SERIES: A REVIEW OF HUMITE GROUP OF MINERALS AND NEW Ca-ANALOGUES

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The humite mineral group comprises orthorhombic or monoclinic nesosilicates  $nA_2SiO_4 \times A(F,OH)_2$  ( $n = 1, 2, 3$  or  $4$ ) where  $A = Mg, Fe^{2+}, Mn^{2+}, Zn, Ca,$  and others. Corresponding structures are based on hexagonal closed packed O arrays containing zig-zag chains of edge sharing octahedra and isolated tetrahedra. The whole group can be classified by the dominant octahedral cations: true humites - Mg silicates and Ca- or Mn- analogues. They can also be characterized as structure types with 1, 2, 3 or 4 silicate layers, indicated by  $n$  in the general group formula. However, most interesting is the classification of humite group minerals as polysomatic series. The latter concept was developed by J.B. Thompson (1978) who recognised that any crystal can be sliced into the slabs [1], and that in some cases slabs of the one structure can be combined with a slabs of another. Results are hybrid structures called polysomes. Humite-group structure can be represented as members of a polysomatic series constructed from slabs of the olivine  $Mg_2SiO_4$  (composed of two slabs of type O, thus olivine has the notification OO) and slabs of the norbergite  $Mg_3SiO_4(F,OH)_2$  (composed of two slabs of type N, thus norbergite has the notification NN) structures. The structure of chondrodite  $Mg_5(SiO_4)_2F_2$ , another group member, can be constructed from one slab of olivine and one of norbergite. Thus, the polysomatic notation for this mineral is NO. In the same way humite  $Mg_7(SiO_4)_3F_2$ : NOO and clinohumite  $Mg_9(SiO_4)_4F_2$ :NOOO can be characterized. At the end of the year 2008, two new calcium minerals of the humite group have been approved by the CNMNC IMA: chegemite  $Ca_7(SiO_4)_3(OH)_2$  (IMA2008–38) [2] – the calcium and hydroxyl analogue of humite, and  $Ca_5(SiO_4)_2F_2$  (IMA2008–45) [3]– the fluorine analogue of reinhardbraunsite, with the chondrodite structure-type. The crystal chemistry of the olivine and norbergite-like slabs in Ca-analogues of the group, as well as new minerals are compared.

[1] J. B. Thompson, *American Mineralogist*, 63 (1978), 239-249.

[2] E. V. Galuskin, V. M. Gazeev, B. Lazic, T. Armbruster, I. O. Galuskina, A. E. Zadov, N. N. Pertsev, R. Wrzalik, P. Dzierzanowski, A. G. Gurbanov, G. Bzowska, *European Journal of Mineralogy*, 21 (2009), 1045-1059.

[3] I. O. Galuskina, B. Lazic, T. Armbruster, E. V. Galuskin, V. M. Gazeev, A. E. Zadov, N. N. Pertsev, L. Ježak, R. Wrzalik and A. G. Gurbanov, *American Mineralogist* 94 (2009), 1361–1370.

## POLISOMATSKE SERIJE: ANALIZA HUMITSKE GRUPE MINERALA I NOVIH Ca - ANALOGA

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Kao grupa minerala humiti se sastoje od rombičnih i monokliničnih nezosilikata opšte formule  $nA_2SiO_4 \times A(F,OH)_2$  ( $n = 1, 2, 3,$  or  $4$ ) gde je  $A = Mg, Fe^{2+}, Mn^{2+}, Zn, Ca,$  itd. Njihove strukture se zasnivaju na heksagonalnom najgušćem pakovanju kiseonika, a sadrže cik-cak lance oktaedara povezanih ivicama i izolavane tetraedre. Cela grupa može biti podeljena prema dominantim oktaedarskim katjonima na: prave humite - Mg silikate i Ca- ili Mn- analoge. Takođe, mogu biti opisani kao različiti strukturni tipovi sa 1, 2, 3, ili 4 silikatna sloja, označena brojem  $n$  u opštoj formuli. Najinteresantnija je klasifikacija humitske grupe minerala kao polisomatske serije čiji koncept je razvio J. B. Thompson (1978), prepoznavši da bilo koja struktura kristala može biti podeljena na delove [1]. Ponekad delovi jedne strukture mogu biti kombinovani sa delovima druge strukture tako da se na kraju dobije hibridna struktura zvana polizom. Strukture minerala humitske grupe mogu se predstaviti kao članovi polisomatke serije sastavljene od delova olivina  $Mg_2SiO_4$  (sastoji se od dva dela tipa O, zbog toga se označava sa OO) i delova norbergita  $Mg_3SiO_4(F,OH)_2$  (dva dela tipa N, zato se označava sa NN). Struktura hondrita  $Mg_5(SiO_4)_2F_2$ , još jednog člana grupe, može biti izgrađena od jednog sloja olivina i jednog sloja norbergita. Zbog toga je polisomatska oznaka hondrita NO. Na isti način mogu se opisati minerali humit  $Mg_7(SiO_4)_3F_2$  kao NOO i klinohumit  $Mg_9(SiO_4)_4F_2$  kao NOOO. Krajem 2008. godine dva nova Ca-minerala humitske grupe odobrena su od strane međunarodne komisije CNMNC IMA. To su čegemit  $Ca_7(SiO_4)_3(OH)_2$  (IMA2008–38) [2] – kalcijum-humit sa hidroksil grupom, i  $Ca_5(SiO_4)_2F_2$  (IMA2008–45) [3] – flouritski rajnhardbraunsit, sa hondritskom strukturom. Kristalo-hemijske osobine olivinskih i norbergitskih slojeva među novim i starim kalcijumskim članovima humitske grupe su analizirani.

[1] J. B. Thompson, *Am. Mineral.*, 63 (1978), 239-249.

[2] E. V. Galuskin, V. M. Gazeev, B. Lazic, T. Armbruster, I. O. Galuskina, A. E. Zadov, N. N. Pertsev, R. Wrzalik, P. Dzierzanowki, A. G. Gurbanov, G. Bzowska, *Eur. J. Mineral.*, 21 (2009), 1045-1059.

[3] I. O. Galuskina, B. Lazic, T. Armbruster, E. V. Galuskin, V. M. Gazeev, A. E. Zadov, N. N. Pertsev, L. Ježak, R. Wrzalik and A. G. Gurbanov, *Am. Mineral.*, 94 (2009), 1361–1370.

## MODULATED STRUCTURE AND PHASE TRANSITIONS OF $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$

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In previous years the phase relationships in the binary system  $\text{SrO-Ga}_2\text{O}_3$  have been re-investigated in more detail [1]. This interest can be at least partially attributed to the fact that alkaline earth gallates are potential host materials for the production of luminescent compounds. The crystal structure of  $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$  was studied by *in situ* single-crystal X-ray diffraction in the temperature range 298–673 K. At ambient conditions the compound shows a (3+1)-dimensional modulated structure in superspace group  $\text{C}2/c(0\beta 0)s0$  [ $a = 34.9145(13)$ ,  $b = 7.9369(2)$ ,  $c = 15.9150(7)$  Å and  $\beta = 103.551(3)^\circ$ ] with a modulation wave-vector of  $\mathbf{q} = 0.4288(2)\mathbf{b}^*$ . Further high-temperature experiments at 503 K revealed a change in the diffraction pattern: the incommensurate satellite reflections had disappeared, but new commensurate superstructure reflections emerged at positions which double the  $a$  and  $b$  lattice constants [ $a = 70.005(4)$ ,  $b = 15.901(1)$ ,  $c = 15.982(1)$  Å,  $\beta = 103.618(1)^\circ$ ]. In addition, a second phase transition was identified between 503 and 673 K. This high-temperature phase does not show any of the superstructure reflections. Thus, the cell is similar to  $\alpha\text{-Sr}_{10}\text{Ga}_6\text{O}_{19}$  [2]. Crystals showing a combination of diffraction patterns originating from both superstructures can be obtained by cooling from 500 K. Probably, this phenomenon is caused by the formation of a "multi-phase" crystal.

[1] M. Zinkevich, *Int. J. Mater. Res.* 98 (2007), 574–579

[2] V. Kahlenberg, *J. Solid State Chem.* 160 (2000), 421–429

## MODULISANA STRUKTURA I FAZNI PRELAZI JEDINJENJA $\text{Sr}_{10}\text{Ga}_6\text{O}_{19}$

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U prethodnim godinama odnosi faza u binarnom sistemu SrO-Ga<sub>2</sub>O<sub>3</sub> često su iznova detaljnije ispitivani [1]. Ovaj interes može se bar delimično pripisati činjenici da su zemnoalkalni galati potencijalni domaćini-materijali za proizvodnju luminescentnih jedinjenja. Kristalna struktura jedinjenja Sr<sub>10</sub>Ga<sub>6</sub>O<sub>19</sub> proučavana je *in situ* rendgenskom difrakcijom na monokristalu u temperaturnom opsegu od 298 do 673 K. U ambijentalnim uslovima jedinjenje pokazuje (3+1)-dimenzionalnu modulisanu strukturu u super-prostornoj grupi C2/c(0β0)s0 [ $a = 34,9145(13)$ ,  $b = 7,9369(2)$ ,  $c = 15,9150(7)$  Å i  $\beta = 103,551(3)^\circ$ ] sa vektorom modulacije  $q = 0,4288(2) b^*$ . Dalji visokotemperaturni eksperimenti su na 503 K otkrili promene na difrakcionoj slici: Nproporcionalno modulisane satelitske refleksije su nestale, a nove proporcionalno modulisane, superstrukturne refleksije pojavile su se na pozicijama koje udvostručuju  $a$  i  $b$  parametar rešetke [ $a = 70,005(4)$ ,  $b = 15,901(1)$ ,  $c = 15,982(1)$  Å,  $\beta = 103,618(1)^\circ$ ]. Osim toga, drugi fazni prelaz je identifikovan između 503 i 673 K. Ova visokotemperaturna faza ne pokazuje satelitske refleksije i slična je fazi  $\alpha$ -Sr<sub>10</sub>Ga<sub>6</sub>O<sub>19</sub> [2]. Hlađenjem od 500 K dobijaju se kristali koji pokazuju kombinaciju satelitskih refleksija obe modulisane superstrukture istovremeno. Ovo je verovatno uslovljeno stvaranjem „višefaznog” kristala.

[1] M. Zinkevich, *Int. J. Mater. Res.* 98 (2007), 574–579

[2] V. Kahlenberg, *J. Solid State Chem.* 160 (2000), 421–429

## STRUCTURE AND DFT ANALYSIS OF THE [Ni(H<sub>2</sub>O)<sub>6</sub>][Ni(ed3a)(H<sub>2</sub>O)]<sub>2</sub>·2H<sub>2</sub>O COMPLEX

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In this report we have been studied the structure of complex nickel(II) with ed3a type of ligand (ed3a = ethylenediamine-*N,N,N'*-triacetate ion). Each asymmetric unit of [Ni(H<sub>2</sub>O)<sub>6</sub>][Ni(ed3a)(H<sub>2</sub>O)]<sub>2</sub>·2H<sub>2</sub>O unit cell consisted of three moieties: an anionic [Ni(ed3a)(H<sub>2</sub>O)]<sup>-</sup> complex, a half cationic hydrated nickel complex and a solvate water molecule. The *cis*-equatorial [Ni(ed3a)(H<sub>2</sub>O)]<sup>-</sup> entity contains a Ni(II) atom in a distorted octahedral N<sub>2</sub>O<sub>4</sub> environment. There are two longer equatorial bonds Ni–N12 (2.1108(13) Å) and Ni–O12 (2.123(1) Å). The other distances in this anionic complex are within the range from 2.0185(10) to 2.0820(12) Å and as expected comparable with those obtained for related ed3a-type complexes [1].

Using DFT (Density Functional Theory) method implemented in Gaussian03 [2] program package we have modeled all three possible geometrical isomers (*cis*-equatorial, *cis*-polar and *trans*-equatorial). The results obtained indicate *cis*-equatorial isomer being the most energetically stable one: by 1 kcal/mol related to *cis*-polar and by 2 kcal/mol related to *trans*-equatorial isomer. This fact is in accordance with the geometry found by the X-ray structure analysis.

The results of Ni(ed3a) and Cu(ed3a) [3] X-ray analysis were compared and show [Ni(ed3a)(H<sub>2</sub>O)]<sup>-</sup> being isomorphous with [Cu(ed3a)(H<sub>2</sub>O)]<sup>-</sup>. Surprisingly, their similarity is so evident that it crosses to almost identity (RMS = 0.0460). Furthermore, we extracted coordinated ed3a ligands from these complexes and made up their overlay by the use of Hyperchem program package. In such a way overlay shows even better fit (RMS error of 0.01243).

The major reason for this feature we should seek in extremely unfavourable presence of three five-membered rings in the equatorial plane (two acetate and one diamine ring) due to considerable strain effect. As a cosequence *cis*-equatorial isomer (two five-membered rings in the equatorial plane) dominates in all the metal *M*-ed3a complexes [*M* = Co(III), Cr(III), Cu(II)] [1, 3-4] prepared so far.

[1] N. Sakagami, S. Kaizaki, *J. Chem. Soc., Dalton Trans.* (1992), 291

[2] M. J. Frisch et al., Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford, CT, 2004

[3] Z. Matovic, A. Meetsma, V. Miletic, P. van Koningsbruggen, *Inorg. Chim. Acta* 360 (2007) 2420

[4] D. Radanović, *Coord. Chem. Rev.*, 54 (1984), 159

## СТРУКТУРА И ДФТ АНАЛИЗА КОМПЛЕКСА [Ni(H<sub>2</sub>O)<sub>6</sub>][Ni(ed3a)(H<sub>2</sub>O)]<sub>2</sub>·2H<sub>2</sub>O

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У овом раду изучавана је структура комплекса никла(II) са ed3a лигандом (ed3a = етилендиамин-*N,N,N'*-триацетато јон). Свака асиметрична јединица јединичне ћелије једињења [Ni(H<sub>2</sub>O)<sub>6</sub>][Ni(ed3a)(H<sub>2</sub>O)]<sub>2</sub>·2H<sub>2</sub>O састоји се од три компоненте: анјонског [Ni(ed3a)(H<sub>2</sub>O)]<sup>-</sup> комплекса, половине хидратисаног катјона никла као и солватног молекула воде. *Cis*-екваторијална [Ni(ed3a)(H<sub>2</sub>O)]<sup>-</sup> јединица садржи атом никла у деформисаном октаедарском N2O4 окружењу. У јону су присутне две дуже екваторијалне Ni–N12 (2,1108(13) Å) и Ni–O12 (2,123(1) Å) везе док се остале дужине веза крећу од 2,0185(10) до 2,0820(12) Å и у опсегу су поредивом са осталим комплексима *M*-ed3a типа[1].

Употребом ДФТ (Density Functional Theory) методе имплементиране у Gaussian03 [2] програму извршено је у овом раду моделовање могућих геометријских изомера (*cis*-екваторијални, *cis*-поларни и *trans*-екваторијални). Резултати моделовања указују да је *cis*-екваторијални изомер енергетски стабилнији од остала два и то за 1 kcal/mol у односу на *cis*-поларни и 2 kcal/mol у односу на *trans*-екваторијални изомер, што је у сагласности са геометријом верификованом рендгенском структурном анализом.

Поређењем резултата рендгенске структурне анализе Ni(ed3a) и Cu(ed3a) [3] комплексних јона утврђено је да су јони [Ni(ed3a)(H<sub>2</sub>O)]<sup>-</sup> и [Cu(ed3a)(H<sub>2</sub>O)]<sup>-</sup> изоморфни и да сличност прелази готово у идентичност (грешка преклапања RMS = 0,0460), а екстракцијом структура ed3a лиганата из матичних комплекса никла и бакра и њиховим преклапањем употребом Hyperchem програма нађено је још боље слагање (RMS = 0,0124).

Разлог оваквог понашања ed3a лиганата треба тражити у крајње неочекиваном присуству три петочлана прстена у екваторијалној равни комплексног јона (два ацетатна и један диамински). Ово има за последицу присуство израженог напона у равни тако да код свих до сада добијених ed3a комплекса [*M* = Co(III), Cr(III), Cu(II)] [1, 3-4] доминира *cis*-екваторијални изомер (два петочлана прстена у екваторијалној равни).

