ISSN 0354-5741

СРПСКО КРИСТАЛОГРАФСКО ДРУШТВО
SREBIAN CRYSTALLOGRAPHIC SOCIETY

XIII КОНФЕРЕНЦИЈА СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА

Изводи радова

XIII CONFERENCE OF THE SERBIAN CRYSTALLOGRAPHIC SOCIETY

Abstracts

НОВИ САД – NOVI SAD
2006.

XIII КОНФЕРЕНЦИЈА СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА
Изводи радова
XIII CONFERENCE OF THE SERBIAN CRYSTALLOGRAPHIC SOCIETY
Abstracts

Издавач - Publisher
- Српско Кристалографско Друштво,
Ђушина 7, 11 000 Београд, Србија и Црна Гора, тел./факс: 635 – 217
- Serbian Crystallographic Society
Đušina 7, 11 000 Belgrade, Serbia and Montenegro, phone/fax: 381 – 11 – 635 – 217

За издавача – For the publisher
Љиљана Карановић – Ljiljana Karanović

Технички уредник – Technical editor:
Агнеш Капор – Agneš Kapor
Оливера Клисурић – Olivera Klisurić

Издавање ове публикације омогућено је финансијском помоћи Департмана за физику (ПМФ, Нови Сад), Природно-математичког факултета (Универзитет у Новом Саду) и Министарства за науку и заштиту животне среднине Републике Србије.
This publication is financially supported by Department of Physics (Faculty of Sciences, Novi Sad), Faculty of Sciences (Univresity of Novi Sad) and Ministary of Science and Environmental Protetction of the Republic of Serbia.

ISSN 0354-5741

Штампа – Printing:
“СИМБОЛ”
Петроварадин
“SIMBOL”
Petrovaradin

Тираж – Copies: 100
Нови Сад – Novi Sad
2006

XIII КОНФЕРЕНЦИЈА
СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА
Нови Сад, 01. – 03. 6. 2006.

XIII CONFERENCE
OF THE SERBIAN CRYSTALLOGRAPHIC SOCIETY
Novi Sad, 01. – 03. 6. 2006.

НАУЧНИ ОДБОР / SCIENTIFIC COMMITTEE:

- Слободанка Станковић, ПМФ, Нови Сад
- Братислав Антић, ИНН "Винча", Винча
- Дејан Полети, ТФ Београд
- Љиљана Карановић, РГФ Београд
- Александар Кременовић, РГФ Београд
- Снежана Зарић, ХФ Београд
- Срећко Трифуновић, ПМФ Крагујевац

ОРГАНИЗАЦИОНИ ОДБОР / ORGANIZING COMMITTEE:

- Александра Росић, РГФ Београд
- Оливера Клисурић, ПМФ Нови Сад
- Агнеш Капор, ПМФ Нови Сад
- Срђан Ракић, ПМФ Нови Сад
- Горан Богдановић, ИНН "Винча", Винча

CONTENTS – САДРЖАЈ

PLENARY LECTURES – ПЛЕНАРНА ПРЕДАВАЊА

ORAL PRESENTATIONS – САОПШТЕЊА

PLENARY LECTURES
ПЛЕНАРНА ПРЕДАВАЊА

STRUCTURAL INFORMATION FROM TRANSITION-METAL SULFUR COMPLEXES MODELING POTENTIAL INTERMEDIATES OF BIOLOGICAL N_2 FIXATION: PRINCIPLES *VERSUS* COPIES

Frank W. Heinemann[a] **and Dieter Sellmanna**

[a]Institut für Anorganische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 1, D-91058 Erlangen, Germany

The red-hot temperatures and high pressures of the Haber-Bosch process (500 °C, 200 bar) reflect the chemical inertness of the N_2 molecule, but are in strong contrast to the mild conditions (20°C, 1 bar, redox potential ~ -500mV) of the biological N_2 fixation catalyzed by Fe/Mo, Fe/V, or FeFe nitrogenases, and this discrepancy represents a persistent challenge for chemists.

The first low molecular weight transition metal dinitrogen complex has been reported in 1964 [1] and since then numerous N_2 complexes have been prepared and characterized. While in some of these complexes the N_2 ligand could be reduced to give nitrogen hydrogen species even down to ammonia, none of the synthetic chemical systems truly works catalytic. In 1992 the X-ray structure of FeMo nitrogenase was solved and a very recent and more precise structure determination was published in 2002.[2] But even the elucidation of the FeMo cofactor of nitrogenases has not afforded a detailed understanding of the mechanism of biological N_2 fixation. In the search for transition metal complexes modeling nitrogenase-like activity it has become clear that such compounds must realize the *principles* that govern the reactivity of metalloenzyme centers rather than being structural copies. These principles include structural features like the sulfur coordination of the metal centers. Beyond this, model complexes have to (i) be robust and stable in the absence of proteins, (ii) exhibit vacant sites for the coordination and activation of substrates, (iii) possess Brønsted acid-base properties for the transfer of protons, (iv) be redox active for the transfer of electrons and (v) enable the electron transfer at mild redox potentials.[3]

A series of transition metal complexes of related sulfur ligands with nitrogenase relevant co-ligands such as N_2, N_2H_2, N_2H_4, and NH_3 has been investigated by means of X-ray crystallography. The crystallographic characterization of these complexes and the discussion of their structural features gives valuable information on how the necessary principles can be realized in low molecular weight complexes. This, in turn, might be helpful in achieving a better understanding of nitrogenase functionalities and the future development of highly active low molecular weight catalysts.

[1] A. D. Allen, C. V. Senoff, *Chem. Comm.,* 621 (1965)
[2] J. Kim, D. C. Rees, *Science,* 297 (2002), 1696.
[3] D. Sellmann, J. Sutter, in *Progress in Inorganic Chemistry*, Vol. 52 (Eds. E. I. Stiefel), John Wiley and Sons, Hoboken, NJ, (2004) 585.

WHAT BRINGS AROMATIC RING CLOSER TO METAL ATOM? THE CASE OF METAL COMPLEXES.

Zoran D. Tomić

'Vinča' Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, PO Box 522, 11001 Belgrade, Serbia and Montenegro
e-mail: zorant@vin.bg.ac.yu

To succeed in design of solid material with desired physical and chemical properties, the necessary prerequisite is capability to 'predict crystalline architectures from knowledge of chemical composition [1]. While there is a growing interest in developing theoretical models capable to predict crystal structure, the complexity of the problem makes this task still heavily dependent on collecting data relevant to the consideration of crystal packing modes. Systematic structural analysis of closely related molecules has revealed that some types of intermolecular interactions occurs more frequently and consequently can be considered as the determining factor for the association of molecules in the solid state. These includes hydrogen bonds, stacking interactions, agostic interactions, H···H and Au···Au interactions, to mention some of the most investigated. In this work we will focus on the interactions involving metal-chelate and phenyl ring, which until recently has not been recognized as the factor important for the consideration of crystal packing.

Report of the crystal structure of bis[acetone-1-naphthoylhydrazinato(-1)]copper(II) complex [2] point to the interesting observation about its intermolecular contacts. The copper is four coordinated in a square-planar arrangement, thus leaving the axial directions open to approach by neighboring molecules. Interestingly, the atom found to be the closest to the copper in the axial direction was not one of those known to have affinity towards copper atoms i.e. N or O, or Cu atom, but the aromatic carbon from the naphthalene fragment. It is positioned at a distance of 3.185(3) Ǻ from the copper, forming angles with other atoms expected for the octahedral coordination. The facts that this distance is shorter than the sum of the van der Waals radii (4.05 Ǻ), that angles resemble those expected for axially coordinated atom, and known 'plasticity' of the copper coordination sphere, gave reason to suspect that this may be an example of weakly coordinated aromatic carbon. Inspection of literature reveals the few similar observations, and in all these reports this arrangement has been described as a weak bond between the copper and aromatic carbon. However the spatial relations of the closest chelate and phenyl rings as well as disposition of charges in both rings strongly supported the assumption that these interactions involve not only the copper atom but also the whole chelate ring. To investigate more closely this type of contacts we perform the database studies of the square-planar copper complexes [3] with aim to find out how frequent is this type of contact. We confirmed the role of chelate-phenyl stacking interaction as an important factor in this contact. For the investigated data set we found that in about 60%, the Cu-C(phenyl) distance is bellow the sum of van der Waals radii of copper and carbon atoms. This indicate the relative importance of this type of interaction for the association of square-planar copper complexes in the solid state. In order to establish whether the presence of the chelate ring influence the geometry of this contacts, we analyze statistical distributions and correlations of the various geometrical parameters describing this contact. The results support assumption that Cu···C(aromatic) contacts are strongly influenced by the interaction between the chelate and phenyle rings. To find out whether these interactions are unique to the copper complexes or present in other systems also, we extend this analysis on the square-planar complexes including all transition metals [4]. To have a criteria for the presence of interaction common for all metal atom types the parameter Δ have been defined, representing the difference between the sum of the van der Waals radii of the respective atoms, and the observed metal-carbon distance. In cases where $\Delta>0$ it is supposed that interaction exist and *vice versa*. In was found that in the complexes with chelate rings, there is a larger percentage of structures with a metal-carbon distance below the sum of the van der Waals radii ($\Delta > 0$) than in the complexes without chelate rings. The other important geometrical parameter is the dihedral angle between the mean plane of the phenyl ring and the mean coordination plane consisting of metal and coordinated atoms. The distribution of this angle in structures with and without chelate rings shows a clear difference and is in accordance with the presence of interaction between the chelate and phenyle rings.

Identification of the interactions important for consideration of association of molecules is the first step in crystal engineering and should be followed by the analysis of factors which could be a tool for 'tailoring' the association of molecules toward the specific crystal structure. As an illustration of this task we will point to the sensitivity of the described stacking contacts to the size of the aromatic system present in the molecule.

The crystal structure of dichloro(2-hydroxy-1-naphtaldehyde-3-methylisothio semicarbazonato)iron(III) complex [5], is an interesting example both for preference towards the stacking contacts even in the presence of strong hydrogen bond donors and acceptors, and for the influence of the size of the aromatic system on the spatial relations between the neighboring molecules. In spite of the presence of fragment likely to form hydrogen bonds, it turns out that a unique multi-stacked π,π interaction occurs between chelate rings, forming a chain along the b axis of the crystal. How this arrangement could be influenced by the size of aromatic system can be seen in the crystal structure of the similar iron complex, with the same coordination sphere, but one aromatic ring less in the organic ligand. There is again multi-stacked π,π interaction and formation of chains, however spatial relations of the neighbouring molecules are changed and correlate with the different properties of the aromatic systems present.