[1] N. Sakagami, S. Kaizaki, *J. Chem. Soc., Dalton Trans.* (1992), 291

[2] M. J. Frisch et al., Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford, CT, 2004

[3] Z. Matovic, A. Meetsma, V. Miletic, P. van Koningsbruggen, *Inorg. Chim. Acta* 360 (2007) 2420

[4] D. Radanović, *Coord. Chem. Rev.*, 54 (1984), 159

## META-AUTUNITE FROM A LI-PEGMATITE OF THE CER Mt., SERBIA

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Meta-autunites from a Li-pegmatite mineralization of the Cer Mt. granitoid massif near Šabac have been investigated as the first occurrence of this mineral in Serbia. The crystals of 1–2 mm in diameter appear as yellow plates. The mineral was found in a Li-pegmatite zone of the locality Konjuša (NE from the top Trojanov grad, 607 m) associated with albite, quartz, spodumene, mica, garnet, tourmaline and columbite-tantalite minerals.

Chemical composition of meta-autunite was determined by SEM/EDX analysis, and confirmed that it is a Ca-member. The water in the structure of the mineral was characterized by IR spectroscopy. Even though meta-autunite shows intensive cleavage parallel to (001), single crystal X-ray diffraction measurements taken on several crystals revealed its tetragonal symmetry, space group  $P4/nmm$  (129),  $a = 6.989(4)$ ,  $c = 8.433(6)$  Å. The structure solution easily revealed the uranyl and phosphate polyhedral layer similar to that in autunite structure [1] and nearly identical to the one found in [2]. On the other hand, the absence of significant positive peaks in differential Fourier map as well as the abrupt decrease of the intensity of the reflections with increasing diffraction angle lead us to the conclusion that the  $\text{Ca}^{2+}$  cations and  $\text{H}_2\text{O}$  molecules found between the two successive  $[(\text{UO}_2)(\text{PO}_4)]^-$  layers are strongly disordered, as it was the case in previous investigations of meta-autunite structure [2].

Consequently, the meta-autunite from Cer Mt. locality was investigated using the Rietveld X-ray powder pattern fitting method. The results obtained confirmed the known tetragonal symmetry and unit cell dimensions. Meanwhile, XRPD experiment revealed the inhomogeneity of the meta-autunite investigated. By using the Le Bail method, it was shown that the observed powder pattern consists of three tetragonal hydrate phases with different  $c$  unit cell parameters, evidenced for the first time.

[1] A. Locock, P. Burns, *Am. Mineral.*, 88 (2003), 240–244

[2] E. S. Makarov, V. I. Ivanov, *Doklady Akad. Nauk. SSSR*, 132 (1960), 673–676



## META-AUTUNIT IZ Li-PEGMATITA PLANINE CER, SRBIJA

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Meta-autuniti iz Li-pegmatitske mineralizacije granitoidnog masiva planine Cer kraj Šabca ispitivan je kao prva pojava ovog minerala u Srbiji. Oni se pojavljuju kao žuti pločasti kristali 1-2 mm u prečniku. Mineral se nalazi u asocijaciji sa albitom, kvarcom, spodumenom, liskunima, granatom, turmalinom i mineralima iz serije kolumbit-tantalit u Li-pegmatitskoj zoni lokaliteta Konjuša (SI od kote Trojanov grad, 607 m).

Hemijski sastav meta-autunita određen je SEM/EDX analizom i utvrđeno je da je Ca-član. IC spektroskopija je korišćena za karakterizaciju vode u strukturi ovog minerala. Meta-autunit pokazuje savršenu cepljivost paralelno (001). Rendgenskom difrakcijom na nekoliko monokristala određena je tetragonalna simetrija, prostorna grupa  $P4/nmm$  (129),  $a = 6,989(4)$ ,  $c = 8,433(6)$  Å. Rešavanjem kristalne strukture otkriven je sloj koji grade koordinacioni poliedri urana i fosfora, sličan sloju u strukturi autunita [1] i gotovo identičan sloju određenom u ranijem ispitivanju [2]. Sa druge strane, odsustvo maksimuma u diferentnoj Furijeovoj mapi, kao i naglo opadanje intenziteta refleksija sa povećanjem difrakcionog ugla ukazuju na neuređenost  $Ca^{2+}$  katjona i  $H_2O$  molekula koji se nalaze između dva susedna  $[(UO_2)(PO_4)]^-$  sloja, kao što je to bio slučaj u prethodnom ispitivanju strukture meta-autunita [2].

Meta-autunit iz lokaliteta planine Cer ispitan je i Ritveldovom metodom. Dobijeni rezultati potvrdili su tetragonalnu simetriju i parametre jedinične ćelije. Međutim, rendgenska difrakcija na prahu je otkrila nehomogenost ispitivanog meta-autunita. Fitovanje Le Belovom (Le Bail) metodom po prvi put je pokazano da se dijagram praha sastoji od tri tetragonalne hidratne faze različitog  $c$ -parametra jedinične ćelije.

[1] A. Locock, P. Burns, *Am. Mineral.*, 88 (2003), 240–244

[2] E. S. Makarov & V. I. Ivanov, *Doklady Akad. Nauk. SSSR*, 132 (1960), 673–676

## HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURE OF $\text{Cd}_{1.16}\text{Zn}_{2.34}(\text{AsO}_4)(\text{HAsO}_4)_2$

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Using hydrothermal method (Teflon-lined steel autoclave,  $T = 473$  K, 72 hours) title compound crystallised as colourless prismatic crystals up to 100  $\mu\text{m}$  in length from an aqueous mixture of  $\text{Cd}(\text{OH})_2$ ,  $5\text{ZnO} \cdot 2\text{CO}_3 \cdot 4\text{H}_2\text{O}$  and  $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ . The crystal structure was refined using single-crystal X-ray diffraction data (CCD detector,  $\text{MoK}\alpha$  radiation, 298 K,  $2\theta_{\text{max}} = 52.74^\circ$ ). The refinement on  $F^2$  (146 free parameters) yielded  $R_1 = 0.0253$ ,  $wR_2 = 0.0416$  using 1939 unique reflections; for 1787 observed reflections with  $I \geq 2\sigma(I)$ ,  $R_1 = 0.0206$ . *Crystal data:* space group  $C2$ ,  $a = 12.2496(4)$ ,  $b = 12.4915(3)$ ,  $c = 6.8156(2)$  Å,  $\beta = 113.6220(2)^\circ$ ,  $V = 955.51(5)$  Å<sup>3</sup>,  $Z = 2$ . The crystal structure was solved from a racemic twin ( $x = 0.50(2)$ ). All H atoms were found in a difference Fourier map and successfully refined as riding atoms, with restraints on the O–H bond distances of 0.82(2) Å.  $U_{\text{iso}}(\text{H})$  values were fixed at 1.5  $U_{\text{eq}}(\text{O})$ .

$\text{Cd}_{1.16}\text{Zn}_{2.34}(\text{AsO}_4)(\text{HAsO}_4)_2$  is related to the alluaudite-like compounds. They adopt general formula  $A1A2M1M2_2(X1O_4)(HX2O_4)_2$ . In minerals,  $A$ -position is mostly occupied with Na, Ca, Mn,  $M$ -position with Mn, Fe, Al, Mg, and  $X$  with P. Synthetic members show much broader chemical variability. Alluaudites crystallise monoclinic, and the most common space group is  $C2/c$ . The crystal structure consists of kinked chains of edge-sharing  $M1$  and  $M2$  octahedra that are stacked parallel to  $[101]$  and are connected by the  $X1O_4$  and  $HX2O_4$  tetrahedra in the  $b$ -direction. These interconnected chains form channels parallel to  $c$ -axis, where the large  $A1$  and  $A2$  cations are located.

The new compound represents previously unknown structure variant among alluaudites. The symmetry reduction from  $C2/c$  to  $C2$  was noticed and it is probably the consequence of the incorporation of different cation types and quantities. In the  $\text{Cd}_{1.16}\text{Zn}_{2.34}(\text{AsO}_4)(\text{HAsO}_4)_2$  site  $A1$  is empty. In the  $A2$  site are situated Cd atoms. The  $M1$  site is shared between Zn and Cd, and the  $M2$  site is filled with Zn.

*Financial support of the Austrian Science Foundation (FWF) (Grant T 300-N19) and the Ministry for Science and Technological Development of the Republic of Serbia (Project Nos. 142030 and 19002) are gratefully acknowledged.*

## ХИДРОТЕРМАЛНА СИНТЕЗА И КРИСТАЛНА СТРУКТУРА



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Безбојни призматични кристали величине до 0,10 mm добијени су као производ реакције између компонената  $\text{Cd}(\text{OH})_2$ ,  $5\text{ZnO} \cdot 2\text{CO}_3 \cdot 4\text{H}_2\text{O}$  и  $3\text{As}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$  уз додатак дестиловане воде. Кристали су синтетисани хидротермалном методом у тефлонским судовима у аутоклавима (473 K, 72 h). Прикупљени су дифракциони подаци на монокристалу (Мо Ка рендгенско зрачење, CCD равни детектор, 298 K,  $2\theta_{\text{max}} = 52,74^\circ$ ) и утањена је структура. Утањивањем 146 параметра добијени су следећи R-параметри:  $R_1 = 0,0253$ ,  $wR_2 = 0,0416$  за укупно 1939 рефлексије и  $R_1 = 0,0206$  за 1787 рефлексија са  $I \geq 2\sigma(I)$ . Кристалографски подаци: просторна група C2,  $a = 12,2496(4)$ ,  $b = 12,4915(3)$ ,  $c = 6,8156(2)$  Å,  $\beta = 113,6220(2)^\circ$ ,  $V = 955,51(5)$  Å<sup>3</sup>,  $Z = 2$ . Важно је напоменути да се током утањивања структуре дошло до закључка да је реч о рацематском близанцу ( $x = 0,50(2)$ ). Положаји водоника утањени су коришћењем благих ограничења O—H везе од 0,82(2) Å. Термални параметри водоника су били фиксирани на вредност која је 1,5 већа од термалних параметара носећих атома кисеоника (модел јашућег атома).

$\text{Cd}_{1,16}\text{Zn}_{2,34}(\text{AsO}_4)(\text{HAsO}_4)_2$  има структуру сличну минералу алуаудиту. Општа формула алуаудита је  $A1A2M1M2_2(X1O_4)(HX2O_4)_2$ . У минералима A-положаје најчешће заузимају Na, Ca, и Mn, M-положаје Mn, Fe, Al и Mg, а X = P, док је у синтетичким једињењима са алуаудитским типом структуре хемијска разноврсност много већа. Алуаудити кристалишу моноклинично, најчешће у просторној групи C2/c. Тродимензионалну мрежу чине извијени ланци M1-октаедара и парова M2-октаедара, који деле заједничке ивице и пружају се дуж правца [101], а међусобно су повезани X1O<sub>4</sub> HX2O<sub>4</sub>-тетраедрима и формирају слојеве нормалне на b-осу. Кроз повезане слојеве 3D мреже протежу се канали дуж осе c у којима су смештени велики A1 и A2 катјони. Новосинтетисано једињење представља до сада непознати структурни варијетет алуаудита. Разлика у врсти и количини катјона највероватније је условила да се симетрија редукује са просторне групе C2/c до C2. A1 положај у  $\text{Cd}_{1,16}\text{Zn}_{2,34}(\text{AsO}_4)(\text{HAsO}_4)_2$  је празан. У положају A2, смештени су атоми кадмијума. Положај M1 је мешовит између цинка и кадмијума, док је положај M2 немешовит и припада само цинку.

Аутори овог рада захваљује се Научном Фонду Републике Аустрије (FWF) (Пројекат Т300-N19) и Министарству науке и технолошког развоја Републике Србије (Пројекти 142030 и 19002) на финансијској помоћи.

## TITANIUM OXIDE MATERIALS FOR GREENER ENVIROMENT

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<sup>a</sup>Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia; <sup>b</sup>Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia; <sup>c</sup>IHIS, Science and Technology Park Zemun a.d., Research and Development Centre, Batajnički put 23, 11080 Belgrade, Serbia; <sup>d</sup>Institute of Technical Sciences of the SASA, 11000 Belgrade, Knez Mihailova 35, 11000 Belgrade, Serbia; <sup>e</sup>Centre for Multidisciplinary Studies, University of Belgrade, Kneza Višeslava 1a, 11000 Belgrade, Serbia  
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Pollution, or contamination of environment by man-made substances, tends to become a major problem of our civilization. There are many types of pollution, although in this work we will mention only three: air, water and land/soil pollution, and discuss possible solutions for it. Major sources of air contamination are motor vehicle exhaust, as well as heat and power generator facilities. For water pollution the most dangerous are hazard industries, petroleum products and agricultural chemicals, while land/soil is mainly damaged by mining and agriculture.

Titanium oxides are very promising materials to solve multiple environmental problems due to its properties, relatively low price, and various potential or commercial applications. Titanium dioxide (anatase) has photocatalytic properties. Photocatalysis is a well-known process mostly in use to degrade or transform organic and inorganic compounds, e.g. for water purification. Anatase is also a good candidate for dye sensitized solar cells. A mixture of some other titanium oxides known as Ebonex<sup>®</sup> is used as commercial electrode material, for the last 20–30 years. This material satisfy roughly all conditions to be a bipolar plate in bipolar lead acid batteries. Another solution for electric or hybrid vehicles are Li-ion batteries in which for negative electrodes lithium titanium oxides, especially  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , have many advantages.

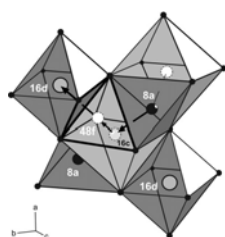


Fig.1: Crystal structure of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

Our current studies dedicated to synthesis, characterisation and possible application of mentioned materials will be present in this work. Mechanochemical and/or hydrothermal treatment followed by solid state reactions were applied for synthesis. Samples were characterised by XRPD, TG/DTA, SEM/EDS and particle size analysis. Quality of hydrothermally prepared anatase powder was investigated by degradation of C.I. Reactive Orange 16 dye under UV illumination. The prepared mixtures of Magnéli oxides identical or similar to Ebonex<sup>®</sup> powder were proceeded into plastic-bonded foil electrodes using low density polyethylene or polyethylene glycol. The electrodes were tested for corrosion stability in real lead acid accumulator conditions and their conductivity was measured. Lithium titanium oxides were prepared by solid state reactions and hydrothermal lithiation of anatase and rutile using different concentrations of LiOH. The samples were characterized by XRPD in order to define the capacity of intercalation and Li ion diffusion pathways.

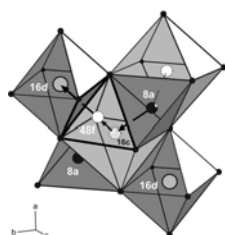
## OKSIDI TITANA – MATERIJALI ZA ZDRAVIJU ŽIVOTNU SREDINU

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Zagađenje životne sredine koje je prouzrokovano od strane čoveka sve više postaje ozbiljan problem. Postoji mnogo tipova zagađenja, ali u ovom radu će biti pomenuta samo tri glavna: zagađenje vazduha, vode i zemljišta, kao i moguća rešenja problema. Glavni izvori zagađenja vazduha su izduvni gasovi motornih vozila, energetska postrojenja i toplane, dok su za vodu najštetniji industrijski otpadi i razni pesticidi koji se koriste u poljoprivredi. Zagađenje zemljišta uglavnom prouzrokuju jalovine iz rudnika i poljoprivredne aktivnosti.

Zbog svojih osobina, relativno niske cene i mogućih ili komercijalnih upotreba, materijali bazirani na oksidima titana mogu višestruko da smanje problem zagađenja. Titan dioksid (anatas) je fotokatalizator, što možemo iskoristiti za uklanjanje raznih organskih i neorganskih otpada iz vode uz pomoć UV zračenja. Osim toga, dobar je kandidat za upotrebu u „dye sensitized“ solarnim ćelijama. Smeša nekih drugih oksida titana, poznata kao Ebonex<sup>®</sup>, u komercijalnoj je upotrebi poslednjih 20–30 godina, sa svojim karakteristikama zadovoljava skoro sve uslove da se koristi i kao strujni kolektor bipolarno konstruisanog olovnog akumulatora. Ovo bi naravno moglo da omogući manje aerozagađenje koje potiče od izduvnih gasova prevoznih sredstava. Druga opcija za električne i hibridne automobile su litijum–jonske baterije gde litijum-titan-oksidi, posebno  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , pokazuju određene prednosti u odnosu na ostale materijale.



Sl. 1: Kristalna struktura  $\text{Ti}_2\text{O}_3$ .