On the basis of the above observations we may say that in the square planar complexes metal-aromatic carbon contacts are in most cases consequence of chelate-phenyl stacking interactions. With regard to the usability of this interaction for rationalization of the crystal packing, it is important to stress its relatively frequent observation, which is indication of energetically favorable arrangement, and possibility to tailor the mode of association of the molecules by varying the properties of the aromatic systems.

[1] C. V. Krishnamohan Sharma, Crystal Growth & Design, 2 (2002) 465.
[2] Z. D. Tomić, V. M. Leovac, S. V. Pokorni, D. Zobel, S. D. Zarić, Eur. J. Inorg. Chem. (2003) 1222.
[3] Z. D. Tomić, S. B. Novaković, S. D. Zarić, Eur. J. Inorg. Chem. (2004) 2215.
[4] Z. D. Tomić, D. Sredojević, S. D. Zarić, Crystal Growth & Design, 6 (2006) 29.
[5] Z. D. Tomić, V.M.Leovac, Ž. K. Jaćimović, G.Giester, S. D. Zarić, Inorg, Chem. Comm., (2006) in press.

ŠTA UTIČE NA PRIBLIŽAVANJE AROMATIČNOG PRSTENA METALNOM ATOMU?

Zoran D. Tomić

Institut za nuklearne nauke "Vinča", Laboratorija za teorijsku fiziku i fiziku čvrstog stanja, P.Fah 522, 11001 Beograd, Srbija i Crna Gora
e-mail: zorant@vin.bg.ac.yu

U istraživanjima usmerenim ka sintezi molekulskih materijala sa željenim fizičkim i hemijskim svojstvima nameće se potreba da se na osnovu poznavanja strukture molekula predvidi način njihovog udruživanja u kristalu [1] Predloženo je nekoliko pristupa u rešavanju ovog problema, a naročita pažnja je usmerena ka formulisanju teorijskih modela koji bi omogućili brže i potpunije ispitivanje različitih mogućnosti za sintezu materijala sa željenom strukturom (svojstvima). Međutim složenost problema čini da su i dalje napori u ovoj oblasti u velikoj meri oslonjeni na eksperimentalna istraživanja i utvrđivanje načina na koji strukturna svojstva izolovanih molekula utiču na način njihovog udruživanja u čvrstom stanju. Značajni rezultati su ostvareni primenom sistematske analize strukturnih parametara, uz primenu statističkih metoda, koja omogućava da se analizom velikog broja kristalnih struktura uoče oni činioci koji u većoj meri utiču na način udruživanja molekula u čvrstom stanju. Tako je ukazano na ulogu koju imaju vodonične veze, interakcije aromatičnih prstenova, H···H ili Au···Au interakcije, da pomenemo samo neke od najčešće ispitivanih. U ovom radu ćemo skrenuti pažnju na interakcije između metala koji su deo helatnog prstena, i aromatskog prstena, koje do nedavno nisu sistematski ispitivane.

U kristalnoj strukturi bis[aceton-1-naftoilhidrazonato(-1)]bakar(II) kompleksa [2] opaženo je da se na rastojanju 3.185(3) Å od atoma bakra nalazi atom ugljenika iz naftalenskog prstena. Uglovi koje ovaj atom gradi sa ostalim koordinovanim atomima su bliski onima koji se očekuju kod oktaedarski koordinovanog atoma. Ono što je donekle neočekivano je da bakar ne ostvaruje intermolekulski kontakt sa nekim od atoma za koje se zna da često formiraju takve kontakte kakvi su u ovom slučaju atomi N, O ili Cu iz susednog molekula, pa se postavlja pitanje da li se može govoriti o postojanju interakcije između aromatskog ugljenika i bakra u ovom kristalu. Ono što ide u prilog ovakvoj pretpostavci je i poznata osobina ‘’plastičnosti’’ koordinacione sfere bakra. Pregledom literature ustanovljeno je da je u nekoliko slučajeva saopšteno opažanje sličnih strukturnih fragmenata, i protumačeno kao posledica postojanja slabe interakcije između atoma Cu i aromatičnog ugljenika. Međutim detaljnija analiza položaja dva susedna prstena, helatnog i fenilnog, i izračunavanje raspodele naelektrisanja u njima, ukazala je na mogućnost da je Cu···C kontakt u ovom slučaju posledica interakcije između helatnog i fenilnog prstena. Da bi se ustanovilo kakva je verovatnoća formiranja ovakvog kontakta i utvrdili činioci koji utiču na njegovo pojavljivanje izvršena je analiza geometrijskih parametara koji opisuju medjusobni položaj dva najbliža molekula u kristalnim strukturama kvadratno-planarnih kompleksa Cu [3]. Za ovu i ostale analize opisane u ovom radu korišćeni su podaci koji se nalaze u Kristalografskoj banci podataka u Kembridžu. Opaženo je da je u približno 60% analiziranih struktura, ispitivano Cu···C rastojanje manje od zbira van der Valsovih poluprečnika bakra i ugljenika. Statistička analiza parametara koji opisuju položaj najbližih molekula je u skladu sa pretpostavkom o postojanju interakcije između helatnog i fenilnog prstena. Isti metod je primenjen i na analizu kvadratno-planarnih kompleksa koji obuhvataju sve prelazne metale [4]. Da bi isti kriterijum za postojanje interakcije mogao da bude primenjen na strukture koje sadrže različite metale definisan je parametar Δ koji je jednak razlici između zbira van der Valsovih poluprečnika atoma Cu i C, i opaženog Cu···C rastojanja. Kada je $\Delta>0$ može se govoriti o postojanju interakcije. Poređenje raspodele vrednosti ovog parametra u strukturama sa i bez helatnog prstena pokazuje da prisustvo helatnog prstena pospešuje interakciju između atoma Cu i C. Uočava se i jasna razlika u međusobnom položaju srednje koordinacione ravni i fenilnog prstena u zavisnosti od toga da li je u molekulu prisutan helat ili ne. U prisustvu helata ove ravni teže da se postave približno paralelno, što odgovara pretpostavci o postojanju helat-fenil interakcije. Kod struktura u kojima nema helatnog prstena uočljiva je težnja da se dve ravni postave približno normalno.

Uočavanje intermolekulskih interakcija koje su važne za razumevanje udruživanja molekula u kristalu je prvi korak u pokušajuma da se opaženi strukturni raspored u kristalu protumači u odnosu na strukturu izolovanog molekula. Da bi na tu strukturu moglo da se utiče potrebno je poznavati i šta utiče na svojstva ispitivane interakcije. Analize opisane u ovom radu su pokazale da je jedan od činioca koji utiče na geometriju intermolekulskih kontakata kvadratno-planarnih kompleksa, i veličina aromatskog sistema. Primer za to je kristalna struktura dihloro(2-hidroksi-1-naftaldehid-3-metilizotiosemikarbazonato) gvožđe(III) kompleksa [5]. Ovaj molekul sadrži strukturne fragmente za koje se može pretpostaviti da će formirati vodonične veze međutim pokazalo se da je struktura koja se formira posledica višeslojnog uređivanja molekula kao posledica interakcije između helatnih prstenova. Kako se na ovakav raspored molekula može uticati može se videti poređenjem sa strukturom kompleksa čija je osnovna razlika u odnosu na pomenuti odustvo jednog C_6 prstena. I u ovom slučaju dolazi do obrazovanja višeslojnog ‘’molekulskog lanca’’ ali je međusobni položaj susednih molekula različit i može se protumačiti kao posledica različitih veličina aromatskih sistema.

Opisani rezultati ukazuju da kontakte između atoma metala i ugljenika iz fenilnog prstena ne treba posmatrati kao posledicu interakcije pojedinačnih atoma Cu i C već se mora uzeti u obzir interakcija helatnih i fenilnih prstenova čiji su ovi atomi deo. Činjenica da se ovi kontakti pojavljuju u relativno velikom broju struktura ukazuje da je njihovo obrazovanje energetski povoljno u ispitivanom tipu kompleksa, i da se uticajem na njihova svojstva može uticati na način udruživanja kvadratno-planarnih kompleksa u čvrstom stanju.

[1] C. V. Krishnamohan Sharma, Crystal Growth & Design, 2 (2002) 465.

[2] Z. D. Tomić, V. M. Leovac, S. V. Pokorni, D. Zobel, S. D. Zarić, Eur. J. Inorg. Chem. (2003) 1222.

[3] Z. D. Tomić, S. B. Novaković, S. D. Zarić, Eur. J. Inorg. Chem. (2004) 2215.

[4] Z. D. Tomić, D. Sredojević, S. D. Zarić, Crystal Growth & Design, 6 (2006) 29.

[5] Z. D. Tomić, V.M.Leovac, Ž. K. Jaćimović, G.Giester, S. D. Zarić, Inorg, Chem. Comm., (2006) in press.

ELECTROSTATIC POTENTIAL AS AN EXPERIMENTAL OR A THEORETICAL TOOL FOR A BETTER UNDERSTANDING OF DRUG INTERACTIONS

Nour Eddine Ghermani[a] and Anne Spasojevic – de Biré[b]

[a]*Laboratoire Physico-chimie, Pharmacotechnie, Biopharmacie, UMR 8612 du CNRS, Paris-Sud, Faculté de pharmacie, 92296 Châtenay-Malabry, France*
[b]*Laboratoire "Structures Propriétés et Modélisation des Solides", UMR 8580 du CNRS, Ecole Centrale Paris, 92295 Châtenay-Malabry, France*

High-resolution X-ray diffraction and theoretical calculations allow a fine characterization of these electronic and electrostatic properties in crystals, which is essential to the understanding and prediction of the interaction of drugs with the biological targets (pharmacology) and excipients (formulation). This fundamental approach can have important consequences for practical applications in the areas of drug design or drug delivery. The Laboratoire Structures, Propriétés et Modélisation des Solides, SPMS (UMR 8580, CNRS / Ecole Centrale Paris), who will lead the proposed project, has developed a dual experimental and theoretical expertise in this field. Since 2002, we have expanded our approach combining high-resolution X-ray diffraction and *ab initio* calculations to the characterization of pharmaceutical solids through a joint research group ("*Pharmaceutical Materials*") involving SPMS and the Laboratoire de Physico-chimie, Pharmacotechnie, Biopharmacie, PPB (UMR 8612 – CNRS / Paris Sud) of the Faculté de Pharmacie of Châtenay-Malabry. Our collaborative work has enabled us to answer several questions posed by medicinal chemists or galenists, in particular relative to the following topics:

- Electronic and electrostatic properties of racemic ibuprofen [1]
- Electronic and electrostatic properties of a complex of zinc aspirin [2]
- Understanding of the crystallization of busulfan, a pediatric cancer chemotherapeutic drug, and development of a new formulation (encapsulation in a cyclodextrine derivate) [3]
- Understanding of the reactivity toward nucleophile agent: a putative intermediary product in the total synthesis of cephalotaxine (antileukemic agent) [4]
- Electronic and electrostatic properties of co-crystal of decavanadate – cytosine, compound implied in the activity or inhibition of various enzymes (phosphotransferases, Ca^{2+} ATP-ase, adenylate kinase, and others) [5]
- Experimental and theoretical electrostatic properties of salicyladehyde thiosemicarbazone, a pharmacophore of trombopoietin mimics, one of the simplest ligands in the thiosemicarbazone family [6]
- Experimental and theoretical electrostatic properties of styrylquinoline-based compounds as new inhibitors in the integrase of the HIV-1 [7,8].

In this talk we will present results concerning the above-cited compounds.

In the abstract, we will focus on our work on the electrostatic properties of HIV-1 integrase inhibitors [7,8] in collaboration with the team of d'Angelo (Laboratoire BIOCIS, UMR 8076, CNRS - Paris-Sud). The most promising candidate from the point of view of its therapeutic indicators (*in vitro* inhibition, *ex vivo* and toxicity) is (E)-8-hydroxy-2-[2-(4,5-dihydroxy-3-methoxyphenyl)-ethenyl]-7-quinoline carboxylic acid. This compound is in pre-clinical development phase (Bio-Alliance star-up). Crystals are very small and air sensitive. Single X-ray diffraction has permitted the determination of the molecular structure of the inhibitor, evidencing its zwiterionic character, but the quality of the crystals was not sufficient for high resolution even with experiments using ESRF synchrotron radiation. The two precursors have also being crystallized and the electron density has been determined. Experimental – theory (HF and DFT) comparisons have shown that there is no electronic delocalization between the two fragments when the spacer is ethylenic. Experiments have been conducted to synthesize several compounds similar to I changing the nature of the spacer and also the functional groups on the hydroxylated aromatic ring [9]. In complement, a systematic approach based on Kohonen neural network was also explored [10]. While conclusions on the role of these groups arose and then allowed for the synthesis of optimized molecules, the influence of the spacer on the activity of the inhibitors remained unclear. Among a hundred quinolines derivatives already synthesized we selected and compared molecules which exhibit various ability to inhibit the integrase. By means of first principals quantum chemistry computations, we aim at drawing from this comparison electrostatic criteria enable to predict which molecules are likely to be active. From our results we try to conclude to what extend their structure play a role in the reactional mechanism.

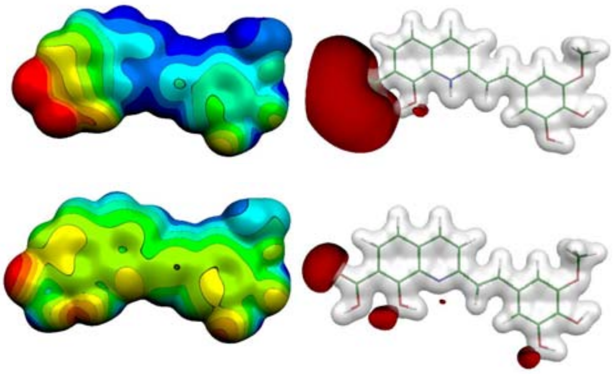


Figure : Electrostatic theoretical potential on the molecular surface (right) and isosurfaces of one integrase inhibitor. Zwiterionic form (up) and non-zwiterionic form (down). [8]

[1] BOUHMAIDA N., DUTHEIL M., GHERMANI N. E. and BECKER P. *«Gradient vector field and properties of the experimental electrostatic potential: application to Ibuprofen drug molecule. »*, J. Chem. Phys., **2002**, 116, 6196-6204

[2] SPASOJEVIC - DE BIRE A., BOUHMAIDA N., KREMENOVIC A., MORGANT G. and GHERMANI N. E. *«Experimental Electron Density and Electrostatic Potential Analysis of Zinc(Aspirinate)2(H2O)2 Complex: a 3d10 Metal Bonding to a Drug-ligand. »*, J. Phys Chem. A, **2002**, 106, 12170-12177

[3] GHERMANI N. E., SPASOJEVIC - DE BIRÉ A., BOUHMAIDA N., OUHARZOUNE S., BOULIGAND J., LAYRE A., GREF R. and COUVREUR P. *« Molecular Reactivity of the Busulfan Through its Experimental Electrostatic Properties in the Solid State. »*, Pharmaceutical Research, **2004**, 21, 598-607

[4] PIZZONERO M., KELLER L., DUMAS F., OUREVITCH M., MORGANT G., GHERMANI N. E., SPASOJEVIC - DE BIRE A., BOGDANOVIC G. and d'ANGELO J. *«Crystallographic/Electron Density Characterizations and Reactions with Nucleophiles of □-Enaminonitriles Possessing a Pyrrolobenzazepine Core. »*, J. Org. Chem., **2004**, 69, 4336-4350

[5] BOSNJAKOVIC-PAVLOVIC N., CORREIA I., TOMAZ I., BOUHMAIDA N., AVECILLA F., SPASOJEVIC-DE BIRÉ A., MIOC U., PESSOA J., GHERMANI NE. *« Structure et Propriétés Electrostatiques d'un Complexe Décavanadate-Cytosine. »,* Colloque de l'Association Française de Cristallographie, AFC 2003. Caen (F), july **2003**

[6] NOVAKOVIC S., COURCOT B., FRAISSE B., LEOVAC V., BOGDANOVIC G.A., SPASOJEVIC-DE BIRÉ A., *« Experimental and theoretical electrostatic properties of salicylaldehyde thiosemicarbazone. », 5th World Meeting on Pharmaceutics Biopharmaceutics and Pharmaceutical Technology,* Geneva (CH), march **2006**

[7] FIRLEY D., FRAISSE B., ZOUHIRI, F., SPASOJEVIC - DE BIRE A., DESMAËLE D., D'ANGELO J. and GHERMANI N. E. *«7-Carboxylato-8-hydroxy-2-methylquinoliniummonohydrate and 7-carboxy-8-hydroxy-2-methylquinolinium chloridemonohydrate at 100 K »,* Acta Crystallogr., **2005**, C61, o154-o157

[8] FIRLEY D., COURCOT B., GILLET J.M., FRAISSE B., ZOUHIRI F., DESMAELE D., D'ANGELO J., GHERMANI N. E., "*Experimental/Theoretical Electrostatic Properties of a Styrylquinoline-Type HIV-1 Integrase Inhibitor and Its Progenitors*", Journal of Physical Chemistry B, **2006**, **110**, 537-547.

[9] BENARD, C., ZOUHIRI, F., NORMAND-BAYLE, M., DANET, M., DESMAËLE, D., LEH, H., MOUSCADET, J.F., MBEMBA, G., THOMAS, C.M., BONNENFANT, S., LE BRET, M. D'ANGELO, "*Linker-modified quinoline derivatives targeting HIV-1 integrase: synthesis and biological activity"J.* Bioorg. Med. Chem. Lett., **2004**, **14**, 2473-2476

[10] POLANSKI, J., ZOUHIRI, F., JEANSON, L., DESMAËLE, D., D'ANGELO, J., MOUSCADET, J.F., GIELECIAK,R., GASTEIGER, J. LE BRET, M. *"Use of the Kohonen neural network for rapid screening of ex vivo anti-HIV activity of styrylquinolines*" J.Med.Chem. **2002**, **45**, 4647-4654

ORAL PRESENTATION
САОПШТЕЊА

STRUCTURE OF HEXAAQUA (μ-1,2,4,5-BENZENETETRA-CARBOXYLATO)-BIS(2,2'-DIPYRIDYLAMINE)DINICKEL(II) HEXAHYDRATE DMSO SOLVATE AT 173 K

D. Poleti [a], **Lj. Karanović** [b], **A. Kremenović** [b], **J. Rogan** [a]

[a] *Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia and Montenegro*
[b] *Faculty of Mining and Geology, Đušina 7, Belgrade, Serbia and Montenegro*
e-mail: dejan@tmf.bg.ac.yu

Structure of the title complex has been published recently [1]. However, due to presence of wide channels (about 3.5×4.7 Å) parallel to the *b*-axis we had a problem to model some disordered solvent molecules. Instead, the contribution of these molecules to the structure factors was removed by the SQEEZE procedure implemented in program PLATON [2]. To resolve this ambiguity it was necessary to recollect single crystal X-ray diffraction data at low temperature (–100 ºC) and the results of this new structure determination are reported here.

At low temperature a predictable decrease (≈1.4 %) of unit cell volume was observed. However, in addition to expected H_2O molecules one DMSO molecule with a half occupation was found in crystal lattice channels. Since these molecules are located around the symmetry center, they are close to each other and cannot coexist at the same time. Therefore, this (minor) part of the structure is noncentrosymmetric, though the remaining main part is centrosymmetric. Besides, one O atom from uncoordinated COO groups is also found to be disordered.

Crystal data are as follows: $C_{32}H_{50}N_6Ni_2O_{21}S_1$, $M_r = 1004.26$, triclinic system, space group $P{-1}$, $a = 9.290(1)$, $b = 10.863(1)$, $c = 11.997(2)$ Å, $\alpha = 67.40(1)$, $\beta = 77.04(1)$, $\gamma = 84.79(1)$ º, $V = 1089.2(3)$ Å^3, $Z = 1$, $F(000) = 524$, $\rho_x = 1.531$ g cm^{-3}, $\mu = 0.998$ mm^{-1}, $S = 1.179$, $R_1 = 0.0606$ for 3189 reflections with $I>2\sigma(I)$, $wR_2 = 0.1237$ for 3972 independent reflections and 351 refined parameters.

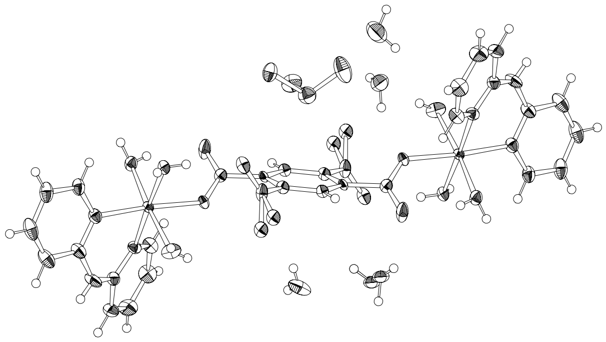


Figure 2. Binuclear complex unit and asymmetric part of lattice solvent molecules.
Slika 2. Bunuklearna kompleksna jedinka i asimetrični deo molekula rastvarača.