U ovom radu će biti prikazana naša dosadašnja ispitivanja pomenutih materijala koja uključuju sinteze, karakterizaciju i ispitivanja potencijalne primene. Sinteze su uglavnom izvođene mehanohemijskim i/ili hidrotermalnim tretmanom praćenim reakcijama u čvrstom stanju. Uzorci su karakterisani XRPD, TG/DTA, SEM/EDS analizama, a određivana je i raspodela veličine čestica. Mogućnost primene pripremljenog anatasa proverena je razgradnjom narandžaste boje (C. I. Reactive Orange 16) pod UV zračenjem. Od pripremljenih smeša Manjelijevih oksida koje su slične komercijalnom Ebonex<sup>®</sup> prahu napravljeni su tzv. „plastic-bonded“ strujni kolektori koristeći polietilen niske gustine ili polietilenglikol kao vezivo. Izvršena su ispitivanja korozione stabilnosti ovih strujnih kolektora u uslovima karakterističnim za olovni akumulator, a merena je i provodnost uzoraka. Uzorci litijum-titan-oksida pripremani su reakcijama u čvrstom stanju ili hidrotermalnom litijacijom anatasa i rutila pomoću LiOH različitih koncentracija. Uzorci su karakterisani XRPD analizom u cilju definisanja kapaciteta interkalacije i puteva difuzije litijum jona.



**POSTER PRESENTATIONS**

**ПОСТЕРСКА СЕКЦИЈА**

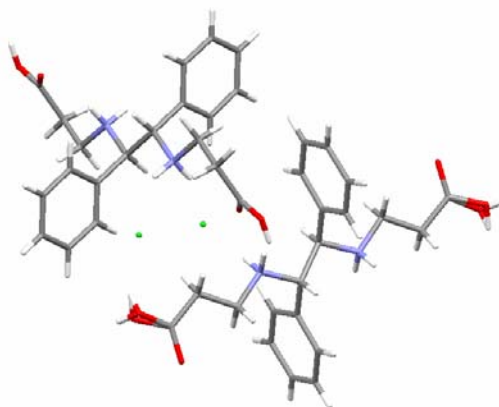
## CRYSTAL STRUCTURE OF 1,2-DIPHENYL-ETHYLENEDIAMINE-*N,N'*-DI-3-PROPANOIC ACID DIHYDROCHLORIDE

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Z. Ratković<sup>a</sup>, S. R. Trifunović<sup>a</sup>**

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Tetradentate ligand 1,2-diphenyl-ethylenediamine-*N,N'*-di-3-propanoic acid, (H<sub>2</sub>-1,2-dphedp) was prepared by direct reaction between 3-chloro-propanoic acid and 1,2-diphenyl-ethylenediamine in a molar ratio 2:1. The title compound was obtained as dihydrochloride from mother solution after acidification up to pH = 1. Crystals suitable for X-ray crystal structure analysis were obtained by slowly evaporation from an ethanol-water solution of H<sub>2</sub>-1,2-dphedp·2HCl.

The compound crystallizes as a dimer with three water molecules and four molecules of HCl. Crystallographic data: C<sub>40</sub>H<sub>52</sub>N<sub>4</sub>O<sub>11</sub>Cl<sub>4</sub>, triclinic system, space group  $P\bar{1}$ ,  $a = 8.699(2)$ ,  $b = 10.086(2)$ ,  $c = 13.461(2)$  Å,  $\alpha = 104.14(2)$ ,  $\beta = 105.79(2)$ ,  $\gamma = 100.75(2)$ °,  $V = 1060.6(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 1.420$  g cm<sup>-3</sup>,  $\mu(\text{CuK}\alpha) = 3.076$  mm<sup>-1</sup>,  $F(000) = 476$ ,  $\alpha = 1.5418$  Å. Data collection:  $3.513^\circ < \theta < 70.626^\circ$ , number of parameters: 282,  $R_1 = 0.107$ ,  $wR_1 = 0.327$  for 4006 reflections with  $I > 2\sigma(I)$ .





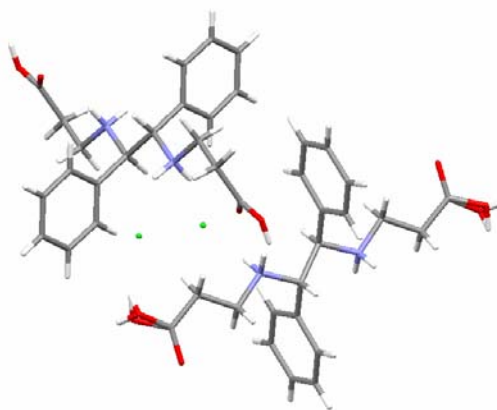
## KRISTALNA STRUKTURA 1,2-DIFENIL-ETILENDIAMIN-*N,N'*-DI- -3-PROPANSKE KISELINE DIHIDROHLORIDA

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Tetradentatni ligand 1,2-difenil-etilendiamin-*N,N'*-di-3-propanska kiselina, (H<sub>2</sub>-1,2-dpheddp) pripremljen je reakcijom između 3-hlor-propanske kiseline i 1,2-difenil-etilendiamina u molskom odnosu 2:1. Jedinjenje je dobijeno kao dihidrohlorid iz matičnog rastvora zakiseljavanjem do pH = 1. Kristali pogodni za rendgensku strukturnu analizu dobijeni su sporim uparavanjem voda-etanolskog rastvora H<sub>2</sub>-1,2-dpheddp·2HCl.

Dobijeno jedinjenje je kristalísalo kao dimer sa tri molekula vode i četiri molekula HCl. Kristalografski podaci: C<sub>40</sub>H<sub>52</sub>N<sub>4</sub>O<sub>11</sub>Cl<sub>4</sub>, triklinički sistem, prostorna grupa  $P\bar{1}$ ,  $a = 8,699(2)$ ,  $b = 10,086(2)$ ,  $c = 13,461(2)$  Å,  $\alpha = 104,14(2)$ ,  $\beta = 105,79(2)$ ,  $\gamma = 100,75(2)$  °,  $V = 1060,7(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc.}} = 1,420$  g cm<sup>-3</sup>,  $\mu(\text{CuK}\alpha) = 3,076$  mm<sup>-1</sup>,  $F(000) = 476$ ,  $\lambda = 1,54184$  Å. Opseg snimanja:  $3,513^\circ < \theta < 70,625^\circ$ , broj parametara: 282,  $R_1 = 0,107$ ,  $wR_1 = 0,327$  za 4006 refleksija sa  $I > 2\sigma(I)$ .



**HYDROTHERMAL SYNTHESIS OF  $M1$ – $M2$ –H–VANADATES**  
**( $M1 = \text{Ca}^{2+}, \text{Pb}^{2+}, M2 = \text{Mn}^{2+,3+}, \text{Fe}^{2+,3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}$ ):**  
**CRYSTAL STRUCTURE OF  $(\text{Zn}_{1.86}\text{Cd}_{0.14})(\text{VO}_4)(\text{OH})$**

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The investigations on hydrothermal synthesis and crystal-chemistry of synthetic vanadates compounds in the system  $M1^{2+}$ – $M2^{2+}$ –V–O–(H) ( $M1^{2+} = \text{Ca}, \text{Pb}; M2^{2+} = \text{Mn}, \text{Fe}, \text{Ni}, \text{Co}, \text{Cu}, \text{Zn}, \text{Cd}$ ) were performed at Faculty of Mining and Geology, University of Belgrade between December 2009 and March 2010. Up to now, only 12 members of this system are known of which four are anhydrous compounds, where  $M1 = \text{Ca}$ . From eight members with  $M1 = \text{Pb}$  four are hydrated and found as minerals.

During the study, seven syntheses have been performed in parallel runs using up to 12 autoclaves and 78 different mixtures of oxides, hydroxides, carbonates, nitrates, chlorides, sulphates of the relevant  $M1$  and  $M2$  cations and  $\text{V}_2\text{O}_5$ . The vanadate compounds were synthesized under autogeneous pressure in Teflon-lined stainless steel autoclaves at temperatures ranging from 160 to 200 °C (7 - 14 days, pH > 5, distilled water as a medium).

All crystalline compounds from the first 54 mixtures were tested by single-crystal X-ray diffraction. As a result 2 new compounds,  $(\text{Zn}_{1.86}\text{Cd}_{0.14})(\text{VO}_4)(\text{OH})$  and  $\text{Zn}_5(\text{VO}_4)_2(\text{OH})_4$ , in addition to the 12 previously known ones, were obtained. However, none of them contains both  $M1$  and  $M2$  ions in its crystal structure. This is probably a consequence of the low solubility of the used  $M1$ -salts, which were mostly oxides and hydroxides. In the new synthesis performed in March 2010, small amounts ( $\sim 0.2 \text{ cm}^3$  pro mixture) of ethylenediamine were used in order to increase the pH value of the mixtures and improve the solubility of the starting and/or intermediate compounds.

New zinc cadmium vanadate  $(\text{Zn}_{1.86}\text{Cd}_{0.14})(\text{VO}_4)(\text{OH})$  is orthorhombic, s. g.  $Pnma$  ( $a = 14.702(3)$ ,  $b = 6.0511(12)$ ,  $c = 8.9469(18)$  Å,  $V = 759.8(3)$  Å<sup>3</sup>,  $Z = 4$ ). It is isostructural with adamite-type phases  $[\text{Zn}_2(\text{XO}_4)(\text{OH})]$ ,  $\text{X}^{5+} = \text{P}, \text{As}, \text{V}$  and topologically related to the minerals descloizite  $\text{PbZn}(\text{VO}_4)(\text{OH})$  and tsumcorite  $\text{PbZn}_2(\text{AsO}_4)_2(\text{H}_2\text{O})$  [1 and references therein]. In its crystal structure,  $[\text{Zn}_3\text{O}_6]_n$  octahedral chains are interconnected by  $\text{VO}_4$  tetrahedra to form a  $[\text{Zn}_3(\text{OH})\text{VO}_4]$  framework. The voids are filled by  $\text{Zn1/Cd1}$  and  $\text{Zn2}$  cations with octahedral and trigonal bipyramidal coordination, respectively.

*Financial support of the Austrian Science Community (ÖFG) (Grant MOEL 413) and the Ministry for Science and Technological Development of the Republic of Serbia (Projects Nos. 142030 and 19002) are gratefully acknowledged.*

[1] X. Wang, L. Liu, A. J. Jacobson, *Z. Anorg. Allg. Chem.*, 624 (1998), 1977-1981.

**ХИДРОТЕРМАЛНА СИНТЕЗА  $M1-M2-H$ -ВАНАДАТА  
( $M1 = Ca^{2+}, Pb^{2+}, M2 = Mn^{2+,3+}, Fe^{2+,3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$ ):  
КРИСТАЛНА СТРУКТУРА  $(Zn_{1,86}Cd_{0,14})(VO_4)(OH)$**

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Хидротермална синтеза и кристалохемијска испитивања супстанци из система  $M1^{2+}-M2^{2+}-V-O-(H)$  ( $M1^{2+} = Ca, Pb; M2^{2+} = Mn, Fe, Ni, Co, Cu, Zn, Cd$ ) урађени су на Рударско-геолошком Факултету Универзитета у Београду у периоду од 1. децембра 2009. до 1. марта 2010. године. Систем броји 12 познатих супстанци од којих су 4 безводни представници са  $M1 = Ca$ . Од преосталих осам чланова са  $M1 = Pb$ , четири су минерали и само су они хидратисани.

У току ове студије урађено је седам синтеза. Као почетни материјал за синтезу коришћено је 78 различитих мешавина оксида, хидроксида, карбоната, нитрата, хлорида и сулфата  $M1$  и  $M2$  катјона са  $V_2O_5$ . Синтезе су рађене у распону температура од 160 до 200 °C под аутогеним притиском у тефлонским судовима који су били стављени у аутоклаве од нерђајућег челика (7 – 14 дана, pH > 5, дестилована вода је коришћена као растварач).

Кристални материјал из првих 54 мешавина испитан је уз помоћ рендгенске дифракције на монокристалу. Нађене су две нове супстанце:  $(Zn_{1,86}Cd_{0,14})(VO_4)(OH)$  и  $Zn_5(VO_4)_2(OH)_4$ . Нажалост, ни једна од њих нема и  $M1$  и  $M2$  у својој структури. То је вероватно последица слабе растворљивости коришћених оксида и хидроксида  $M1$ . У циљу повећавања pH почетних мешавина и самим тим повећавања растворљивости почетних супстанци и међупроизвода насталих у току синтеза урађеним марта 2010. коришћене су мале количине (~ 0.2 cm<sup>3</sup> по мешавини) етилендиамина.

$(Zn_{1,86}Cd_{0,14})(VO_4)(OH)$  кристалише ромбично, п. г. *Pnma* ( $a = 14,702(3)$ ,  $b = 6,0511(12)$ ,  $c = 8,9469(18)$  Å,  $V = 759,8(3)$  Å<sup>3</sup>,  $Z = 4$ ). Изоструктуран је са сустанцама из групе адамита  $[Zn_2(XO_4)(OH)]$ ,  $X^{5+} = P, As, V$  и тополошки сличан са минералима десклозитом  $PbZn(VO_4)(OH)$  и цумкуруитом  $PbZn_2(AsO_4)_2(H_2O)$  [1 и цитирана литература]. Његова кристална структура изграђена је од октаедарских  $[Zn_3O_6]_n$  ланца повезаних преко  $VO_4$  тетраедара у  $[Zn_3(OH)VO_4]$  мрежу. Шупљине су попуњене  $Zn1/Cd1$  и  $Zn2$  катјонима који имају октаедарску и тригонално-бипирамидалну координацију.

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[1] X. Wang, L. Liu, A. J. Jacobson, *Z. Anorg. Allg. Chem.*, 624 (1998), 1977-1981.

## THEORETICAL STUDY OF O-H... $\pi$ AND N-H... $\pi$ INTERACTIONS WITH ACETYLACETONATO CHELATES

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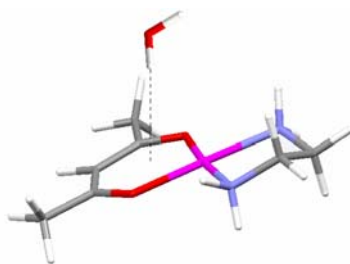
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The noncovalent interactions of  $\pi$ -systems have been extensively studied in recent years. They are important for many molecular systems from molecular biology to crystal engineering [1]. It has been observed that planar chelate rings with delocalized  $\pi$ -bonds can be involved in noncovalent interactions in a manner similar to that in organic aromatic rings, indicating that the chelate rings could have aromatic character. CH/ $\pi$  interactions with acetylacetonato chelates were described in our previous papers [2,3].

In this work we report on OH/ $\pi$  and NH/ $\pi$  interactions with acetylacetonato ligands in transition metal complexes. Both interactions were studied by searching and analyzing crystal structures in the Cambridge Structural Database (CSD) and by quantum chemical calculations. Quantum chemical calculations were done on model systems. The systems were made from the crystal structures of acetylacetonato complexes in the way that large groups in complexes were substituted by hydrogen atoms and the energies were calculated for interactions of these systems with water and ammonia molecules.

A number of crystal structures with both types of interactions were found in CSD. Quantum chemical calculations on a few model systems show that energies of OH/ $\pi$  and NH/ $\pi$  interactions with acetylacetonato chelate ring are similar to energies of CH/ $\pi$  interactions.



[1] T. Steiner, *Angew. Chem.* 41 (2002), 48-76

[2] M. K. Milcic, V. B. Medakovic, D. N. Sredojevic, N. O. Juranic, S. D. Zarić, *Inorg. Chem.* 45 (2006), 12.

[3] G. A. Bogdanovic, A. Spasojevic-de Bire, S. D. Zarić, *Eur. J. Inorg. Chem.* (2002) 1599-1602.

## ТЕОРИЈСКО ПРОУЧАВАЊЕ О-Н/ $\pi$ И N-Н/ $\pi$ ИНТЕРАКЦИЈА СА АЦЕТИЛАЦЕТОНАТНИМ ХЕЛАТИМА

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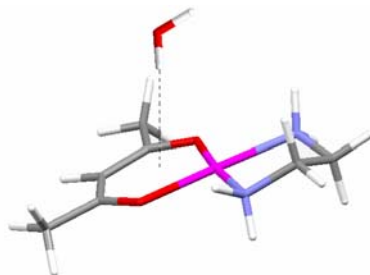
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Последњих година нековалентне интеракције  $\pi$ -система предмет су интензивног проучавања. Оне имају велики значај за многе молекулске системе, од молекуларне биологије до кристалног инжењеринга [1]. Примећено је да планарни хелатни прстенови са делокализованим  $\pi$ -везама могу да учествују у нековалентним интеракцијама на сличан начин као и органски ароматични прстенови, што указује на то да би ови хелатни прстенови могли имати ароматичан карактер. СН/ $\pi$  интеракције са ацетилацетонатним хелатима описане су у нашим ранијим радовима [2,3].

У овом раду проучавали смо ОН/ $\pi$  и NH/ $\pi$  интеракције са ацетилацетонатним лигандима у комплексима прелазних метала. Обе врсте интеракција проучаване су претрагом и анализирањем кристалних структура преузетих из Кембричке банке података (CSD) и помоћу квантно хемијских прорачуна. Квантно хемијски прорачуни су извршени на модел системима. Системи су направљени на основу кристалних структура ацетилацетонатних комплекса тако што су веће групе замењене атомима водоника, а потом су израчунате интеракције оваквих система са молекулима воде и амонијака.

У Кембричкој банци података пронађене су структуре за оба типа интеракција. Квантно хемијски прорачуни извршени на неколико модел система показали су да су енергије ОН / $\pi$  и NH/ $\pi$  интеракција са ацетилацетонатним хелатима сличне као и енергије као и СН/ $\pi$  интеракција.



[1] T. Steiner, *Angew. Chem.* 41 (2002), 48-76

[2] M. K. Milcic, V. B. Medakovic, D.N. Sredojevic, N.O. Juranic, S.D. Zanic, *Inorg.Chem.* 45 (2006), 12.

[3] Bogdanovic GA, Spasojevic-de Bire A, Zanic SD *Eur. J. Inorg. Chem.* 2002, 1599-1602.

# CHELATE-CHELATE STACKING INTERACTIONS IN CRYSTAL STRUCTURES OF SQUARE-PLANAR TRANSITION METAL COMPLEXES

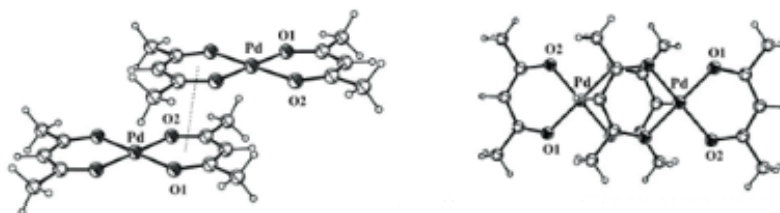
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Noncovalent interactions of aromatic and other  $\pi$ -systems are very important in various molecular systems, from biomolecules to crystal engineering [1]. In transition metal complexes planar chelate rings with delocalized  $\pi$ -bonds can form stacking interactions similar to aromatic organic molecules. Our previous results show that stacking interactions between chelate and C<sub>6</sub>-aromatic rings exist in crystal structures of square-planar transition-metal complexes [2-4].

In this work we found evidences of chelate-chelate stacking interactions analyzing crystal structures from the Cambridge Structural Database (CSD). Our study showed that chelate-chelate stacking interactions occur in large number of crystal structures of neutral square-planar complexes that possess planar five and/or six-membered chelate rings. We separately analyzed structures with isolated and fused chelate rings because size of the planar system has influence on the stacking interactions.

By searching the Cambridge Structural Database (CSD), using the defined search criteria, 2322 structures of square-planar complexes in which chelate rings are part of extended  $\pi$ -system were found, while in 892 of these structures we observed stacking interactions between two chelate rings. In case of isolated chelate rings 151 structures were found and in 63 of them there are stacking interactions between chelate rings. In crystal structures with fused chelate rings there are three main conformations of interacting chelate rings: *parallel*, *cross* and *antiparallel*, while in structures with isolated chelate rings there are very small number of examples with *cross* conformations.



- [1] T. Steiner, *Angew. Chem. Int. Ed.* 41 (2002), 48-76.  
[2] Z. D. Tomić, D. N. Sredojević, S. D. Zarić, *Cryst. Growth Des.* 6 (2006), 29-31.  
[3] D. N. Sredojević, Z. D. Tomić, S. D. Zarić, *Cent. Eur. J. Chem.* 5 (2007), 20-31.  
[4] D. N. Sredojević, G.A. Bogdanović, Z. D. Tomić, S. D. Zarić, *CrystEngComm.* 9 (2007) 793-798.

# HELAT-HELAT STEKING INTERAKCIJE U KRISTALNIM STRUKTURAMA KVADRATNO-PLANARNIH KOMPLEKSA PRELAZNIH METALA

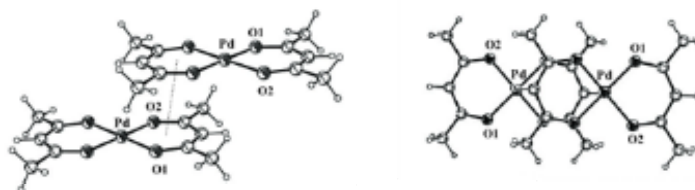
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Nekovalentne interakcije aromatičnih i drugih  $\pi$ -sistema igraju veoma važnu ulogu u različitim molekulskim sistemima od biomolekula do kristalnog inženjeringa [1]. U kompleksima prelaznih metala planarni helatni prstenovi sa delokalizovanim  $\pi$ -vezama mogu da grade steking interakcije slično aromatičnim organskim molekulima. Naši predhodni rezultati su pokazali da se steking interakcije između helatnih i C<sub>6</sub>-aromatičnih prstenova javljaju u kristalnim strukturama kvadratno-planarnih kompleksa prelaznih metala [2-4].

U ovom radu dati su dokazi o postojanju helat-helat steking interakcija analiziranjem kristalnih struktura iz Kembričke strukturne baze podataka (CSD). Naše istraživanje je pokazalo da helat-helat steking interakcije postoje u velikom broju kristalnih struktura neutralnih kvadratno-planarnih kompleksa koji poseduju planarne petočlane ili šestočlane helatne prstenove. Posebno su analizirane strukture sa izolovanim i kondenzovanim helatnim prstenovima zato što veličina planarnog sistema ima uticaja na steking interakcije.

Pretražujući CSD, koristeći definisane kriterijume pretrage, pronađene su 2322 strukture kvadratno-planarnih kompleksa u kojima su helatni prstenovi deo proširenog  $\pi$ -sistema, dok su u 892 strukture pronađene steking interakcije između helatnih prstenova. U slučaju izolovanih helatnih prstenova pronađena je 151 struktura, dok u 63 strukture postoje steking interakcije između helatnih prstenova. U kristalnim strukturama koje poseduju kondenzovane helatne prstenove postoje tri glavne konformacije interagujućih helatnih prstenova: *paralelne*, *prelazne* i *antiparalelne* dok u strukturama sa izolovanim helatnim prstenovima postoji veoma mali broj struktura sa prelaznom konformacijom.



[1] T. Steiner, *Angew. Chem. Int. Ed.* 41 (2002), 48-76.

[2] Z. D. Tomić, D. N. Sredojević, S. D. Zarić, *Cryst. Growth Des.* 6 (2006), 29–31.

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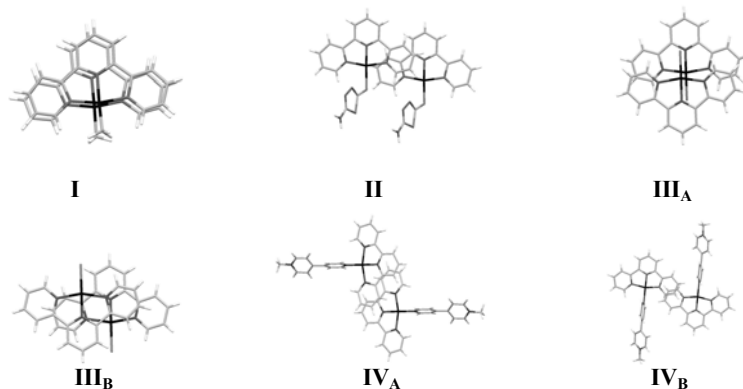
## PACKING CLASSIFICATION OF TERPYRIDYL SQUARE-PLANAR COMPLEXES

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Stacking interactions are generally studied between aromatic organic molecules or fragments, however, other planar molecules and fragments can be also involved in stacking interactions. It was shown that planar chelate rings can form stacking interactions with aromatic organic rings [1]. Recently, we showed that water molecule forms parallel alignment interactions with C<sub>6</sub> aromatic rings [2].

Here we analyze the geometry of  $\pi$ - $\pi$  stacking interactions between the terpyridyl ligands of square-planar transition metal complexes in crystal structures from the Cambridge Structural Database (CSD) [3]. Terpyridine molecule coordinating to a metal ion forms large planar system of five rings, three pyridine fragments and two chelate rings. We classified overlaps of terpyridyl ligands in several types (I, II, III<sub>A</sub>, III<sub>B</sub>, IV<sub>A</sub> and IV<sub>B</sub> type) and analyzed mode of the packing in the crystal structures, where the distance between two centers of pyridine fragments was limited to 4.6 Å. In most of structures, interacting ligands are oriented "head to tail" and the overlapping includes also the chelate ring. The most numerous are interactions with overlap types III<sub>A</sub> and III<sub>B</sub>. Further analysis of packing in crystal structures showed that these stacking interactions form stacking series and dimers.



[1] Z. D. Tomić, D. Sredojević, S. D. Zarić, *Cryst. Growth Des.* 6 (2006), 29–31.

[2] B. D. Ostojić, G. V. Janjić, S. D. Zarić, *Chem. Commun.* 48 (2008), 6546-6548.

[3] G. V. Janjić, J. Andrić, A. Kapor, Ž. D. Bugarčić, S. D. Zarić, *Crystengcomm*, in press.



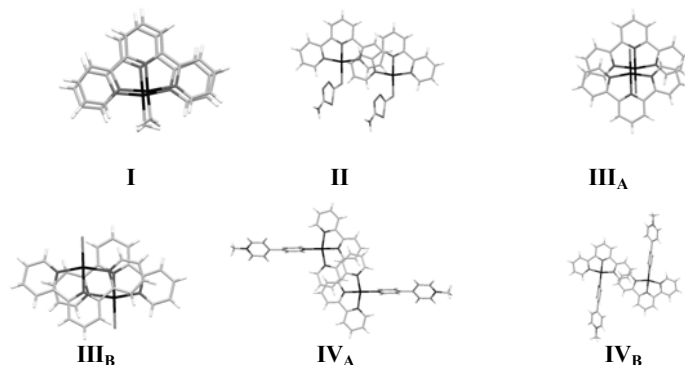
## KLASIFIKACIJA PAKOVANJA TERPIRIDINSKIH KVADRATNO-PLANARNIH KOMPLEKSA

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Steking interakcije uobičajeno su ispitivane između organskih molekula ili fragmenata, mada je primećeno da i drugi planarni molekuli mogu biti uključeni u njih. Naime, pokazano je da planarni helatni prstenovi mogu graditi steking interakcije sa aromatičnim organskim prstenovima [1]. Nedavno, pokazano je da molekul vode, takođe može da se paralelno orijentiše u odnosu na C6- aromatični prsten [2].

U ovom radu prikazani su rezultati geometrijske analize  $\pi$ - $\pi$  steking interakcija između terpiridinskih liganada u kristalnim strukturama kvadratno-planarnih kompleksa [3]. Kristalne strukture su dobijene pretragom Kembričke banke podataka (CSD), a analizirane su samo one strukture u kojima su međumolekulska rastojanja između centara piridinskih fragmenata kraća od 4,6 Å. Molekul terpiridina, koordinovanjem za jon metala, formira veliki planarni system, koji se sastoji od tri piridinska i dva helatna prstena. Klasifikovana su sva preklapanja u nekoliko tipova ( tip I, II, III<sub>A</sub>, III<sub>B</sub>, IV<sub>A</sub> i IV<sub>B</sub>) i analizirani su načini pakovanja u kristalnim strukturama. U većini struktura, interagujući ligandi imaju „glava-rep” orijentaciju, a u preklapanju obično učestvuju i helatni prstenovi. Najbrojnije su interakcija sa III<sub>A</sub> i III<sub>B</sub> tipom preklapanja. U daljoj analizi pokazano je da se interagujući terpiridinski ligandi pakuju tako da formiraju ili steking nizove ili dimere.



[1] Z. D. Tomić, D. Sredojević, S. D. Zarić, *Cryst. Growth Des.* 6 (2006), 29–31.

[2] B. D. Ostojić, G. V. Janjić, S. D. Zarić, *Chem. Commun.* 48 (2008), 6546-6548.

[3] G. V. Janjić, J. Andrić, A. Kapor, Ž. D. Bugarčić, S. D. Zarić, *Crystengcomm*, u štampi

## CRYSTAL AND MOLECULAR STRUCTURE OF [Cr(edda)(acac)] COMPLEX

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The crystal and molecular structure of *s-cis*-[Cr(edda)(acac)] complex (edda = ethylenediamine-N,N'-diacetate, acac = acetylacetonate) has been determined, strong intermolecular hydrogen bonds were found, and the chelate ring conformations were shown to be comparable to those found in other structures containing the Cr(edda)<sup>+</sup> fragment (retrieved from September 2009 update of CSD).

X-ray data were obtained on a monocrystal (0.52×0.42×0.40 mm) at 150 K, with a Bruker SMART 1K CCD diffractometer. The structure is monoclinic, space group P2<sub>1</sub>/c, with unit cell dimensions: *a* = 10.2588(9) Å, *b* = 15.801(3) Å, *c* = 8.7015(11) Å, and β = 101.201(9)°, *Z* = 4. The structure was solved by direct method (SIR97) and refined by full matrix least squares using the SHELXTL program. The result shows a slightly distorted octahedral coordination and symmetrical *cis* (*s-cis*) configuration of edda. All values of bond lengths and valence angles are in agreement with the metric data on all complexes of Cr(III) with edda ligand reported so far. The values of all endocyclic torsional angles in *s-cis*-[Cr(edda)(acac)] show that the chelate ring conformations are almost identical to those found in other structures containing the Cr(edda)<sup>+</sup> fragment.

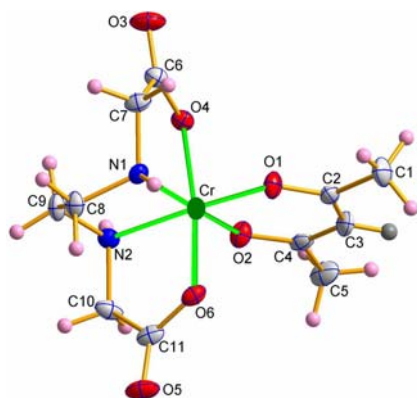


Fig. 1: *s-cis*-[Cr(edda)(acac)]

Each molecule of *s-cis*-[Cr(edda)(acac)] in the crystal structure forms two pairs of strong intermolecular hydrogen bonds (between tertiary NH groups and oxygen ligand atoms of the carboxylic group, thus binding to the neighbouring molecules on both sides. In this way, *s-cis*-[Cr(edda)(acac)] molecules form infinite linear strands parallel to the crystallographic *a* axis, in which the adjacent

molecules have opposite absolute configurations. Achiral (syndiotactic) stereochemistry of the strands is the requirement of the centrosymmetric crystal lattice.

Molecular-mechanics calculations show a slight preference for the *s-cis*-[Cr(edda)(acac)] isomer (approx. 2.05 kcal/mol) with respect to the other theoretically possible isomer, the unsymmetrical-*cis* (*u-cis*), which accounts for the prevalence of *s-cis* configuration in crystal structures.

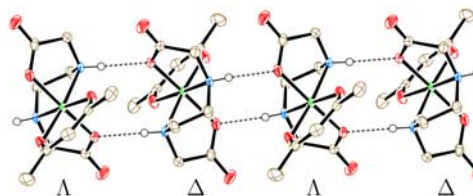


Fig. 2: Hydrogen bonds in *s-cis*-[Cr(edda)(acac)]

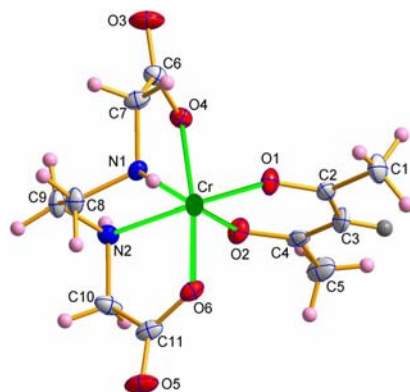
## KRISTALNA I MOLEKULSKA STRUKTURA [Cr(edda)(acac)] KOMPLEKSA

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Opisana je kristalna i molekulska struktura *s-cis*-[Cr(edda)(acac)] kompleksa (edda = etilendiamin-N,N'-diacetat, acac = acetilacetonat), nađene su jake intermolekulske vodonične veze, upoređene su konformacije helatnih prstenova sa onima koje postoje u ostalim strukturama sa koordinovanim Cr(edda)<sup>+</sup> fragmentom (iz CSD od septembra 2009.).