[1] J. Rogan, D. Poleti, Lj. Karanović, *Z. anorg. allg. Chem.*, **632** (2006) 133-139
[2] P. v.d. Sluis, A.L. Spek, *Acta Crystallogr.* **A46** (1990) 194-201; A.L. Spek, *J. Appl. Cryst.*, **36** (2003) 7-13

STRUKTURA HEKSAAKVA (μ-1,2,4,5-BENZENTETRAKARBOKSILATO)-BIS(2,2'-DIPIRIDILAMIN)DINIKAL(II)-HEKSAHIDRATA-DMSO SOLVATA NA 173 K

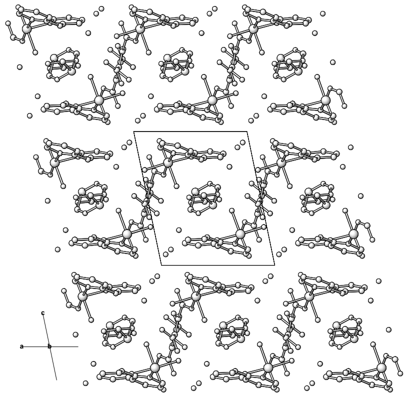
D. Poleti[a], **Lj. Karanović**[b], **A. Kremenović**[b], **J. Rogan**[a]

[a] *Tehnološko-metalurški fakultet, Karnegijeva 4, 11000 Beograd*
[b] *Rudarsko-geološki fakultet, Đušina 7, 11000 Beograd*
e-mail: dejan@tmf.bg.ac.yu

Mada je struktura navedenog kompleksa objavljena nedavno [1], zbog postojanja širokih kanala (oko 3.5×4.7 Å) paralelnih sa *b*-osom postojali su problemi pri modelovanju nekih neuređenih molekula rastvarača. Zbog toga je doprinos tih molekula strukturnim faktorima uklonjen pomoću procedure SQEEZE iz programa PLATON [2]. Da bi se rešili navedeni problemi bilo je nužno da se prikupljanje podataka ponovi na niskoj temperaturi (–100 ºC). Novi rezultati utačnjavanja strukture prikazani su u ovom radu.

Na niskoj temperaturi došlo je do predvidljivog smanjenja zapremine jedinične ćelije (≈1,4 %). Međutim, uz očekivane molekule H_2O u kanalima je nađen i jedan molekul DMSO sa okupacijom 0,5. Pošto su svi ti molekuli smešteni oko centra simetrije, oni su suviše blizu jedni drugima da bi mogli postojati u istoj jediničnoj ćeliji. Sledi da taj (manji) deo strukture mora biti necentrosimetričan, dok je ostatak strukture centrosimetričan. Osim toga, jedan atom O iz nekoordinirane COO-grupe takođe je statistički podeljen na dva položaja.

Kristalografski podaci: $C_{32}H_{50}N_6Ni_2O_{21}S_1$, $M_r = 1004{,}26$, triklinični sistem, prostorna grupa $P{-}1$, $a = 9{,}290(1)$, $b = 10{,}863(1)$, $c = 11{,}997(2)$ Å, $\alpha = 67{,}40(1)$, $\beta = 77{,}04(1)$, $\gamma = 84{,}79(1)$ º, $V = 1089{,}2(3)$ Å^3, $Z = 1$, $F(000) = 524$, $\rho_x = 1{,}531$ g cm^{-3}, $\mu = 0{,}998$ mm^{-1}, $S = 1{,}179$, $R_1 = 0{,}0606$ za 3189 refleksija sa $I > 2\sigma(I)$, $wR_2 = 0{,}1237$ za 3972 nezavisne refleksije i 351 utačnjavani parametar.



Slika 1. Pakovanje molekula, projekcija duž *b*-ose.
Figure 1. Crystal packing along *b*-axis.

[1] J. Rogan, D. Poleti, Lj. Karanović, *Z. anorg. allg. Chem.*, **632** (2006) 133-139
[2] P. v.d. Sluis, A.L. Spek, *Acta Crystallogr.* **A46** (1990) 194-201; A.L. Spek, *J. Appl. Cryst.*, **36** (2003) 7-13

CRYSTAL STRUCTURE OF *O,O'*-DI*ISO*PROPYL-(*S,S*)-ETHYLENEDIAMMONIUM-*N,N'*-DI-2-PROPANOATE CHLORIDE

Bojana B. Krajčinović[a], Goran N. Kaluđerović[a,b], Dirk Steinborn[b], Christoph Wagner[b], Srećko R. Trifunović[c], Zoran M. Miodragović[d] and Tibor J. Sabo[d]

[a]*Department of Chemistry, Institute of Chemistry, Technology and Metallurgy, Studentski trg 16, 11000 Belgrade, Serbia & Montenegro;* [b]*Institut für Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle, Germany;* [c]*Department of Chemistry, Faculty of Science, University of Kragujevac, 34000 Kragujevac, Serbia & Montenegro:* [d]*Faculty of Chemistry, University of Belgrade, P.O. Box 158, 11001 Belgrade, Serbia & Montenegro*
e-mail: bokilik@chem.bg.ac.yu

The title compound was synthesized by standard procedure of Fisher esterification. Namely, hydrogen chloride was introduced into a flask containing absolute isopropyl alcohol. Then, (*S,S*)-ethylenediamine-*N,N'*-di-2-propanic acid was suspended in absolute alcohol saturated with HCl, and the suspension was reflucted for 16 h. After that, the suspension was filtered and the filtrate was left on room temperature for several days. Crystals of [dip(*S,S*)eddpH_2]Cl_2 suitable for X-ray structure analysis were obtained.

Crystallographic data: $C_{14}H_{30}Cl_2N_2O_4$, orthorhombic system, space group $P22_12_1$, $a = 5.0876(8)$, $b = 9.4982(18)$, $c = 20.414(5)$ Å, $V = 986.5(3)$ Å^3, $Z = 2$, $D_c = 1.216$ Mg/m^3, $\mu(\mathrm{Mo}K\alpha) = 0.346$ mm^{-1}, F(000) = 388. Data collection: $2.00 < \theta < 25.95°$, no. of parameters: 124, $R_1 = 0.059$, $wR_2 = 0.1548$ for 1828 reflections with $I > 2\sigma(I)$.

The crystal consists of three species: one dicationic, dip(*S,S*)eddp^{2+} (*O,O'*-di*iso*propyl-(*S,S*)-ethylenediammonium-*N,N'*-di-2-propanoate) and two Cl^- anions. All of the mentioned species are involved in H-bonding (H(0A)$\cdots$Cl = 3.127(4) Å, N–H(0A)$\cdots$Cl = 165°; H(0B)$\cdots$Cl = 3.120(4) Å, N–H(0B)$\cdots$Cl = 164°), and these interactions led to building a one-layer structure. The angle between NC1C1N and NClNCl planes is 90°.

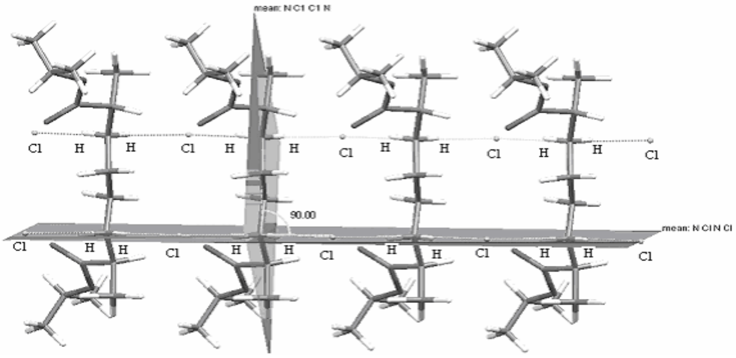


Fig. 1. Hydrogen bonding of [dip(*S,S*)eddpH_2]Cl_2

KRISTALNA STRUKTURA (*O,O'*-DI*IZO*PROPIL-(*S,S*)--ETILENDIAMMONIUM-*N,N'*-DI-2-PROPANOAT) HLORIDA

Bojana B. Krajčinović[a], Goran N. Kaluđerović[a,b], Dirk Steinborn[b], Christoph Wagner[b], Srećko R. Trifunović[c], Zoran M. Miodragović[d] and Tibor J. Sabo[d]

[a]*Centar za hemiju, Institut za hemiju, tehnologiju i metalurgiju, Studentski trg 16, 11000 Beograd, Srbija i Crna Gora;* [b]*Institut für Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle, Germany;* [c]*Departman za hemiju, PMF, Univerzitet u Kragujevcu, 34000 Kragujevac, Srbija i Crna Gora;:* [d]*Hemijski fakultet, Univerziet u Beogradu, P.O. Box 158, 11001 Beograd, Srbija i Crna Gora*
e-mail: bokilik@chem.bg.ac.yu

O,O'-di*izo*propil-(*S,S*)-etilendiamin-*N,N'*-di-2-propanoat sintetisan je standardnom Fisher-ovom esterifikacijom. Gasoviti hlorovodonik je uvođen u balon koji sadrži apsolutni izo-propanol, zatim je (*S,S*)-etilendiamin-*N,N'*-di-2-propanska kiselina suspendovana u apsolutnom alkoholu zasićenim hlorovodonikom. Suspenzija je refluktovana 16 sati. Posle toga suspenzija je procеđena i filtrat je ostavljen na sobnoj temperaturi nekoliko dana. Dobijeni su kristali pogodni za rendgensku strukturnu analizu.

Kristalografski podaci: $C_{14}H_{30}Cl_2N_2O_4$, rombičan sistem, prostorna grupa $P22_12_1$, $a = 5{,}0876(8)$, $b = 9{,}4982(18)$, $c = 20{,}414(5)$ Å, $V = 986{,}5(3)$ Å^3, $Z = 2$, $D_c = 1{,}216$ Mg/m^3, $\mu(\mathrm{Mo}K\alpha) = 0{,}346$ mm^{-1}, F(000) = 388. Opseg: $2{,}00 < \theta < 25{,}95°$, broj parametara: 124, $R_1 = 0{,}059$, $wR_2 = 0{,}1548$ za 1828 refleksija sa $I > 2\sigma(I)$.

Dobijeni monokristali se sastoje iz tri hemijske vrste: jednog dikatjona, dip(*S,S*)eddp^{2+} (*O,O'*-di*izo*propil-(*S,S*)-etilendiammonijum-*N,N'*-di-2-propanoat) i dva anjona hlora. Sve pomenute vrste učestvuju u vodoničnom vezivanju (H(0A)$\cdots$Cl = 3,127(4) Å, N–H(0A)$\cdots$Cl = 165°; H(0B)$\cdots$Cl = 3,120(4) Å, N–H(0B)$\cdots$Cl = 164°), što je dovelo do građenja jednoslojne strukture. Ugao između NC1C1N and NClNCl ravni iznosi 90°.

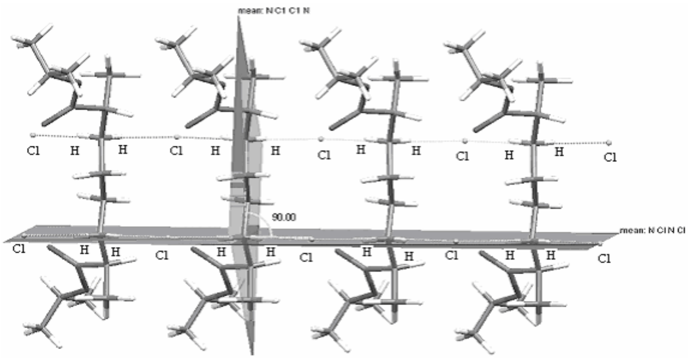


Fig. 1. Vodonično vezivanje [dip(*S,S*)eddpH_2]Cl_2

THE CRYSTAL STRUCTURE OF COMPLEX [NI(S,S-eddp)]×2H_2O

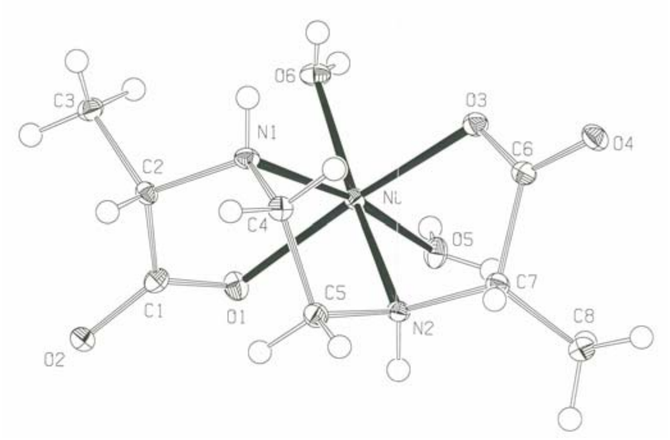
S. Trifunović[a], M. Stanković[a], Z. Matović[a], G. Vasić[a], A. Meetsma[b], P. J. van Koningsburggen[b]

[a]*Faculty of Science, University of Kragujevac, R. Domanovic 12, P.O.Box, 60, SCG;* [b]*Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Groningen NL-9747, The Netherland*
e-mali: srecko@kg.ac.yu

The complex [Ni(S,S-eddp)]×2H_2O was obtained in reaction of nickelhloride–-hexahidrate and ethylenediamine-*N,N`*-di-S,S-2-propionic acid (S,S-eddp) in molar ratio 1:1 at 65°C and pH = 7. This green crystals was undergone to elemental microanalyisis and X-ray sructure analysis.

The experimental results of the elemental analysis for C, H, N are in accordance with calculated values. Found (%): C, 32.57; H, 6.16; N, 9.48. Calculated: C, 32.36; H, 6.11; N, 9.44.

The structure of the complex was solved and refined using SHELXL program. Results of structure refinement of complex compound: $C_8H_{18}N_2NiO_6$, M_r = 296.93, monoclinilc, space group $P2_1$, crystal size 0.14×0.12×0.09 mm, block shape and green coloured, $a = 7.5532(5)$, $b = 9.1933(6)$, $c = 8.2722(5)$ Å, $\beta = 100.225(1)°$, $V = 565.29(6)$ Å^3, $Z = 2$, $\rho = 1.773$ gcm^{-3}, $F(000) = 312$, $\mu = 17.35$ cm^{-1}, $\lambda(\mathrm{MoK}_\alpha) = 0.71073$ Å, T = 100(1) K, 5182 reflection measured, $GOOF = 1.055$, $wR_2(F^2) = 0.0689$ for 2671 unique reflections and 226 parameters, 1 restraints and $R_1(F) = 0.0270$ for 2596 reflections obeying $F_0 \geq 4\sigma(F_0)$ criterion of observability.



KRISTALNA STRUKTURA KOMPLEKSA [NI(S,S-eddp)]×$2H_2O$

S. Trifunović[a], M. Stanković[a], Z. Matović[a], G. Vasić[a], A. Meetsma[b], P. J. Koningsbruggen[b]

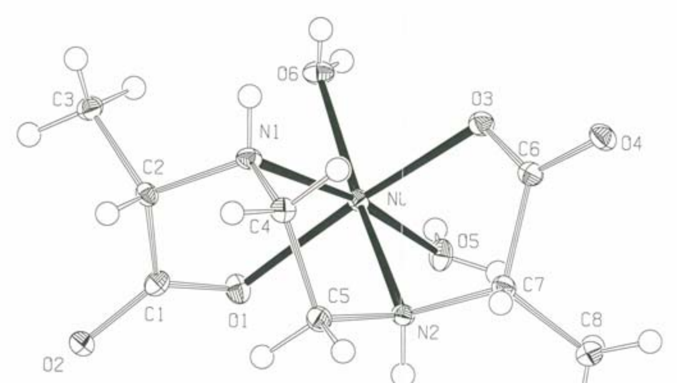
[a]*Prirodno-matematički fakultet, Univerzitet u Kragujevcu, R. Domanovića 12, P.O. Box 60, SCG;* [b]*Institut za Organsku i molekularnu neorgansku hemiju,Univerzitet u Groningenu, Groningen NL-9747,Holandija;*
e-mail: srecko@kg.ac.yu

Kompleks [Ni(S,S-eddp)]×$2H_2O$ je dobijen u reakciji nikal-hlorida-heksa-hidrata i etilendiamin-*N,N'*-di-S,S-2-propionske kiseline (S,S-eddp) u molskom odnosu 1:1, na temperaturi 65 °C i pH = 7. Sastav kompleksa je određen elementarnom mikroanalizom, a struktura rendgenskom strukturnom analizom.

Eksperimentalni rezultati elementarne mikroanalize za C, H, N su u saglasnosti sa teorijski izračunatim vrednostima. Nađeno (%)C, 32,57; H, 6,16; N, 9,48. Izračunato (%): C, 32,36; H, 6,11; N, 9,44.

Kristalna struktura kompleksa je rešena i utačnjena korišćenjem SHELXL programa.

Rešavanjem kristalne strukture kompleksa dobijeni su sledeći podaci: $C_8H_{18}N_2NiO_6$, M_r = 296,93, monokliničan, prostorna grupa $P2_1$, veličina kristala 0,14 × 0,12 × 0,09 mm, a = 7,5532(5), b = 9,1933(6), c = 8,2722(5) Å, β = 100,225(1)°, V = 565,29(6) Å^3, Z = 2, ρ = 1,773 gcm^{-3}, $F(000)$ = 312, μ = 17,35 cm^{-1}, $\lambda(\mathrm{MoK}_{\alpha}^{-})$ = 0,71073 Å, T = 100(1) K, izmerene su 5182 refleksije, *GooF* = 1,055, $wR_2(F^2)$ = 0,0689 za 2671 nezavisnih refleksija i 226 parametra, a $R_1(F)$ = 0,0270 za 2596 opaženih refleksijasa $F_0 \geq 4.0\sigma(F_0)$.



SYNTHESIS AND CRYSTAL STRUCTURE OF $SR_4CU_3(ASO_4)_2(ASO_3OH)_4{\cdot}3H_2O$

Tamara Mihajlović

Institut für Mineralogie und Kristallographie, Universität Wien – Geozentrum, Althanstrasse 14, 1090 Wien, Austria
e-mail: tamara.mihajlovic@univie.ac.at

The new compound $Sr_4Cu_3(AsO_4)_2(AsO_3OH)_4{\cdot}3H_2O$ was synthesised under hydrothermal conditions from a mixture of $Sr(OH)_2$, CuO, As_2O_5 and H_2O using Teflon-lined stainless steel autoclaves (493 K, 2 days). It crystallised as blue transparent prismatic crystals up to 0.15 mm in length together with a small amount of $Sr(AsO_3OH)$ [1]. It is the first Sr-Cu arsenate in the system SrO–CuO–As_2O_5–H_2O and represents a new structural type.

The crystal structure of $Sr_4Cu_3(AsO_4)_2(AsO_3OH)_4{\cdot}3H_2O$ was determined by single-crystal X-ray diffraction (298 K, Mo$K\alpha$, $2\theta_{max} = 60°$): space group $C2/c$, $a = 18.536(4)$, $b = 5.179(1)$, $c = 24.898(5)$ Å, $\beta = 101.28(3)°$, $V = 2344.0(8)$ Å^3, $Z = 4$. The refinement with 204 free parameters yielded $R_1(F) = 0.0292$, $wR_2(F^2) = 0.0694$ for the 3428 unique reflections, and $R_1(F) = 0.0211$ for the 2864 observed reflections with $F_o^2 \geq 4\sigma(F_o^2)$ [2].

The crystal structure of $Sr_4Cu_3(AsO_4)_2(AsO_3OH)_4{\cdot}3H_2O$ is related to a group of compounds formed by Cu(II)-XO$_4$ ($X = P^{5+}$, As^{5+}) layers linked by Me cations [Me = alkali or alkaline earth metal, Pb(II) or Ag(I)] and partly by hydrogen bonds [3]. These layers involve Cu_3O_{12} units formed by one square-planar coordinated Cu atom on the symmetry centre corner-connected to two Cu atoms in [5]-coordination. Distinct patterns and links of the Cu_3O_{12} groups by XO$_4$ tetrahedra were observed.

In the title compound the stacked [$Cu_3(As(2)O_4)(As(3)O_3OH)$] layers with Cu_3O_{12} groups arranged parallel to each other are interconnected by two distinct SrO_8 polyhedra, by one $As(1)O_4$ tetrahedron, and partly by hydrogen bonds. These layers show an *ABAB* stacking sequence. The SrO_8 polyhedra are distorted square antiprisms with average bond distances of 2.630 and 2.631 Å. The central Cu(1) atom of the Cu_3O_{12} group is square-planar coordinated with an average bond length of 1.964 Å. The terminal Cu(2) atom features a [3+1+1] coordination resulting in a distorted trigonal bipyramid: the two shortest Cu–O bonds represent the axis, whereas equatorial O–Cu(2)–O angles are 101.23(8), 115.52(7) and 144.86(8)°. The arsenate terahedra are fairly regular. The average As–O bond distances vary from 1.686 to 1.693 Å. The H atoms were detected in a difference Fourier map at plausible positions and their atomic coordinates were refined successfully.

Financial support of the Austrian Science Foundation, FWF (Grant P15875-N03) is gratefully acknowledged.