Difraktometrijski podaci dobijeni su na monokristalu (0,52×0,42×0,40 mm) na 150 K, pomoću Bruker SMART 1K CCD difraktometra. Struktura je monoklinična, prostorna grupa je P2<sub>1</sub>/c, a dimenzije jedinične ćelije su *a* = 10,2588(9) Å, *b* = 15,801(3) Å, *c* = 8,7015(11) Å, β = 101,201(9)°, Z=4. Struktura je rešena direktnom metodom (SIR97) i utačnjena pomoću programa SHELXTL. Rezultati pokazuju da je ispitivani kompleks

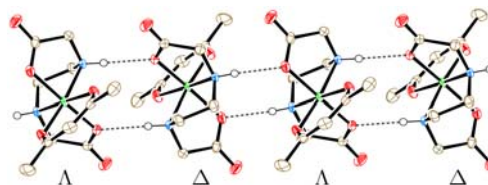


Slika 1. *s-cis*-[Cr(edda)(acac)]

približno oktaedarske strukture i da ima simetričnu-*cis* (*s-cis*) konfiguraciju. Sve vrednosti dužina veza i uglova dobro se slažu sa metričkim podacima svih do sada poznatih kompleksa Cr(III) sa edda ligandom. Vrednosti svih endocikličnih torzionih uglova *s-cis*-[Cr(edda)(acac)] pokazuju da su konformacije helatnih prstenova skoro identične u svim strukturama koje sadrže Cr(edda)<sup>+</sup> fragment.

Svaki molekul *s-cis*-[Cr(edda)(acac)] u kristalnoj strukturi formira dva para jakih intermolekulskih vodoničnih veza, između tercijarne NH grupe i koordinovanog kiseonika karbo-ksilne grupe, čime se vezuje za susedne molekule s obe strane. Na taj način, molekuli *s-cis*-

[Cr(edda)(acac)] formiraju linearne lance koje se prostiru paralelno kristalografskoj *a* osi i u kojima susedni molekuli imaju suprotne apsolutne konfiguracije. Ahiralna (sindiataktična) stereochemija ovih lanaca je uslovljena centrosimetričnom prirodom kristalne rešetke.



Slika 2. Vodonične veze u *s-cis*-[Cr(edda)(acac)]

Molekulsko-mehanički proračuni pokazuju da je *s-cis*-[Cr(edda)(acac)] izomer nešto stabilniji (za 2,05 kcal/mol) od drugog teorijski mogućeg, nesimetričnog *cis* (*u-cis*) izomera, što objašnjava dominantno javljanje *s-cis* konfiguracija u kristalnim strukturama.

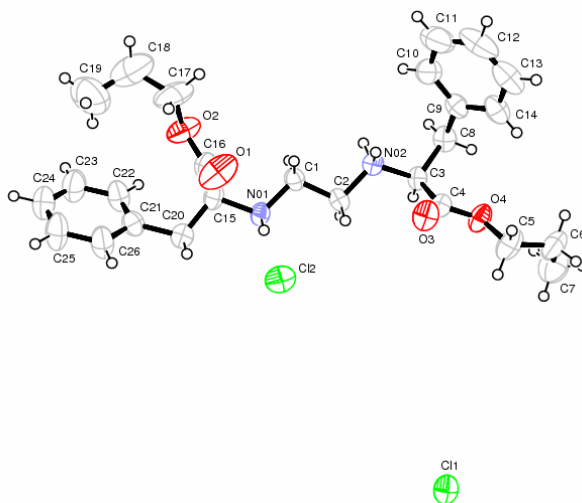
# SYNTHESIS AND CRYSTAL STRUKTURE OF *O,O'*-DIPROPYL-ETILENDIAMINE-*N,N'*-DI-*S,S'*-(2,2'-DIBENZYL)- -ACETATE DIHYDROCHLORIDE

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In reaction of etilendiamine-*N,N'*-di-*S,S'*-(2,2'-dibenzyl)-etanoic acid and absolute 1-propanol, saturated with gaseous HCl *O,O'*-dipropyl-etilendiamine-*N,N'*-di-*S,S'*-(2,2'-dibenzyl)-acetate dihydrochloride was obtained. In order to get crystals for X-ray structure analysis, the white powder was resolved in small amount of dry 1-propanol and left for a several days.

Crystallographic data: C<sub>26</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>·2HCl monoclinic system, space group P2<sub>1</sub>, a = 5.2333(5) Å, b = 15.577 (2) Å, c = 16.8148 (19) Å, α = 90°, β = 94.495 (10), γ = 90°, V = 1366.5 Å<sup>3</sup>, Z = 2, μ(MoKα) = 2.401 mm<sup>-1</sup>, F(000) = 548, crystal size 0.2615 x 0.0364 x 0.0097 mm, R1 = 0.0521 and wR2 = 0.1162 (for 5288 reflections with I > 2σ (I)). In the crystal exist intermolecular hydrogen bonds: N(01)-H(01A)···Cl(2) (H···A = 2.26 Å), N(02)-H(02B)···Cl(1) (H···A = 2.20 Å).



**SINTEZA I KRISTALNA STRUKTURA**  
***O,O'*-DIPROPIL-ETILENDIAMIN-*N,N'*-DI-*S,S'*-(2,2'-DIBENZIL)**  
**-ACETAT DIHIDROHLORIDA**

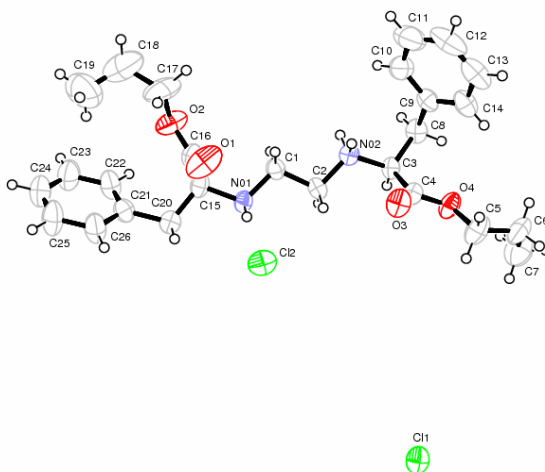
**D. P. Dimitrijević<sup>a</sup>, J. Vujić<sup>b</sup>, S. Garsija-Granda<sup>c</sup>, L. Menéndez-Taboada<sup>c</sup>, S. R. Trifunović<sup>a</sup>**

<sup>a</sup>Institut za hemiju, Prirodno-matematički fakultet, Univerzitet u Kragujevcu, Radoja Domanovića 12, 34 000, Kragujevac, Republika Srbija; <sup>b</sup>Agronomski Fakultet, Univerzitet u Kragujevcu, Svetog Save 65, 3200 Čačak, Republika Srbija; <sup>c</sup>Univerzitet u Ovijedu, Hemijski fakultet, Španija  
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U reakciji etilendiamin-*N,N'*-di-*S,S'*-(2,2'-dibenzil)-etanske kiseline i apsolutnog 1-propanola (zasićenog hlorovodonikom) dobijen je *O,O'*-dipropil-etilendiamin-*N,N'*-di-*S,S'*-(2,2'-dibenzil)-acetat dihidrohlorid. Kristali pogodni za rendgensku strukturu analizu dobijeni su stajanjem rastvora *O,O'*-dipropil-etilendiamin-*N,N'*-di-*S,S'*-(2,2'-dibenzil)-acetat dihidrohlorida za vreme od nekoliko dana u maloj zapremini apsolutnog 1-propanola.

Kristalografski podaci: C<sub>26</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>·2HCl monoklinični sistem, prostorna grupa P2<sub>1</sub>, a = 5,2333(5) Å, b = 15,577 (2) Å, c = 16,8148 (19) Å, α = 90°, β = 94,495 (10), γ = 90°, V = 1366,5 Å<sup>3</sup>, z = 2, μ(MoKα) = 2,401 mm<sup>-1</sup>, F(000) = 548, veličina kristala 0,2615 x 0,0364 x 0,0097 mm, R1 = 0,0521 and wR2 = 0,1162 (za 5288 refleksija sa I>2σ(I)).

U kristalu postoje jake intermolekulske vodonične veze: N(01)-H(01A)···Cl(2) (H···A = 2,26 Å), N(02)-H(02B)···Cl(1) (H···A = 2,20 Å).



## SYNTHESIS AND CHARACTERIZATION OF NANOSIZED $\text{Bi}_2\text{O}_3$

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Nanosized  $\text{Bi}_2\text{O}_3$  powder was successfully synthesized by applying the method based on self-propagating room temperature reaction (SPRT) between bismuth(III) nitrate [ $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ] and sodium hydroxide (NaOH). X-ray powder diffraction (XRPD) and Rietveld's structure refinement method were applied to characterize prepared powder (Fig. 1). It revealed that synthesized material is single phase monoclinic  $\alpha\text{-Bi}_2\text{O}_3$ , space group  $P2_1/c$ , with unit cell parameters  $a = 5.84605(4)$ ,  $b = 8.16339(6)$ ,  $c = 7.50788(6)$  Å and  $\beta = 112.9883(8)^\circ$ . Powder particles were of nanometric size (about 50 nm). Raman spectral studies conformed that obtained powder is a single phase  $\alpha\text{-Bi}_2\text{O}_3$ . Specific surface area of obtained powder was measured by Brunauer-Emmet-Teller (BET) method.

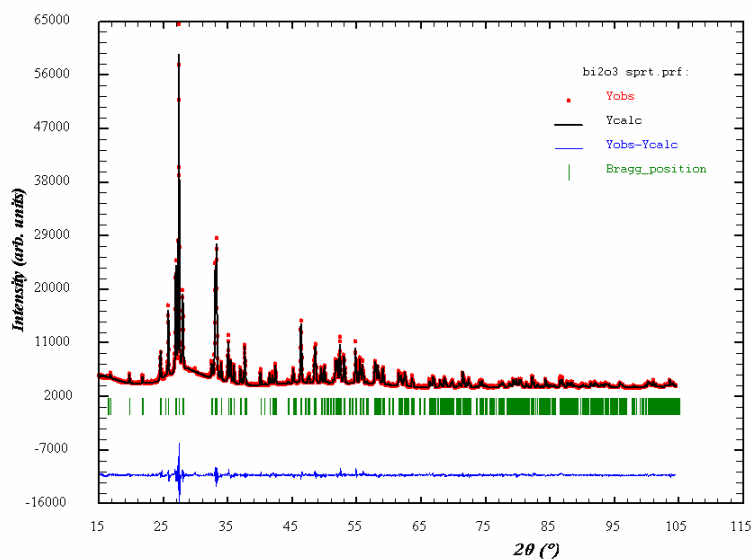


Figure 1. XRPD pattern after the refinement procedure using Rietveld's method

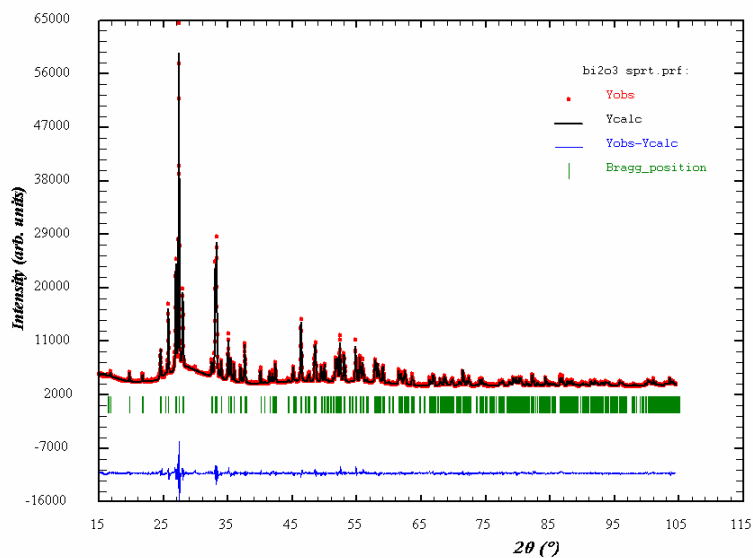
## SINTEZA I KARAKTERIZACIJA NANOČESTIČNOG $\text{Bi}_2\text{O}_3$

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<sup>a</sup>Institut za nuklearne nauke "Vinča", P.O.Box 522, Beograd; <sup>b</sup>Rudarsko geološki fakultet, Dušina 7, Beograd

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Nanočestični prah  $\text{Bi}_2\text{O}_3$  dobijen je primenom samostalno propagirajuće sinteze na sobnoj temperaturi (SPRT metoda). Kao početni reagensi korišćeni su bizmut(III)-nitrat [ $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ] i natrijum hidroksid (NaOH). Sintetizovani  $\text{Bi}_2\text{O}_3$  snimljen je na rendgenskom difraktometru za prah, a struktura je utačnjena Ritveldovom metodom (slika 1), pri čemu je nađeno da je dobijen monofazni  $\alpha\text{-Bi}_2\text{O}_3$  koji kristališe monoklinično, u prostornoj grupi  $P2_1/c$ . Utačnjavanjem su dobijeni sledeći parametri kristalne rešetke:  $a = 5,84605(4)$ ,  $b = 8,16339(6)$ ,  $c = 7,50788(6)$  Å i  $\beta = 112,9883(8)^\circ$ . Dobijeni prah ima kristalite nanometarske veličine (oko 50 nm). Metodom Ramanske spektroskopije potvrđeno je da je sintetizovani prah monofazni  $\alpha\text{-Bi}_2\text{O}_3$ . Primenom BET metode izmerena je i specifična površina dobijenog nanočestičnog  $\alpha\text{-Bi}_2\text{O}_3$ .



Slika 1. Dijagram praha nakon Ritveldovog utičnjavanja

## X-RAY DIFFRACTION STUDY OF CATION ORDERING AND CRYSTALLITE SIZE WITH THERMAL ANNEALING OF MECHANOCHEMICALLY PREPARED $\text{ZnFe}_{1.95}\text{Yb}_{0.05}\text{O}_4$

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<sup>a</sup>Faculty of Technical Sciences, University of Novi Sad, Trg D. Obradovića 6, 21000 Novi Sad, Serbia; <sup>b</sup>Institute of Nuclear Sciences "Vinča", Solid State Physics Laboratory, P. O. Box 522, 11001 Belgrade, Serbia; <sup>c</sup>Faculty of Mining and Geology, Laboratory for Crystallography, University of Belgrade, Đušina 7, 11000 Belgrade, Serbia; <sup>d</sup>University of Ljubljana, Faculty of Chemistry and Chemical Technology, 1000 Ljubljana, Slovenia  
e-mail: milicavv@uns.ac.rs

Mechanochemical synthesis of  $\text{ZnFe}_{1.95}\text{Yb}_{0.05}\text{O}_4$  was performed in a planetary ball mill "pulverisette 4" equipped with tungsten carbide bowls and balls. X-ray powder diffraction (XRPD) data (*in situ* and *ex-situ* measurements) of the samples were collected on a PANalytical X'pert PRO MPD diffractometer. XRPD data were used for the refinement of the structure parameters (lattice parameters and cations occupancies), as well as for microstructure (crystallite size and microstrain) determination. The collected XRPD data of as-prepared sample confirmed mechanochemical synthesis of spinel, as well as the presence of hematite and tungsten carbide. Three phases Rietveld refinement and microstructure determination were done by using Fullprof computer program. Percentage of both hematite and tungsten carbide phases was less than 2 % together. It was found that crystallite size increases from  $\approx 7$  nm to  $\approx 11$  nm with the increase of annealing temperature up to 600 °C.

The increase of unit cell with the increase of temperature of thermal annealing was evident in both regimes. Parameters of linear tendency  $a = a_0 + k \cdot t$  were: *in situ*  $a_0 = 8.435(2)$  Å,  $k = 6.6(5) \cdot 10^{-5}$  Å/°C; *ex-situ*  $a_0 = 8.435(1)$  Å,  $k = 1.2(2) \cdot 10^{-5}$  Å/°C. Changes of lattice parameter for *in situ* regime were related to: (i) simple thermal expansion, (ii) changes in cation distribution, (iii) crystallite size effect, and (iv) valence changes of polyvalent ions. *Ex-situ* unit cell change was related to the effects (ii), (iii) and (iv). Both crystallite size effect and valence changes had the same influence on *in situ* and *ex-situ* regimes.

Found cation distribution for both regimes showed ordering tendency with the increase of temperature, leading to normal spinel structure. Occupation parameters of  $\text{Fe}^{3+}$  at octahedral sites for *ex-situ* measurements were slightly lower than corresponding *in situ* values. After disregarding this difference, the linear thermal expansion coefficient was calculated. The obtained value was  $6.4(6) \cdot 10^{-6}$  1/°C.