[1] T. Mihajlović, H. Effenberger, *Z. Kristallogr. Suppl. Issue*, **22** (2005), 73
[2] G. M. Sheldrick, SHELX-97, a program for the solution and refinement of crystal structures. University of Göttingen, Germany (1997)
[3] H. Effenberger, *J. Solid State Chem.*, **142** (1999), 6-13

СИНТЕЗА И СТРУКТУРА $SR_4CU_3(ASO_4)_2(ASO_3OH)_4\cdot 3H_2O$

Тамара Михајловић

Institut für Mineralogie und Kristallographie, Universität Wien – Geozentrum, Althanstrasse 14, 1090 Wien, Austria
e-mail: tamara.mihajlovic@univie.ac.at

Једињење $Sr_4Cu_3(AsO_4)_2(AsO_3OH)_4\cdot 3H_2O$ синтетисано је хидротермалном методом тако што је смеша $Sr(OH)_2$, CuO, As_2O_5 и H_2O стављана у тефлонске судове и загревана у аутоклавима од нерђајућег челика 2 дана на T = 493 K. Једињење је искристалисало у виду плавих, прозрачних, призматичних кристала дужине до 15 mm заједно са мањом количином $Sr(AsO_3OH)$ [1]. Оно представља, како први Sr-Cu арсенат у систему $SrO–CuO–As_2O_5–H_2O$, тако и нови структурни тип.

Структура $Sr_4Cu_3(AsO_4)_2(AsO_3OH)_4\cdot 3H_2O$ решена је директним методама коришћењем података добијених рендгенском дифракцијом на монокристалу (298 K, Mo$K\alpha$, $2\theta_{max}$ = 60°): просторна група $C2/c$, a = 18,536(4), b = 5,179(1), c = 24,898(5) Å, β = 101,28(3)°, V = 2344,0(8) $Å^3$, Z = 4. Утачњавање са 204 варирана параметра дало је следеће R-вредности: $R_1(F)$ = 0,0292, $wR_2(F^2)$ = 0,0694 за 3428 независних рефлексија и $R_1(F)$ = 0,0211 за 2864 рефлексије са $F_o^2 \geq 4\sigma(F_o^2)$ [2].

$Sr_4Cu_3(AsO_4)_2(AsO_3OH)_4\cdot 3H_2O$ је структурно близак групи супстанци које садрже Cu(II)-XO_4 (X = P^{5+}, As^{5+}) слојеве повезане Me катјонима [Me = алкални или земноалкални метал, Pb(II) или Ag(I)] и делимично водоничним везама [3]. Ови слојеви садрже Cu_3O_{12} групе изграђене од једног атома бакра који лежи у центру симетрије и има квадратно-планарну координацију, а који је даље повезан са још два атома бакра у координацији 5. Познати су различити модели повезивања Cu_3O_{12} група XO_4 тетраедрима.

Слојеви $[Cu_3(As(2)O_4)(As(3)O_3OH)]$ повезани су помоћу два различита SrO_8 полиедра, једним $As(1)O_3OH$ тетраедром и делимично водоничним везама, тако да је сваки други слој идентичан (*ABAB* повезивање). Посматрано по слојевима, Cu_3O_{12} групе су паралелне једна у односу на другу. Полиедри SrO_8 су деформисане квадратне антипризме са $\langle Sr(1/2)–O\rangle$ = 2,630/2,631 Å. Централни Cu(1) атом из Cu_3O_{12} групе у квадратно-планарној координацији има $\langle Cu(1)–O\rangle$ = 1,964 Å. Терминални Cu(2) атоми имају [3+1+1] координацију. $Cu(2)O_5$ координациони полиедар је деформисана тригонална бипирамида: две најкраће Cu(2)–O везе су осе бипирамиде, а екваторијални O–Cu(2)–O углови су 101,23(8), 115,52(7) и 144,86(8)°. Тетраедри AsO_4 су прилично правилни, а просечна дужина As–O веза варира од 1,686 до 1,693 Å. Атоми водоника су нађени на Фуријеовој мапи и њихове координате су успешно утачњене.

Аутор се захваљује аустријском фонду за науку, FWF (пројекат P15875-N03).

[1] T. Mihajlović and H. Effenberger, *Z. Kristallogr. Suppl. Iss.*, **22** (2005) 73

[2] G. M. Sheldrick, SHELX-97, a program for the solution and refinement of crystal structures. University of Göttingen, Germany (1997)

[3] H. Effenberger, *J. Solid State Chem.*, **142** (1999) 6-13

SYNTHESIS AND STRUCTURAL STUDY OF IRON(II)-FUMARATE

T. Džomić[a], V. Nikolić[b], S. Rakić[a], M. Mitrić[c], A. Kapor[a]

[a]*Faculty of Science, University of Novi Sad, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia and Montenegro*
[b]*Faculty of Technology, University of Niš, Bul. Oslobođenja 124, 16000 Leskovac, Serbia and Montenegro*
[c]*"Vinča" Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, 11001 Belgrade, P.O. Box 522, Serbia and Montenegro* ;
e-mail: tanjicak2000@yahoo.com

Iron(II)-fumarate or Ferrous Fumarate is well known compound in pharmaceutical industry, which is administered orally in the case of iron deficiency. Sample of polycrystalline complex of iron (II)-fumarate was synthesized in the reaction with sodium-fumarate and iron (II)-sulphate. Fe (II) ion easily oxidizes to Fe (III) ion at atmospheric pressure and oxidation intensifies by heating. Thus synthesis was done on temperature of 90^0C at low pressure. The process of oxidation was minimized and contents of Fe (III) ions that are toxic was also minimized in final oral drugs.

Using X-ray powder diffraction method it was established that the synthesized sample under investigation is iron (II)-fumarate. We accepted the values for hkl and calculated unit cell dimensions for the orthorhombic system from paper [1], assumed that space group is $P\,2\,2\,2$ and unit cell dimensions and profile parameters for pattern refined by FullProf [2]. Calculated crystallographic data for orthorhombic system and assumed space group are: a=7.947(2) Å, b=9.648(2) Å, c=11.784(2) Å, V = 903.6(3) $Å^3$.

Calculated dimension of crystallite based on Scherrer's formula is 37(8) nm.

IR spectrum, magnetic susceptibilities and dielectric permeability data were also analyzed. It was concluded that fumaric acid connects both carboxilate ions bidentate with Fe (II) ions. It is assumed that the Fe (II) ion coordinates also two more water molecules. In this case the coordination polyhedron around the Fe (II) ion is slightly distorted octahedron as confirmed by magnetic measurements. This molecular structure forms a polymeric chain.

[1] C.P. Prabhakaran, C.C. Patel, *Indian J. Chem.*, 7 (1968), str. 266-268
[2] J. Rodriguez-Carvajal, T. Roisnel, J. Gonzalez-Platas, L.C. Chapon, *FullProf.2k* (Version 2.90 - Sep2004-LLB JRC)

SINTEZA I STRUKTURNO ISTRAŽIVANJE GVOŽĐE(II)-FUMARATA

T. Džomić[a], V. Nikolić[b], S. Rakić[a], M. Mitrić[c], A. Kapor[a]

[a]*Prirodno-matematički fakultet, Univerzitet u Novom Sadu, Trg Dositeja Obradovića 4, 21000 Novi Sad, Srbija i Crna Gora*
[b]*Tehnološki fakultet, Univerzitet u Nišu, Bul. Oslobođenja 124, 16000 Leskovac, Srbija i Crna Gora*
[c]*Institut za nuklearne nauke "Vinča", Laboratorija za teorijsku fiziku i fiziku kondezovane materije, 11001 Beograd, P. Fah 522, Srbija i Crna Gora*;
e-mail: tanjicak2000@yahoo.com

Gvožđe(II)-fumarat je dobro poznato jedinjenje u farmaceutskoj industriji koje se koristi kao oralni preparat u lečenju i prevenciji nedostataka gvožđa u organizmu. Uzorak polikristalnog kompleksa gvožđe(II)-fumarata je sintetizovan reakcijom natrijum-fumarata i ferosulfata. Pošto Fe(II) jon lako oksidiše pri atmosferskom pritisku do Fe(III) jona, što se dodatno intenzivira zagrevanjem, Sinteza se odvijala na temperaturi od 90^0C pod sniženim pritiskom, da bi se proces oksidacije sveo na minimum, a samim tim znatno snizio i sadržaj Fe(III) jona koji je nepoželjan u gotovim oralnim preparatima.

Rendgenskom difrakcionom metodom praha potvrđeno je da ispitivani sintetizovani uzorak predstavlja gvožđe(II)-fumarat. Vrednosti za hkl i izračunate parametre elementarne ćelije za ortorombični sistem nađene su u radu [1]. Prihvatajući ove podatke kao tačne i pretpostavljajući da je prostorna grupa P 2 2 2, utačnjeni su parametri elementarne ćelije i neki profilni parametri pomoću FullProf programa [2]. Dobijeni kristalografski podaci za ortorombični sistem sa pretpostavljenom prostornom grupom su: a=7,947(2) Å, b=9,648(2) Å, c=11,784(2) Å, V=903,6(3) $Å^3$.

Izračunata je i veličina kristalita pomoću Šererove formule i ona iznosi 37(8) nm.

Analizirani su još i IR spektri, rezultati merenja magnetne susceptibilnosti i dielektrične permeabilnosti uzorka. Rezultati magnetnih merenja ukazuju da se jon Fe(II) u ispitivanom kompleksu nalazi u niskospinskom stanju sa dva nesparena elektrona, što ukazuje da se radi o izduženom oktaedarskom kopleksu. Analizom IR spektra utvrđeno je da se deprotonovana fumarna kiselina vezuje sa oba karboksilna jona asimetrično bidentatno za jone Fe(II) koji koordiniraju i po dva molekula vode. Ovakva struktura dovodi do formiranja umreženog lanca.

[1] C.P. Prabhakaran, C.C. Patel, Indian J. Chem., 7 (1968), str. 266-268
[2] J. Rodriguez-Carvajal, T. Roisnel, J. Gonzalez-Platas, L.C. Chapon, FullProf.2k (Version 2.90 - Sep2004-LLB JRC)

NEW STRUCTURAL MODEL OF γ-BI_2O_3 DOPED WITH PB^{2+} IONS, $BI_{24}PBO_{37}$

A. Hadži-Tonić[a], **D. Poleti**[a], **Lj. Karanović**[b], **I. Petrović-Prelević**[b]

[a]*Faculty of technology and metallurgy, karnegijeva 4, belgrade, serbia and montenegro*
[b]*Faculty of Mining and Geology, Đušina 7, Belgrade, Serbia and Montenegro*
e-mail: hadzi-tonic@tmf.bg.ac.yu

Due to interesting and useful properties, γ-Bi_2O_3 (noncentrosymmetric crystal lattice, space group *I*23, no. 197) has a real or potential application in different fields of electronics and acoustics. This metastable phase can be stabilized at room temperature by doping with different cations.

In this study the possibility to isolate single γ-Bi_2O_3 phase doped with Pb and its crystal structure were investigated. Seven mixtures with different molar ratios of α-Bi_2O_3 (bismite) and PbO (massicot) were homogenized in an agate mortar, heated up to 750 °C and then furnace cooled to the room temperature. The synthesized samples were characterized by X-ray powder diffraction technique. The phase composition of reaction products was as follows:

– $1.67Bi_2O_3\cdot PbO$ and $2.75Bi_2O_3\cdot PbO$ yielded a mixture of γ-Bi_2O_3 and $Bi_8Pb_5O_{17}$, – $6Bi_2O_3\cdot PbO$, $12Bi_2O_3\cdot PbO$, $18Bi_2O_3\cdot PbO$ and $19Bi_2O_3\cdot PbO$ produced γ-Bi_2O_3, – $38Bi_2O_3\cdot PbO$ gave a mixture of γ-Bi_2O_3 and α-Bi_2O_3.

Among four obtained γ-Bi_2O_3, the sample achieved from the $12Bi_2O_3\cdot PbO$ starting mixture was chosen for the Rietveld analysis. As a result, the new structural model of $Bi_{24}PbO_{37}$ phase was proposed. Namely, the structure of a very similar compound $Bi_{24}Pb_2O_{38}$ has already been published [1]. However, very high temperature displacement parameters of Pb^{2+}/Bi^{3+} ions situated in tetrahedral sites at 0,0,0 and ½,½,½ (Wyckoff position 2*a*) shows that the model reported suffers from very serious shortcomings. Though additional cations normally occupy the 2*a* site in most γ-Bi_2O_3 phases, in this case both Pb^{2+} and Bi^{3+} ions have a lone electron pair and cannot be situated in the tetrahedral position. Hence, it was necessary to move slightly these cations from 2*a* to 8*c* position with $x = 0.013(3)$, as it was obtained by the refinement. This is accompanied by introducing an oxygen vacancy resulting in a trigonal pyramidal environment of the 8*c* site.

Initially, the data were refined assuming that only Pb^{2+} occupies a quarter of the 8*c* site with the Bi^{3+} being confined to the 24*f* site. However, since the scattering power of Pb^{2+} and Bi^{3+} ions is very similar it is difficult to obtain the true cation distribution over the 8*c* and 24*f* sites, so the refinement was finished with both positions shared.

At the 24*f* site, the cations are surrounded by five O^{2-} ions making an irregular square pyramid with a short apical Pb/Bi–O distance and a trapezoid-like base. Two additional O^{2-} ions shared between adjacent pyramids are at longer distances, enclosing a highly deformed split-octahedron and leaving the space for stereochemically active Pb/Bi lone electron pair.

[1] A. D. Murray, C. R. A. Catlow, F. Beech, J. Dreenan, *J. Solid State Chem.*, **62** (1986) 290-296

NOVI STRUKTURNI MODEL γ-BI$_2$O$_3$ DOPIRANOG PB^{2+}-JONIMA: BI$_{24}$PBO$_{37}$

A. Hadži-Tonić[a], **D. Poleti**[a], **Lj. Karanović**[b], **I. Petrović-Prelević**[b]

[a] *Tehnološko-metalurški fakultet, karnegijeva 4, beograd, srbija i crna gora*
[b] *Rudarsko-geološki fakultet, Đušina 7, Beograd, Srbija i Crna Gora*
e-mail: hadzi-tonic@tmf.bg.ac.yu

Zahvaljujući svojim fizičkim osobinama, koje su posledica necentrosimetrične kristalne rešetke (prostorna grupa *I*23, br. 197), γ-Bi$_2$O$_3$ se koristi u različitim oblastima elektronike i akustike. Ova, inače metastabilna, faza može se stabilizovati na sobnoj temperaturi dodatkom male količine različitih katjona.

U ovom radu ispitivana je mogućnost dobijanja monofaznog γ-Bi$_2$O$_3$ dopiranog olovom, kao i njegova kristalna struktura. Sedam smeša α-Bi$_2$O$_3$ (bismit) i PbO (masikot), sa različitim molskim odnosima, najpre su homogenizovane u ahatnom avanu, zatim zagrevane do 750 ºC i na kraju postepeno hlađene u peći do sobne temperature. Samleveni uzorci ispitani su metodom rendgenske difrakcije. Određen je sledeći fazni sastav proizvoda:

- polazni sastavi 1,67Bi$_2$O$_3$·PbO i 2,75Bi$_2$O$_3$·PbO dali su smešu γ-Bi$_2$O$_3$ i Bi$_8$Pb$_5$O$_{17}$,
- sa polaznim sastavima 6Bi$_2$O$_3$·PbO, 12Bi$_2$O$_3$·PbO, 18Bi$_2$O$_3$·PbO i 19Bi$_2$O$_3$·PbO dobijen je monofazni γ-Bi$_2$O$_3$,
- polazni sastav 38Bi$_2$O$_3$·PbO dao je smešu γ- i α-Bi$_2$O$_3$.

Ritveldovom analizom γ-Bi$_2$O$_3$, dobijenog od polazne smeše 12Bi$_2$O$_3$·PbO, određen je novi strukturni model za Bi$_{24}$PbO$_{37}$. Treba istaći da je struktura jedinjenja sličnog sastava: Bi$_{24}$Pb$_2$O$_{38}$ već objavljena [1]. Ipak, visoki temperaturni faktori Pb^{2+}/Bi^{3+}-jona koji su bili smešteni u tetraedarsko mesto na 0,0,0 i ½,½,½ (Vikofov položaj 2*a*) pokazuju da raniji model ima velikih nedostataka. Iako u većini γ-Bi$_2$O$_3$ faza katjoni dopanta zauzimaju položaj 2*a*, u ovom slučaju i Pb^{2+}- i Bi^{3+}-jon imaju slobodan elektronski par, pa se ne mogu nalaziti u tretraedarskom okruženju. Stoga je bilo neophodno minimalno izmeštanje ovih katjona iz položaja 2*a* u položaj 8*c* sa vrednošću *x* od 0,013(3) koja je dobijena utačnjavanjem. To je praćeno stvaranjem vakancije na mestu jednog kiseonika čime se dobija trigonalno-piramidalno okruženje Pb^{2+}/Bi^{3+}-jona.

Utačnjavanje je započeto sa pretpostavkom da Pb^{2+}-joni zauzimaju jednu četvrtinu 8*c* položaja, dok su Bi^{3+}-joni isključivo smešteni u položaj 24*f*. Ipak, pošto je moć rasipanja Pb^{2+}- i Bi^{3+}-jona veoma slična, bilo je nemoguće dobiti tačnu raspodelu katjona, tako da je utačnjavanje završeno uz pretpostavku da katjoni dele oba mesta.

Na mestu 24*f*, katjoni su okruženi sa pet O^{2-}-jona čime se formira nepravilna kvadratna piramida sa trapezoidnom bazom i veoma kratkim rastojanjem između Pb^{2+}/Bi^{3+}- i O^{2-}-jona na vrhu piramide. Na većem rastojanju nalaze se još dva O^{2-}-jona koji povezuju susedne piramide, čime se stvara veoma deformisan „split-oktaedar” i dovoljno mesta za stereohemijski aktivan slobodan elektronski par bizmuta, odnosno olova.

[1] A. D. Murray, C. R. A. Catlow, F. Beech, J. Dreenan, *J. Solid State Chem.*, **62** (1986) 290-296

UNUSUAL CATION-π INTERACTIONS. CATION-π INTERACTIONS WITH CHELATE RING AS π SYSTEM - DATABASE STUDY

Miloš Milčić, Vesna Medaković and Snežana Zarić

Department of Chemistry, University of Belgrade, Studentski trg 16, 11000 Belgrade, SCG
e-mail: szaric@chem.bg.ac.yu

Noncovalent interactions involving metal atoms have gained particular attention with the recognition that metal cations can bind to the phenyl ring, and the explanation of this in terms of cation-π interaction.

Cationic transition metal complexes are involved in similar metal-ligand aromatic cation-π interactions, where ligand coordinated to the transition metal interact with π-systems. These MLAC-π interactons have been found in crystal structures of metalo-proteins [1] and transition metal complexes [2].

Receantly, by screening Cambridge Structural Database (CSD) we found a number of structures with C-H···π interactions where π-system of chelate ring is proton acceptor. Calculated energy and geometry observed in crystal structures are comparable with C-H···π interactions where proton acceptor is organic aromatic ring [3].

We searched crystal structures of transition metal complexes from the CSD in order to find specific cation-π interaction, interaction between simple matal cation and chelate ring. Cation-π interactions were identified according to the very restrictive distance and angle criteria. Although in the search we checked for 1st, 2nd and 3rd group cations, the interactions were found only with alkaline metal cations ((Li^+, Na^+ and K^+). Complexes with different central metal atoms are involved in these cation-π interactions. There are cases of the interactions with six membered and five membered chelate rings. To the best of our knowledge this is the first study on cation-π interactions with chelate rings.

[1] S. D. Zarić, D. Popović, E. W. Knapp, *Chem. Eur.* J. **6**, (2000), 213.
[2] M. K. Milčić, S. D. Zarić, *Eur. J. Inorg. Chem.*, (2004), 4327.
[3] V. B: Medaković, M. K. Milčić, G. A. Bogdanović, S. D. Zarić, *J. Inorg. Biochem.* **98**, (2004), 1867.

NEOBIČNE KATJON-π INTERAKCIJE. KATJON-π INTERAKCIJE SA HELATNIM PRSTENOM KAO π SISTEMOM - PROUČAVANJE BANKE PODATAKA

Miloš Milčić, Vesna Medaković i Snežana Zarić

Hemijski fakultet, Univerzitet u Beogradu, Studentski trg 16, 11000 Beograd, SCG
e-mail: szaric@chem.bg.ac.yu

Nekovalentne interakcije u koje su uključeni atomi metala privukli su posebnu pažnju kada je otkriveno da se katjoni metala vezuju za fenilni prsten. Ovo je objašnjeno kao katjon-π interakcije.

Kompleksi prelaznih metala učestvuju u metal-ligand aromatskim katjon-π interakcijama, u kojima ligand koordinovan za centralni metalni jon interaguje sa π-sistemom. Ove MLAC-π interakcije su pronađene u kristalnim strukturama metaloproteina [1] i kompleksa prelaznih metala [2].

Pretraživanjem Kembridžske banke strukturnih podataka (CSD) pronašli smo veliki broj struktura kompleksa prelaznih metala u kojima je π-sistem helatnog prstena uključen u C-H···π interakcije kao akceptor protona. Geometrije tih kompleksa kao i vezivne energije izračunate *ab-initio* metodama su iste kao i kod C-H···π interakcija u kojima je organski aromatični molekul akceptor protona [3]

Pretražili smo strukture kompleksa prelaznih metala u CSD-u da bi pronašli specifičan tip katjon-π interakcija - interakcije između jednostavnih jona metala i helatnog prstena. Za pretraživanje ovih interakcija koristili smo vrlo restriktivne kriterijume za rastojanja i uglove. Iako smo tražili interakcije sa katjonima iz prve, druge i treće grupe periodnog sistema, pronašli smo samo interakcije sa jonima alkalnih metala. Pronađene katjon-π interakcije su uključivale komplekse sa različitim centralnim metalnim jonima kao i različite šestočlane i petočlane helatne prstene. Koliko smo mi upoznati ovo je prvo proučavanje katjon-π interakcija sa helatnim prstenima.