## UTICAJ TEMPERATURE ŽARENJA NA DISTRIBUCIJU KATJONA I VELIČINU KRISTALITA MEHANOHEMIJSKI SINTETISANOG $ZnFe_{1,95}Yb_{0,05}O_4$

M. Vučinić Vasić<sup>a</sup>, B. Antić<sup>b</sup>, A. Kremenović<sup>c</sup>, U Kozmidis Luburić<sup>a</sup>, A. Meden<sup>d</sup>

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Za mehanohemijsku sintezu  $ZnFe_{1,95}Yb_{0,05}O_4$  korišćen je planetarni mlin „pulverisette 4” opremljen posudama i kuglama od volfram-karbida. Difraktogrami praha pri zagrevanju (*in situ* režim) kao i nakon žarenja na različitim temperaturama (*ex-situ* režim) snimljeni su pomoću uređaja PANalytical X'pert PRO MPD. Podaci su korišćeni za utačnjavanje strukturnih parametara kao i za određivanje veličine kristalita i mikronaprezanja. Difraktogram praha snimljen nakon mlevenja potvrdio je nastanak jedinjenja sa spinelnom strukturom, ali i prisustvo hematita i volfram-karbida u malim količinama. Utačnjavanje je vršeno pomoću programa Fullprof polazeći od literaturnih podataka za pomenuti trofazni model. Maseni udeo hematita i volfram-karbida zajedno manji je od 2 %. Utvrđeno je da porast temperature žarenja do 600 °C, utiče na porast veličine kristalita od  $\approx 7$  nm do  $\approx 11$  nm.

Porast parametra elementarne ćelije sa porastom temperature ustanovljen je u oba režima. Parametri linearne zavisnosti oblika  $a=a_0+kt$  iznose: *in situ*  $a_0=8,435(2)$  Å,  $k = 6,6(5)\cdot 10^{-5}$  Å/°C; *ex-situ*  $a_0 = 8,435(1)$  Å,  $k = 1,2(2)\cdot 10^{-5}$  Å/°C. Promena parametra elementarne ćelije u *in situ* režimu je posledica: (i) termičke ekspanzije materijala, (ii) promene u raspodeli katjona, (iii) uticaja veličine kristalita i (iv) mogućih promena valentnosti jona. U *ex-situ* režimu je promena parametra elementarne ćelije povezana sa efektima (ii), (iii) i (iv). Uticaj veličine kristalita i promene valentnosti jona isti je u oba režima rada.

Utvrđena distribucija katjona u oba režima rada pokazuje tendenciju ka uređenju sa porastom temperature, što dovodi do nastanka spinelne strukture sa normalnom raspodelom katjona. Okupacioni parametri  $Fe^{3+}$  jona na oktaedarskim mestima u *ex-situ* režimu neznatno su manji u odnosu na vrednosti u *in situ* režimu rada. Zanemarujući ovu razliku izračunata je vrednost linearnog koeficijenta termičke ekspanzije. Dobijena vrednost iznosi  $6,4(6)\cdot 10^{-6}$  1/°C.

**SYNTHESIS AND CRYSTAL STRUCTURE OF POLYMERIC  
COPPER(II) COMPLEXES WITH 3-METHYL-5-OXO-1-PHENYL-3-  
-PYRAZOLINE-4-CARBOXALDEHYDE THIOSEMICARBAZONE  
AND 5-OXO-3-PHENYL-3-PYRAZOLINE-4-CARBOXALDEHYDE  
THIOSEMICARBAZONE**

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The polymeric ( $\mu$ -chlorido) square-pyramidal copper(II) complexes of a general formula  $\{[\text{Cu}(\text{L})(\mu\text{-Cl})\text{Cl}]\}_n$  were obtained by reaction of the warm alcoholic solutions of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and corresponding thiosemicarbazone ligands (L).

Crystal structure for both compounds was determined using single-crystal X-ray diffraction data collected at 150 K on a Bruker Kappa APEX 2  $I\mu S$  Duo diffractometer (monochromated  $\text{MoK}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). In both crystal structures the Cu(II) complex cations form polymeric chains,  $\{[\text{Cu}(\text{L})\text{Cl}]\}_n^+$ , using Cl1 atom as a bridging ligand. However the Cu-Cl1-Cu' angle is very different for two compounds ( $95.7^\circ$  and  $123^\circ$  for  $[\text{Cu}(\text{PzOPh-tsc})(\mu\text{-Cl})\text{Cl}] \cdot \text{H}_2\text{O}$  and  $[\text{Cu}(\text{PzOMePh-tsc})(\mu\text{-Cl})\text{Cl}]$  respectively). Thiosemicarbazide-based ligand, L, is coordinated as a tridentate ligand with a expected ONS coordination mode and two fused chelate rings (Cu-O-C-C-N and Cu-N-N-C-S).

*Crystallographic data.* Compound 1:  $\text{C}_{11}\text{H}_{13}\text{Cl}_2\text{CuN}_5\text{O}_2\text{S}$ , monoclinic, space group  $\text{P}2_1/c$ ,  $a = 8.3310(6)$ ,  $b = 25.429(2)$ ,  $c = 7.4926(5) \text{ \AA}$ ,  $\beta = 109.472(5)^\circ$ ,  $V = 1496.5(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_x = 1.836 \text{ g cm}^{-3}$ ,  $\mu = 1.969 \text{ mm}^{-1}$ . The refinement on  $F^2$  (199 parameters and 3540 independent reflections),  $R_1 = 0.0257$ ,  $wR_2 = 0.0626$ ,  $S = 1.064$ . Compound 2:  $\text{C}_{12}\text{H}_{13}\text{Cl}_2\text{CuN}_5\text{OS}$ , monoclinic, space group  $\text{P}2_1/c$ ,  $a = 13.074(3)$ ,  $b = 15.573(3)$ ,  $c = 7.654(2) \text{ \AA}$ ,  $\beta = 95.657(5)^\circ$ ,  $V = 1550.9(6) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_x = 1.755 \text{ g cm}^{-3}$ ,  $\mu = 1.894 \text{ mm}^{-1}$ . The refinement on  $F^2$  (200 parameters and 3445 independent reflections),  $R_1 = 0.0526$ ,  $wR_2 = 0.1005$ ,  $S = 0.988$ .

# SINTEZA I KRISTALNA STRUKTURA POLIMERNIH BAKAR(II) KOMPLEKSA SA TIOSEMIKARBAZONIMA 3-METIL-5-OKSO-1-FENIL-3-PIRAZOLIN-4-KARBOKSALDEHIDA I 5-OKSO-3-FENIL-3-PIRAZOLIN-4-KARBOKSALDEHIDA

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Polimerni ( $\mu$ -hlorido) kvadratno-piramidalni bakar(II) kompleksi, opšte formule  $\{[\text{Cu}(\text{L})(\mu\text{-Cl})\text{Cl}]\}_n$  su dobijeni reakcijom toplih alkoholnih rastvora  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  i odgovarajućih tiosemikarbazonskih liganada (L).

Eksperimentalni podaci prikupljeni su na difraktometru za monokristale Bruker Kappa APEX 2  $I\mu S$  Duo (monohromatsko  $\text{MoK}\alpha$  zračenje talasne dužine,  $\lambda = 0.71073 \text{ \AA}$ ) i to na temperaturi od 150 K. Rendgenskom strukturnom analizom određeno je da u obe kristalne strukture bakar(II) kompleksni katjoni formiraju polimerne lance,  $\{[\text{Cu}(\text{L})\text{Cl}]\}_n$ , sa Cl1 atomom kao mostnim ligandom. Međutim Cu-Cl1-Cu' ugao se veoma razlikuje u ovim kompleksima ( $95.7^\circ$  za  $[\text{Cu}(\text{PzOPh-tsc})(\mu\text{-Cl})]\text{Cl} \cdot \text{H}_2\text{O}$  i  $123^\circ$  za  $[\text{Cu}(\text{PzOMePh-tsc})(\mu\text{-Cl})]\text{Cl}$ ). Tiosemikarbazonski ligandi su koordinovani kao tridentatni ligandi sa očekivanom ONS koordinacijom formirajući helatne Cu-O-C-C-C-N i Cu-N-N-C-S prstenove.

*Kristalografski podaci.* Jedinjenje 1:  $\text{C}_{11}\text{H}_{13}\text{Cl}_2\text{CuN}_5\text{O}_2\text{S}$ , monoklinični sistem, prostorna grupa  $\text{P}2_1/\text{c}$ ,  $a = 8.3310(6)$ ,  $b = 25.429(2)$ ,  $c = 7.4926(5) \text{ \AA}$ ,  $\beta = 109.472(5)^\circ$ ,  $V = 1496.5(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_x = 1.836 \text{ g cm}^{-3}$ ,  $\mu = 1.969 \text{ mm}^{-1}$ . Utačnjavanje za  $F^2$  (199 parametara i 3540 nezavisnih refleksija),  $R_1 = 0.0257$ ,  $wR_2 = 0.0626$ ,  $S = 1.064$ . Jedinjenje 2:  $\text{C}_{12}\text{H}_{13}\text{Cl}_2\text{CuN}_5\text{OS}$ , monoklinični sistem, prostorna grupa  $\text{P}2_1/\text{c}$ ,  $a = 13.074(3)$ ,  $b = 15.573(3)$ ,  $c = 7.654(2) \text{ \AA}$ ,  $\beta = 95.657(5)^\circ$ ,  $V = 1550.9(6) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_x = 1.755 \text{ g cm}^{-3}$ ,  $\mu = 1.894 \text{ mm}^{-1}$ . Utačnjavanje za  $F^2$  (200 parametara i 3445 nezavisnih refleksija),  $R_1 = 0.0526$ ,  $wR_2 = 0.1005$ ,  $S = 0.988$ .

## PETAL-LIKE POLYMERIC MANGANESE(II) COMPLEX WITH TEREPHTHALATE ION AND 2,2'-DIPYRIDYLAMINE

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The study of the title polymeric complex,  $[\text{Mn}(\text{tpht})(\text{dipya})_2]_n$ , presents continuation of our studies on synthesis and characterisation of ternary transition metal complexes with dianion of terephthalic (1,4-benzenedicarboxylic) acid, tpht, and some aromatic diamines, as 2,2'-dipyridylamine, dipya [1].

Although the molar ratio of  $\text{Mn}^{2+}$ ,  $\text{tpht}^{2-}$  and dipya in the starting mixture was 1:1:1, the title complex contains two dipya ligands per one Mn. Thus,  $\text{Mn}^{2+}$  ions are in a very deformed octahedral environment consisting of four N atoms from two dipya and two O atoms from different bis-monodentate bridging tpht ligands ( $\text{O}_2\text{N}_2\text{N}'_2$  chromophore) (Fig. 1). In this way, pairs of nonplanar dipya ligands can be described as double petals, which are oriented in zigzag manner with respect to the rest of the polymeric chain running along *c*-axis (Fig. 2). The intrachain Mn–Mn distance is 11.4057(4) Å, typical for tpht complexes [2]. According to this distance, the compound is probably a molecular magnet.

Uncoordinated O atoms from COO groups and the amine H atoms of dipya build hydrogen bonds, N3–H5...O2, which connect adjacent chains. Therefore through hydrogen bonds and  $\pi$ - $\pi$  interactions (at 3.75 Å) the zigzag chains are stacked into three-dimensional architecture in the lattice.

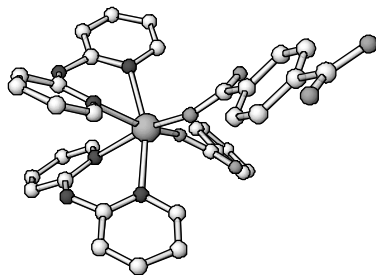


Figure 1. Mn(II) coordination polyhedron.

*Crystal data:*  $\text{C}_{28}\text{H}_{22}\text{MnN}_6\text{O}_4$ ,  $M_r = 561.46$ , monoclinic, space group  $C2/c$ ,  $a = 8.1799(4)$ ,  $b = 16.7500(6)$ ,  $c = 18.9443(7)$  Å,  $\beta = 98,768(4)^\circ$ ,  $V = 2565,29(18)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 1156$ ,  $\rho_x = 1,454$  g cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 0,562$  mm<sup>-1</sup>. The refinement on  $F^2$  (221 parameters) yielded  $R_1 = 0.043$ ,  $wR_2 = 0.077$ ,  $S = 1.00$  for all data, and  $R_1 = 0.031$  for 1973 observed reflections with  $I \geq 2\sigma(I)$ .

[1] J. Rogan, D. Poleti, Lj. Karanović, G. Bogdanović, A. Spasojević-de Biré, D. M. Petrović, *Polyhedron*, 19 (2000), 1415-1421; Lj. Karanović, D. Poleti, J. Rogan, G. A. Bogdanović, A. Spasojević-de Biré, *Acta Crystallogr.*, C58 (2002), m275-m279.

[2] E. G. Bakalbassis, J. Mrozinski, C. A. Tsipis, *Inorg.Chem.*, 24 (1985) 3548-3553.

## LATIČASTI POLIMERNI MANGAN(II)-KOMPLEKS SA TEREFTALAT-JONOM I 2,2'-DIPIRIDILAMINOM

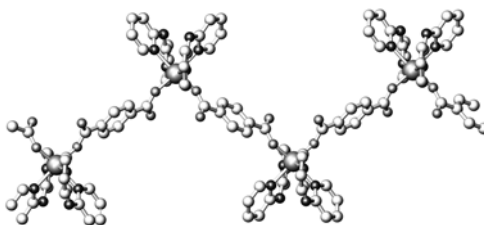
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Navedeni polimerni kompleks,  $[Mn(tpht)(dipya)_2]_n$ , predstavlja nastavak naših istraživanja iz oblasti sinteze i karakterizacije ternernih kompleksa prelaznih metala sa dianjonom tereftalne (1,4-benzendikarboksilne) kiseline, tpht, i nekim aromatičnim diaminima, kao što je 2,2'-dipiridilamin, dipya [1].

Iako je molski odnos  $Mn^{2+}$ ,  $tpht^{2-}$  i dipya u početnoj smeši iznosio 1:1:1, navedeni kompleks sadrži dva dipya liganda po jednom atomu Mn. Tako se  $Mn^{2+}$ -joni nalaze u vrlo deformisanom oktaedarskom okruženju koje čine četiri atoma N iz dva dipya liganda i dva atoma O iz različitih bis-monodentatnih mostovnih tpht liganada ( $O_2N_2N'_2$  hromofora) (slika 1). Na ovaj način, parovi neplanarnih dipya liganada izgledaju kao dvostruke latice sa cik-cak orijentacijom u odnosu na ostatak polimernog lanca koji se proteže duž *c*-ose (slika 2). Rastojanje Mn–Mn unutar lanaca iznosi 11,4057(4) Å, što je tipično za tpht-komplekse [2]. Prema ovom rastojanju, jedinjenje je verovatno molekulski magnet.

Nekoordinirani atomi O iz  $COO^-$ -grupa i aaminski atom H iz dipya grade vodonične veze,  $N3-H5...O2$ , koje povezuju susedne lance. Tako se cik-cak lanci drže vodoničnim vezama i  $\pi-\pi$  interakcijama (na rastojanju 3,75 Å) gradeći trodimenzionalnu arhitekturu u rešetki.



Slika 2. Prikaz cik-cak lanca posmatrano približno duž *a*-ose (*c*-osa je horizontalna).

*Kristalografski podaci:*  $C_{28}H_{22}MnN_6O_4$ ,  $M_r = 561,46$ , monoklinični sistem, prostorna grupa  $C2/c$ ,  $a = 8,1799(4)$ ,  $b = 16,7500(6)$ ,  $c = 18,9443(7)$  Å,  $\beta = 98,768(4)^\circ$ ,  $V = 2565,29(18)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 1156$ ,  $\rho_x = 1,454$  g cm<sup>-3</sup>,  $\mu(Mo K\alpha) = 0,562$  mm<sup>-1</sup>. Utačnjavanje sa  $F^2$  (221 parametar) dalo je  $R_1 = 0,043$ ,  $wR_2 = 0,077$ ,  $S = 1,00$  za sve podatke, i  $R_1 = 0,031$  za 1973 refleksije sa  $I \geq 2\sigma(I)$ .

[1] J. Rogan, D. Poleti, Lj. Karanović, G. Bogdanović, A. Spasojević-de Biré, D. M. Petrović, *Polyhedron*, 19 (2000), 1415-1421; Lj. Karanović, D. Poleti, J. Rogan, G. A. Bogdanović, A. Spasojević-de Biré, *Acta Crystallogr.*, C58 (2002), m275-m279.

[2] E. G. Bakalbassis, J. Mrozinski, C. A. Tsipis, *Inorg. Chem.*, 24 (1985) 3548-3553.

## COMPARISON OF DIFFERENT STATISTICAL METHODS FOR CALCULATION OF AMINO ACID PROPENSITIES TOWARD CERTAIN SECONDARY STRUCTURE TYPES

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The conformational preferences of amino acids are very important for understanding conformational interactions in proteins. Moreover, when used as propensities they can be helpful in predicting secondary and tertiary structures of proteins. Propensity for secondary structures represents an intrinsic property of amino acid, and it is now known that different amino acids have distinct propensities for the adoption of helical, strand, and random coil conformations. Several statistical studies were performed in order to calculate amino acid propensities [1-3].

In our previous work we carried out study of propensities using statistical method [4]. Clear preferences of amino acids towards certain secondary structures based on the study, classify amino acids into four groups:  $\alpha$ -helix preferrers, strand preferrers, turn and bend preferrers, and His and Cys (the latter two amino acids show no clear preference for any secondary structure). Amino acids in the same group have similar structural characteristics at their C $\beta$  and C $\gamma$  atoms that predict their preference for a particular secondary structure.

Here we compare other statistical methods for amino acid propensities with the statistical method which we used in our previous work. Comparison was made on the basis of correlation coefficients ( $\rho(s,p)$ ). As a source of protein data we used structures archived in Protein Data Bank (PDB). The secondary structure assignment was performed by the program DSSP.

[1] P. Y. Chou, G. D. Fasman, *Biochemistry*, 13 (2) (1974), 211–222.

[2] M. Levitt, *Biochemistry*, 17 (1978), 4277–4285.

[3] V. I. Lim, *J.Mol.Biol.*, 88 (1974), 873–846.

[4] S. N. Malkov, M. V. Živković, M. V. Beljanski, M. B. Hall, S. D. Zarić, *J Mol Model*, 14 (2008) 769–775.

## ПОРЕЂЕЊЕ РАЗЛИЧИТИХ СТАТИСТИЧКИХ МЕТОДА ЗА ИЗРАЧУНАВАЊЕ ТЕЖЊЕ АМИНОКИСЕЛИНА ПРЕМА ОДРЕЂЕНОМ ТИПУ СЕКУНДАРНЕ СТРУКТУРЕ

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Преферентност аминокиселина према одређеној конформацији је од изузетног значаја за разумевање конформационих интеракција у протеинима. Штавише, оне могу да буду од помоћи за предвиђање секундарних и терцијарних структура протеина. Склоност ка одређеним секундарним структурама је веома важно својство аминокиселина, и данас се зна да различите аминокиселине имају склоност да се нађу у једној од конформација протеина (хеликс, плочица, завојница). Урађено је и више статистичких проучавања да би се израчунале наведене склоности аминокиселина [1-3].

У нашем ранијем раду проучавали смо преферентност аминокиселина коришћењем статистичког метода [4]. Јасна склоност аминокиселина да се јављају у одређеној секундарној структури омогућава њихово класификовање у једну од четири групе. У прву групу спадају оне које имају тежњу ка  $\alpha$ -хеликсу, у другу ка  $\beta$ -плочици, у трећу спадају оне које имају тежњу ка завијутку, док у четврту групу спадају His и Cys (ове последње две аминокиселине не показују јасну склоност ни према једној конформацији). Аминокиселине из исте групе имају сличне структурне карактеристике у погледу C $\beta$  и C $\gamma$  атома који указују на склоност ка одређеној секундарној структури.

Овде смо упоредили остале статистичке методе за рачунање склоности аминокиселина ка одговарајућој конформацији са статистичком методом коју смо понудили у нашем ранијем раду. Поређење је извршено на основу вредности корелационих коефицијената ( $\rho(s,p)$ ). Као извор података користили смо структуре из Протеинске банке података (PDB). Приписивање секундарних структура извршено је помоћу програма DSSP.

[1] P. Y. Chou, G. D. Fasman, *Biochemistry*, 13 (2) (1974), 211–222.

[2] M. Levitt, *Biochemistry*, 17 (1978), 4277–4285.

[3] V. I. Lim, *J.Mol.Biol.*, 88 (1974), 873–846.

[4] S. N. Malkov, M. V. Živković, M. V. Beljanski, M. B. Hall, S. D. Zarić, *J Mol Model*, 14 (2008), 769–775

## SYNTHESIS AND CRYSTAL STRUCTURE OF PALLADIUM(II) COMPLEX WITH *O,O'*-DIETHYL(*S,S*)-ETHYLENEDIAMINE-*N,N'*-DI-2-(3-METHYL)BUTANOATE

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It is well known that complex compounds of palladium(II) are usually used as model systems for better understanding the interaction of platinum(II) complexes, taking into account that the first complexes are  $10^3$ - $10^5$  times more active than the second ones [1].

The titled compound was obtained in reaction of tetrachloridopalladate(II), *O,O'*-diethyl-*(S,S)*-ethylenediamine-*N,N'*-di-2-(3-methyl)butanoate and lithium hydroxide in a molar ratio 1:1:2, at room temperature. The yellow compound was crystallized from mother solution. The Pd atom was found in a square-planar coordination geometry with one ligand coordinated through one carboxylic oxygen and two nitrogen atoms ( $\kappa^2N,N'$ ,  $\kappa O$  coordination mode). The remaining coordination site is occupied by the chlorido ligand.

Crystallographic data:  $C_{14}H_{25}ClN_2O_4Pd$ ,  $M_r = 427.21$ , orthorhombic system, space group  $P2_12_12_1$ , crystal size  $0.55 \times 0.35 \times 0.18$  mm,  $\rho_x = 1.150$  g cm<sup>-3</sup>,  $Z = 4$ ,  $a = 6.1062(2)$ ,  $b = 10.5325(4)$ ,  $c = 29.115(2)$  Å,  $V = 1872.5(2)$  Å<sup>3</sup>. Diffraction data were collected at room temperature on a Bruker-Smart APEX II diffractometer using graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å).

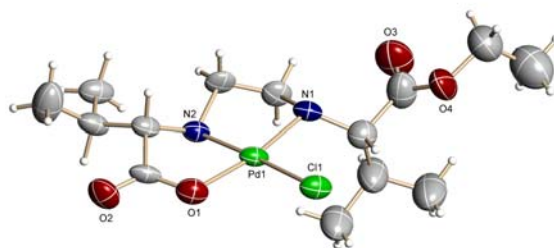


Figure 1. Structure of the complex

[1] T. Rau, R. van Eldik, in A. Sigel and H. Sigelin (Eds), *Metal Ions in Biological Systems*, Markel Dekker, New York, 32 (1996) 339



## SINTEZA I KRISTALNA STRUKTURA KOMPEKSA PALADIJUMA(II) SA *O,O'*-DIETIL-(*S,S*)-ETILNDIAMIN-*N,N'*-DI- -2-(3-METIL)BUTANOATOM

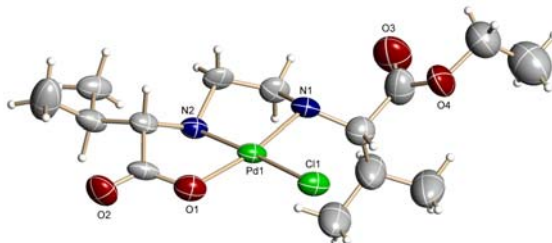
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Dobro je poznato da se kompleksi paladijuma(II) obično koriste kao model molekuli za razumevanje interakcija platina(II) kompleksa, uzimajući u obzir da su prvi kompleksi  $10^3$ - $10^5$  puta reaktivniji nego drugi [1].

Kompeks je dobijen reakcijom tetrahloridopaladata(II) i *O,O'*-dietil-(*S,S*)-etilendiamin-*N,N'*-di-2-(3-dimetil)butanoata i litijum-hidroksida u molaskom odnosu 1:1:2, na sobnoj temperaturi. Žuti kristali dobijeni su iz matičnog rastvora. Formira se kvadratno-planarni kompleks, pri čemu se estar koordinuje preko jednog kaboksilnog kiseonika i preko dva atoma azota ( $\kappa^2N,N'$ ,  $\kappa O$ ). Preostalo koordinaciono mesto zauzima hlorido ligand.

Kristalografski podaci:  $C_{14}H_{25}ClN_2O_4Pd$ ,  $M_r = 427,21$ , rombični sistem, prostorna grupa  $P2_12_12_1$ , veličina kristala  $0,55 \times 0,35 \times 0,18$  mm,  $\rho_x = 1.150$  g cm<sup>-3</sup>,  $Z = 4$ ,  $a = 6,1062(2)$ ,  $b = 10,5325(4)$ ,  $c = 29,115(2)$  Å,  $V = 1872,5(2)$  Å<sup>3</sup>. Eksperimentalni podaci su sakupljeni na sobnoj temperaturi pomoću Bruker-Smart APEX II difraktometra koristeći grafit-monohromatizovano MoK $\alpha$  zračenje ( $\lambda = 0,71073$  Å).



Slika 1. Struktura dobijenog kompleksa

[1] T. Rau, R. van Eldik, in A. Sigel and H. Sigel (Eds), *Metal Ions in Biological Systems*, Markel Dekker, New York, 32 (1996) 339

## TWO POLYMORPHS OF A SYN-FACIAL [TRICARBONYL( $\eta^6$ ; $\eta^1$ -BENZYL)CHROMIUM]MANGANESE TRICARBONYL COMPLEX. A SHORTER Cr-Mn DISTANCE INDUCED FROM THE CRYSTAL PACKING?

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The electronic structure and structural features of a series of 34 electrons *syn*-facial Cr-Mn benzylic complexes were investigated in the light of a statistical study of the geometrical properties of 14 structures obtained by X-ray diffraction analysis. The statistical study shows that the Cr-to-Mn distance  $d_m$  is rather independent of the nature and steric size of the substituents present at the benzylic carbon as well at remote position such as the donor ligand. The distance  $d_m$ , which amounts an average value of *ca.* 3.04 Å is related to a weak but real attractive bonding interaction whereby London dispersion prevails over covalency and donor-acceptor interactions, as suggested by theoretical investigations using density functional theory (DFT) [1,2]. One compound of the 14 compounds of this serie presents the particularity to crystallize in two different polymorphs. One of these structures has been determined through a synchrotron experiment, performed at Soleil [3] at low temperature in order to determine the electron charge density and at consequently the existence of a bond critical point on the metal-metal bond.

The present work presents an analysis of the crystal packing of these polymorphs in order to discuss a structure relationship between the Cr-Mn distance and the crystalline environment of the molecule.

[1] I. Hyla-Kryspin S. Grimm, J. P. Djukić, *Organometalics*, 28 (2008), 1001-1013

[2] J. P. Djukic, C. Michon, A. Berger, M. Pfeiffer, A. de Cian, N. Kyritsakas-Gruber, *J. Organomet. Chem.*, 691 (2006), 846-858

[3] <http://www.synchrotron-soleil.fr/>

**DVA POLIMORFNA SYN-FACIJALNOG KOMPLEKSA  
[TRIKARBONIL( $\eta^6$ ;  $\eta^1$ -BENZIL)HROM]  
TRIKARBONILMANGAN.  
SKRAĆENJE Cr-Mn RASTOJANJA INDUKOVANO KRISTALNIM  
PAKOVANJEM?**

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Elektronska i strukturna svojstva *syn*-facijalnih Cr-Mn benzil-kompleksa ispitivana su na osnovu statističke analize geometrijskih karakteristika 14 kristalnih struktura određenih rendgenskom strukturne analizom. Statistička analiza pokazuje da je rastojanje između atoma Cr i Mn ( $d_m$ ) nezavisno od prirode i veličine ovih atoma, supstituenata prisutnih na benzilnom atomu ugljenika, odnosno supstituenata na udaljenijim atomima liganda. Na osnovu teorijskih DFT („Density functional theory”) izračunavanja [1,2], zaključeno je da se vrednost rastojanja  $d_m$  (koje u proseku iznosi 3.04 Å) može dovesti u vezu sa slabim, ali privlačnim vezivnim interakcijama u kojima Londonove disperzivne sile prevladavaju nad kovalentnim interakcijama, odnosno donora-akceptor interakcijama. Jedno od 14 ispitivanih jedinjenja ima osobinu da kristališe u vidu dva različita polimorfa. Jedna od ovih kristalnih struktura je određena na osnovu eksperimenta difrakcije sinhrotronog zračenja, izvedenog na sinhrotronu „Soleil” [3]. Eksperiment je izveden na niskoj temperaturi (100K) sa ciljem određivanja raspodele elektronske gustine i kasnijem ispitivanju postojanja kritične tačke veze kojom bi se bliže opisala priroda interakcije između atoma metala.

U ovom radu data je analiza kristalnih pakovanja dva polimorfa u cilju razmatranja strukturne veze između Mn-Cr rastojanja i kristalnog okruženja molekula.

[1] I. Hyla-Kryspin S. Grimm, J. P. Djukic, *Organometalics*, (2008), 28, 1001-1013

[2] J. P. Djukic, C. Michon, A. Berger, M. Pfeffer, A. de Cian, N. Kyritsakas-Gruber, *J. Organomet. Chem.*, (2006), 691, 846-858

[3] <http://www.synchrotron-soleil.fr/>

## CRYSTALLOGRAPHIC STATISTICAL STUDIES OF THE DECAVANADATE ANION: TOWARD A PREDICTION OF THE NON-COVALENT INTERACTIONS

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More than 100 structures containing the  $[V_{10}O_{28} H_x]^{6-x}$  anion has already been published. From a geometric point of view, the decavanadate anion  $[V_{10}O_{28}]^{6-}$  appears very rigid with really small variations in interatomic distances or bond angle values.

We have retrieved from the organic-organometallic database (CSD), the protein data base (PDB) and an extensive bibliographic search 30 different crystalline structures, which imply 600 contacts for which the structure is of excellent crystalline quality. In a previous study, we have experimentally determined the electron and electrostatic properties of two decavanadate (figure 1a) based compound  $Na_3V_{10}O_{28}(C_4N_3OH_5)_3(C_4N_3OH_6)_3 \cdot 10H_2O$  [1] and  $(NH_4)_6[V_{10}O_{28}] \cdot 6H_2O$  [2]. From these results we have predicted the preferential non-covalent interactions with the different oxygen atoms of the decavanadate anion. These predictions are confirmed, in this statistical study. The non-covalent interactions are strongly different depending on the oxygen atom type. The Ob and Oc oxygen atoms, for which the electrostatic potential in the vicinity have the lowest value, are involved mainly in the strong O-H...O, N-H...O while Of or Og are mainly involved in weakest hydrogen bonds such as C-H...O or cation interactions. (figure 1b).

These results are important in the context of the various biological applications of the decavanadate such as, for example, inhibition of the  $Ca^{2+}$  ATPase, myosin ATPase, and new development in insulin mimetic.

- [1] a) D. Krstić, M. Colović, N. Bošnjaković-Pavlović, A. Spasojević-de Biré, V. Vasić. *General Physiology and Biophysics*, 28 (2009), 302-308 b) N. Bošnjakovic-Pavlovic, A. Spasojević - de Biré, I. Tomaz, N. Bouhmaida, F. Avecilla, U. Mioč, J. Costa Pessoa, N.E. Ghermani, *Inorganic Chemistry*, 48 (2009), 9742-9753 c) N. Bošnjakovic-Pavlovic, A. Spasojevic - de Biré, *J. Phys. Chem. A*, (2010), in revision  
[2] G. A. Bogdanović, N. Bošnjakovic-Pavlović, A. Spasojević - de Biré, N. E. Ghermani, U. Mioč, *J. Serbian Chem. Soc.*, 72, (2007), 545-554

# KRISTALOGRAFSKA STATISTIČKA ANALIZA DEKAVANADATNOG ANJONA U CILJU PREDVIDJANJA NEKOVALENTNIH INTERAKCIJA

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Više od 100 struktura koje sadrže dekanadatni anjon  $[V_{10}O_{28} H_x]^{6-x}$  je publikovano. Sa geometrijske tačke gledišta, dekanadatni anjon  $[V_{10}O_{28}]^{6-}$  je veoma rigidan, sa veoma malim varijacijama u dužinama veza i uglovima između veza.

Pretraživanjem Kembridžske baze strukturnih podataka (CSD), proteinske baze podataka (PDB) i obimnim ispitivanjem 30 različitih kristalnih struktura koje sadrže dekanadatni anjon, pronašli smo oko 600 kontakata. U prethodnom istraživanju, mi smo eksperimentalno odredili elektronske i elektrostatičke osobine dva dekanadata  $Na_3V_{10}O_{28}(C_4N_3OH_5)_3(C_4N_3OH_6)_3 \cdot 10H_2O$  [1] i  $(NH_4)_6[V_{10}O_{28}] \cdot 6H_2O$  [2]. Na osnovu ovih rezultata mi smo pretpostavili nekovalentne interakcije sa različitim atomima kiseonika dekanadatnog anjona. Ova statistička analiza je potvrdila naše pretpostavke. Neovalentne interakcije su jako zavisne od tipa atoma kiseonika. Atomi kiseonika tipa Ob i Oc, za koje smo našli da elektrostatički potencijal ima najniže vrednosti, grade uglavnom jake O-H...O, N-H...O interakcije dok Of i Og grade slabije C-H...O interakcije.

Ovi rezultati su veoma značajni u cilju objašnjenja biološke aktivnosti dekanadata, kao što je na primer inhibicija  $Ca^{2+}$  ATPaze, miozin ATPaze.

- [1] a) D. Krstić, M. Colović, N. Bosnjaković-Pavlović, A. Spasojević-de Biré, V. Vasić. *General Physiology and Biophysics*, 28 (2009), 302-308 b) N. Bosnjakovic-Pavlovic, A. Spasojević - de Biré, I. Tomaz, N. Bouhmaida, F. Avecilla, U. Mioč, J. Costa Pessoa, N. E. Ghermani, *Inorganic Chemistry*, 48 (2009), 9742-9753 c) N. Bosnjakovic-Pavlovic, A. Spasojevic - de Biré, *J Phys. Chem. A*, (2010), in revision  
[2] G. A. Bogdanović, N. Bosnjakovic-Pavlović, A. Spasojević - de Biré, N. E. Ghermani, U. Mioč, *J. Serbian Chem. Soc.*, 72 (2007), 545-554

## NON PHOTOCHEMICAL LIGHT INDUCED NUCLEATION. A TOOL TO CRYSTALLIZE POLYMORPHS ON DEMAND? APPLICATION TO CARBAMAZEPINE

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There is tremendous pressure on the pharmaceutical industry to understand the polymorphism of drugs in order to control and produce the most stable and effective polymorphs. There is a growing awareness of the effects of polymorphism and pseudo-polymorphism on the properties of drugs, such as their physical and chemical stability, solubility, dissolution rate, bio-availability, and mechanical properties, and their consequences on the manufacturing process. We have developed a fundamental approach to study polymorphism, which combines high-resolution X-ray diffraction and *ab initio* theoretical calculations. That would enable us to study the consequences of drug polymorphism on the physical and chemical properties of drugs. Ideally, the experimental study of polymorphism requires the possibility to crystallize the desired polymorphic forms “at will” and to obtain new, yet uncharacterized phases.

Garetz and Myerson have invented an original nucleation method [1], termed NPLIN, “Non-Photochemical Light-Induced Nucleation” that makes it possible to control the nucleation process. We have already implemented this method at Ecole Centrale Paris and tested it successfully on glycine [2].

Carbamazepine is anti-epileptic drug, a highly polymorphic compound (4 true polymorphs, more than 20 hydrates or solvates) generally studied as a model compound for studying polymorphism. It represents a suitable compound for the demonstration of the feasibility of the NPLIN method for drug compound.

The polymorphs obtained after crystallization under NPLIN method will be discussed according to the hypothesis that the optical Kerr effect is involved in the NPLIN mechanism.

[1] J. Zaccaro, J. Matic, A. S. Myerson, B. A. Garetz, *Cryst. Growth & Des.* 1 (2001) 5-8

[2] This project has been done through the work of ECP-students team small-project during the last years, Thanks to T. Bavière, F. Laeuffer, P. Laignel, F. Synésius (2005-2006), S. Bellani, E. Bothschafter, D. Dregely, S. Hadj-Messaoud (2007-2008), D. Miret (2009) F. Degand, A. Grisey, H. Leterne, T. Rousseau, (2009-2010).

## NUKLEACIJA INDUKOVANA NE-FOTOHEMIJSKOM SVETLOŠĆU. SREDSTVO ZA KRISTALIZACIJU POLIMORFA NA ZAHTEV? PRIMENA KARBAMAZEPINA

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Postoji snažan pritisak na farmaceutsku industriju da savlada polimorfizam lekova kako bi mogla da kontroliše i proizvede najstabilnije i najefikasnije polimorfe. Sve više se shvataju efekti polimorfizma i pseudo-polimorfizma na svojstva lekova, kao što su njihova fizička i hemijska stabilnost, rastvorljivost, brzina rastvaranja (razlaganja), bioraspoloživost, i mehanička svojstva, kao i njihove posledice po proizvodni proces. Razradili smo fundamentalan pristup za izučavanje polimorfizma, koji se sastoji u kombinovanju difrakcije rendgenskih zraka visoke rezolucije i teoretskih proračuna *ab initio*. To nam omogućava da proučimo posledice polimorfizma lekova po fizička i hemijska svojstva lekova. Teoretski gledano, eksperimentalno proučavanje polimorfizma zahteva mogućnost da se kristalizuju željeni polimorfni oblici, „proizvoljno“, i da se dobiju nove, još nespecifične faze.

Garec i Majerson su osmislili originalni metod nukleacije [1], nazvan NPLIN, Nukleacija indukovana ne-fotohemijskom svetlošću“ (“Non-Photochemical Light-Induced Nucleation”) koja omogućava da se proces nukleacije kontroliše. U Ecole Centrale Paris već smo primenili ovaj metod i uspešno ga ispitali na glicinu [2].

Karbamazepin je lek protiv epilepsije, veoma polimorfno jedinjenje (4 prava polimorfa, više od 20 hidrata i rastvora), koje se opšte koristi kao model jedinjenje u izučavanju polimorfizma. Ono predstavlja pogodno jedinjenje za demonstriranje izvodljivosti metoda NPLIN kod jedinjenja lekova. O polimorfima dobijenim nakon kristalizacije po NPLIN metodi razmatraće se shodno pretpostavci da je u NPLIN proceduru uključen optički Kerov efekat.

[1] J. Zaccaro, J. Matic, A. S. Myerson, B. A. Garetz, *Cryst. Growth & Des.* 1 (2001) 5-8

[2] Ovaj projekat je urađen kroz rad studenata ECP – mali projekti, tokom proteklih godina, i zahvaljujući T. Bavière, F. Laeuffer, P. Laignel, F. Synésius (2005-2006), S. Bellani, E. Bothschafter, D. Dregely, S. Hadj-Messaoud (2007-2008), D. Miret (2009) F. Degand, A. Grisey, H. Leterne, T. Rousseau, (2009-2010).

## DISORDER AND HYDROGEN PLACEMENT IN [Cu(PLSC)Cl<sub>2</sub>] COMPOUND

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In general, the hydrogen atoms were visible in the difference map of complex [Cu(PLSC)Cl<sub>2</sub>]. Therefore, they were positioned geometrically and refined in a separate hydrogen cycle (with soft restraints) before inclusion in the refinement using a riding model. The exception was the hydrogen atoms for the oxygen of the disordered -CH<sub>2</sub>OH group. They were not visible in the difference map mainly due to the disordered nature of the entire -CH<sub>2</sub>OH group (Fig. 1). One of the reasons for the disorder can be explained by examining the crystal packing. The hydrogen atom located on N13 of one molecule is pointing directly towards the -CH<sub>2</sub>OH group of the adjacent molecule indicating that it cannot be act as a hydrogen acceptor for the -CH<sub>2</sub>OH group (Figure 2). Attempts to manually add H atoms based on the next nearest hydrogen bond acceptors gave improbable positions for the hydrogen atoms with C-O-H angles close to 170°. Removing H131 would suggest the presence of copper(III) which as well as highly unlikely disagrees with other results. For this reason the hydroxyl hydrogen atoms on the disordered -CH<sub>2</sub>OH group were not include in the final refinement.

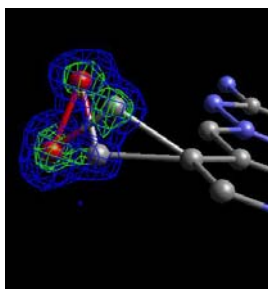


Figure 1. Three dimensional difference electron density map showing the disorder in the -CH<sub>2</sub>OH

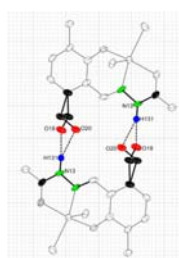


Figure 2. Packing in [Cu(PLSC)Cl<sub>2</sub>] showing the disorder in the -CH<sub>2</sub>OH and the implications for the hydrogen

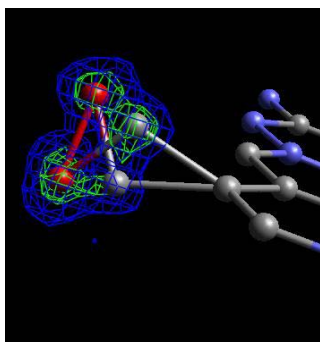


## NEUREDJENOST I POLOŽAJ VODONIKA U [Cu(PLSC)Cl<sub>2</sub>] KOMPLEKSU

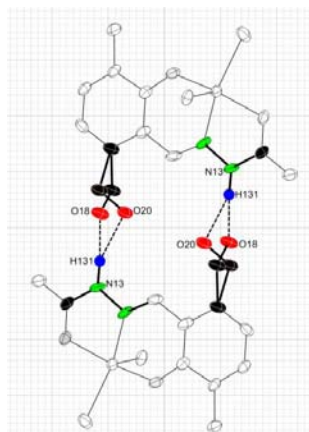
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U principu, atomi vodonika su vidljivi na diferencijalnoj mapi kompleksa [Cu(PLSC)Cl<sub>2</sub>]. Dakle, oni su geometrijski pozicionirani i utučnjeni u posebnom vodoničnom ciklusu (sa blagim ograničenjima) pre uključivanja u preciziranje koristeći "riding model". Izuzetak je bio atom vodonika vezan za kiseonik na -CH<sub>2</sub>OH grupi. Oni nisu bili vidljivi u diferencijalnoj mapi uglavnom zbog neuredjene prirode cele -CH<sub>2</sub>OH grupe (Slika 1). Jedan od razloga za poremećaj može se objasniti proučavanjem kristalnog pakovanja. Atom vodonika vezan za N13 jednog molekula je direktno usmeren ka -CH<sub>2</sub>OH grupi susednih molekula i ne može delovati kao primalac vodonika za -CH<sub>2</sub>OH grupu (Slika 2). Pokušaji da se ručno doda H atom na osnovu sledećeg najbližeg akceptora vodoničnih veza je dao neverovatnu poziciju za atoma vodonika sa C-O-H uglovima blizu 170°. Uklanjanje H131 bi sugerisalo prisustvo bakra(III), što nije u saglasnosti sa drugim rezultatima. Iz tog razloga atomi vodonika na neuređenoj -CH<sub>2</sub>OH grupi nisu bili konačno pozicionirani.



Slika 1. Trodimenzionalna slika koje pokazuje razliku u elektronskoj gustini i neuredjenost -CH<sub>2</sub>OH grupe



Slika 2. Pakovanje u [Cu(PLSC)Cl<sub>2</sub>] pokazuje neuredjenost u -CH<sub>2</sub>OH grupi i implikacije na vodonik

## THE CRYSTAL STRUCTURE OF [Cu(PLSC)(H<sub>2</sub>O)(SO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O COMPLEX

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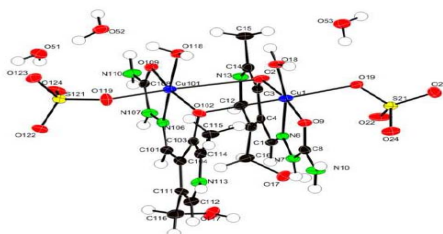
The [Cu(PLSC)(H<sub>2</sub>O)(SO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O was obtained in reaction of copper sulphate pentahydrate and pyridoxal-semicarbazone (PLSC) in molar ratio 1:1. This green crystals was undergone to elemental microanalysis and X-ray structure analysis.

The experimental results of the elemental analysis for C, H, N are in accordance with calculated values. Found C<sub>18</sub>H<sub>34</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>19</sub>S<sub>2</sub> (*Mr* = 857.73) (%): C, 25.27; H, 4.03; N, 13.13. Calculated: C, 25.21; H, 4.00; N, 13.06. The structure of the complex was solved and refined using CRYSTAL 2000 program [1,2].

Results of structure refinement of the [Cu(PLSC)(H<sub>2</sub>O)(SO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O complex compound: triclinic, space group *P*-1, crystal size 0.21 x 0.15 x 0.09 mm<sup>3</sup>, block shape and green coloured, *a* = 9.2575(2) Å, *b* = 9.5857(2) Å, *c* = 17.1333(3) Å,  $\beta$  = 82.9242(9)°, *V* = 1497.16(5) Å<sup>3</sup>, *Z* = 2,  $\rho$  = 1.903 Mg/m<sup>3</sup>, *F*(000) = 880,  $\mu$  = 1.660 mm<sup>-1</sup>,  $\lambda$ (MoK $\alpha$ ) = 0.71073 Å, *T* = 150 K, 18928 reflection measured, *GOOF* = 0.9624,  $wR_2(F^2)$  = 0.1156 for 6800 unique reflections and 443 parameters, 0 restraints and  $R_1(F)$  = 0.0564 for 0.01156 reflections obeying  $F_o \geq 4\sigma(F_o)$  criterion of observability.

[1] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR 92, a program for automatic solution of crystal structures by direct methods, *J. Appl. Crystallogr.*, 27 (1994) 435.

[2] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, J. Prout, D. J. Watkin, CRYSTAL version 12: software for guided crystal structure analysis, *J. App. Crystallogr.*, 36 (2003) 1487.



## KRISTALNA STRUKTURA [Cu(PLSC)(H<sub>2</sub>O)(SO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O KOMPLEKSA

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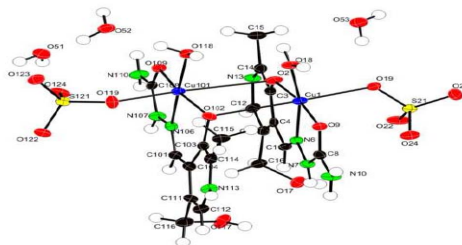
Kompleks [Cu(PLSC)(H<sub>2</sub>O)(SO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O je dobijen u reakciji bakar-sulfata-pentahidrata i piridoksal-semikarbazona (PLSC) u molskom odnosu 1:1. Sastav kompleksa je određen elementalnom mikroanalizom, a struktura rendgenskom strukturnom analizom.

Eksperimentalni rezultati elementalne mikroanalize za C, H, N su u saglasnosti sa teorijski izračunatim vrednostima. Nađeno za C<sub>18</sub>H<sub>34</sub>Cu<sub>2</sub>N<sub>8</sub>O<sub>19</sub>S<sub>2</sub> (*Mr* = 857.73) (%): C, 25,27; H, 4,03; N, 13,13. Izračunato (%): C, 25,21; H, 4,00; N, 13,06. Kristalna struktura kompleksa je rešena i utačnjena korišćenjem CRYSTAL 2000 programa [1,2].

Rešavanjem kristalne strukture kompleksa dobijeni su sledeći podaci: trikliničan, prostorna grupa *P*-1, veličina kristala 0.21 x 0.15 x 0.09 mm<sup>3</sup>, *a* = 9.2575(2) Å, *b* = 9.5857(2) Å, *c* = 17.1333(3) Å, β = 82.9242(9)°, *V* = 1497.16(5) Å<sup>3</sup>, *Z* = 2, ρ = 1.903 Mg/m<sup>3</sup>, *F*(000) = 880, μ = 1.660 mm<sup>-1</sup>, λ(MoKα) = 0.71073 Å, *T* = 150 K, izmerene su 18928 refleksije, *GooF* = 0.9624, *wR*<sub>2</sub>(*F*<sup>2</sup>) = 0.1156 za 6800 nezavisnih refleksija i 443 parametra, a *R*<sub>1</sub>(*F*) = 0.0564 za opaženih refleksija sa 0.01156.

[1] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, SIR 92- a program for automatic solution of crystal structures by direct methods, *J. Appl. Crystallogr.*, 27 (1994) 435.

[2] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, J. Prout, D.J. Watkin, CRYSTAL version 12: software for guided crystal structure analysis, *J. App. Crystallogr.*, 36 (2003) 1487.



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