[1] S. D. Zarić, D. Popović, E. W. Knapp, *Chem. Eur.* J. **6**, (2000), 213-.
[2] M. K. Milčić, S. D. Zarić, *Eur. J. Inorg. Chem.*, (2004), 4327-.
[3] V. B: Medaković, M. K. Milčić, G. A. Bogdanović, S. D. Zarić, *J. Inorg. Biochem.* **98**, (2004), 1867.

THE CRYSTAL STRUCTURE OF K[Cr(S,S-eddp)(ox)]×0.5H$_2$O COMPLEXES

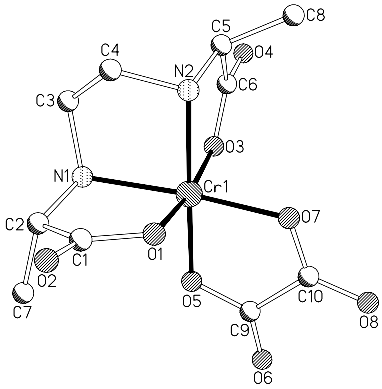
S. R. Trifunović[a], V. V. Glodjović[a] and F. W. Heinemann[b]

[a]Faculty of Science, University of Kragujevac, R. Domanovic 12 P. O. Box 60, Serbia and Montenegro; [b]Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstraβe 1, D-91058 Erlangen, Germany;
e-mail: srecko@kg.ac.yu

The title compound was obtained in reaction of chromium(III)chloride hexahydrate, ethylenediamine-*N,N'*-di-S,S-2-propinic acid and sodium-oxalate in molar ratio 1:1:1.5 at 60° and pH = 5. The compound was crystallized as a semihydrate.

Crystallographic data: $C_{10}H_{15}CrKN_2O_{8.5}$, K[Cr(S,S-eddp)(ox)]×0.5H$_2$O, $M_r = 390.34$, orthortombic system, space group $P2_12_12$ $Z = 4$, $F(000) = 800$, $\rho_x = 1.772$ g/cm, linear absorption coefficient μ(MoKα) = 1.113 mm^{-1}, the lagest diff. peak and hole $\Delta\rho_{max} = 0.265$ eÅ^{-3} and $\Delta\rho_{min} = -0.278$ eÅ^{-3}, $GOOF = 0.947$. Intensities of 3235 unique reflections are collected on a Bruker-Nonius-Kappa CCD diffractometer [λ(MoKα) = 0.71073 Å] in the range $6.7° \leq 2\theta \leq 54.2°$. Crystal size 0.23×0.18×0.14 mm, irregular crystal shape and red colour. Unit cell dimensions: $a = 8.1756(6)$, $b = 26.623(2)$, $c = 6.7215(7)$ Å, $V = 1463.0(2)$ Å^3.

The structure was solved and refined using the program SHELXTL NT 6.12 (Bruker AXS, 2002) 18775 independent reflections $R_1 = 2.95\%$ for 3235 $I > 2\sigma(I)$, $Rw_2 = 6.04\%$ (refinement on F^2) for all reflections and 249 refined parameters.



KRISTALNA STRUKTURA K[Cr(S,S-eddp)(ox)]×0.5H$_2$O KOMPLEKSA

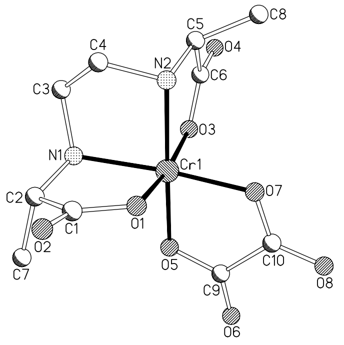
S. R. Trifunović[a], V. V. Glodjović[a], F. W. Heinemann[b]

[a]*Prirodno-matematički fakultet, Univerzitet u Kragujevcu, R. Domanovića 12, P. O. Box 60, SCG;* [b]*Institut za neorgansku hemiju, Univerzitet Erlangen-Nürnberg, Egerlandstraße 1, D-91058 Erlangen, Nemačka*
e-mail: srecko@kg.ac.yu

Kompleks K[Cr(S,S-eddp)(ox)]×0.5H$_2$O dobijen je u reakciji etilendiamin-*N,N′*-di-S,S-2-propionske kiseline (S,S-eddp), hrom(III)hlorida heksahidrata (CrCl$_3$×6H$_2$O) i natrijum-oksalata u molskom odnosu 1:1:1.5. pri pH = 5 i na temperaturi od 60°C. Kompleks kristališe kao semihidrat.

Kristalografski podaci za dobijeni kompleks: $C_{10}H_{15}CrKN_2O_{8,5}$, K[Cr(S,S-eddp)(ox)]×0.5H$_2$O, M_r = 390,34, rombični sistem, prostorna grupa $P2_12_12$, $Z = 4$, $F(000) = 800$, ρ_x = 1,772 g/cm, μ(MoKα) = 1,113 mm^{-1} sa $\Delta\rho_{max}$ = 0,265 i $\Delta\rho_{min}$ = -0,278 eÅ^{-3}, *GOOF* = 0,947. Intenziteti 3235 pojedinačnih refleksija izmereni su pomoću Bruker-Nonius-Kappa CCD difraktometra [λ(MoKα) = 0.71073Å] u opsegu 6,7° ≤ 2θ ≤ 54,2°. Dimenzije kristala su 0,23×0,18×0,14 mm, dok su parametri jedinične ćelije: a = 8,1756(6), b = 26,623(2), c = 6,7215(7) Å, V = 1463,0(2) Å^3.

Struktura je rešena i utačnjena korišćenjem programa SHELXTL NT 6.12 (Bruker AXS, 200) za 18775 nezavisnih refleksija, R_1 = 2,95% za 3235 refleksija sa $I > 2\sigma(I)$, wR_2 = 6,04% za sve refleksije i 249 utačnjavanih parametara.



CRYSTAL PHASES WITH HIGH BI-CONTENT IN BI_2O_3-V_2O_5 SYSTEM AND THEIR TRANSFORMATIONS INDUCED BY THERMAL TREATMENT

A. Hadži-Tonić[a], Lj. Karanović[b], D. Poleti[a], I. Petrović-Prelević[b]

[a] *Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, Serbia and Montenegro*
[b] *Faculty of Mining and Geology, Đušina 7, Belgrade, Serbia and Montenegro*
e-mail: hadzi-tonic@tmf.bg.ac.yu

The possibility to obtain single-phase products of the composition: $12Bi_2O_3{\cdot}V_2O_5$ (Bi:V ratio equal to 12, sample "BiV-12"), $12Bi_2O_3{\cdot}0.8V_2O_5$ (Bi:V = 15, sample "BiV-15") and $12Bi_2O_3{\cdot}0.4V_2O_5$ (Bi:V = 30, sample "BiV-30") was investigated. The products were prepared by high temperature solid state reactions and characterized by XRPD, SEM, and DTA.

The addition of V_2O_5 into α-Bi_2O_3 causes the stabilization of metastable γ-Bi_2O_3 phase down to the room temperature. For the achievement of almost single γ-Bi_2O_3 phase in the sample BiV-12, the annealing at 750 °C for 3 h was required. The final composition was the mixture of γ-Bi_2O_3 [$a_\gamma = 10.2262(3)$ Å] as a predominant phase, some δ-Bi_2O_3-like phase and traces of α-Bi_2O_3. After the same heat treatment, the BiV-15 sample showed the pattern typical for single γ-Bi_2O_3 phase [$a_\gamma = 10.2251(3)$ Å], but in the BiV-30 sample two isostructural γ-Bi_2O_3 phases [$a_{\gamma 1} = 10.2310(7)$, $a_{\gamma 2} = 10.260(1)$ Å] in approximately equal amounts were found.

Since the single-phase product was obtained only for the BiV-15, this sample was further treated at higher temperatures. After heating above the melting point (919 ºC), δ-Bi_2O_3-like structures appeared. All main XRPD peaks correspond to a cubic δ-Bi_2O_3, but the presence of several weak reflections at low 2θ angles that cannot be indexed on the cubic lattice indicated lowering of symmetry and suggested that the true cell may be a superlattice based on pseudo-fcc subcells. Thus, the lattice parameters of δ_r-Bi_2O_3 superstructure are $a = 11.7957(2)$, $c = 28.298(1)$ Å in space group $R3m$. Detailed XRPD studies showed that in addition to the cubic δ-Bi_2O_3 and rhombohedral δ_r-Bi_2O_3 some amount of tetragonal β-Bi_2O_3 phase, with $a = 7.7668(3)$ and $c = 5.6089(3)$ Å, is present as well.As shown by cyclic DTA curves, when products BiV-12 and BiV-15 are heated the γ-$Bi_2O_3 \rightarrow \delta$-$Bi_2O_3$ transition occurs in one step at 774 and 778 ºC, respectively, but on heating of the BiV-30 sample this transition occurs in two steps at 731 and 760 ºC. The first value corresponds well to the transition of pure γ-Bi_2O_3, while the second one could be ascribed to the transition of V-doped γ-Bi_2O_3 phase. On cooling the $\delta \rightarrow \gamma$ transition occurs at 714 - 690 ºC for the first two products, but for the third it takes place again in two steps at 688 and 684 ºC, probably because the δ-Bi_2O_3-like phase transforms into two γ-Bi_2O_3 phases. After heating above the melting point this $\delta \rightarrow \gamma$ transition was not observed. On heating, the δ-Bi_2O_3 phase remains up to 430 ºC when again transforms to γ-Bi_2O_3.

The results of EDS analysis revealed that the V content in BiV-15 sample is 1.65(10) % (calc. 1.42 %), while in BiV-30 sample is 0.84(2) and 0 % for γ_1 and γ_2 phase, respectively.

KRISTALNE FAZE U BI_2O_3-V_2O_5 SISTEMU SA POVEĆANIM SADRŽAJEM BI_2O_3 I NJIHOVE TRANSFORMACIJE TOKOM TERMIČKOG TRETMANA

A. Hadži-Tonić[a], Lj. Karanović[b], D. Poleti[a], I. Petrović-Prelević[b]

[a] *Tehnološko-metalurški fakultet, Karnegijeva 4, beograd, Srbija i Crna gora*
[b] *Rudarsko-geološki fakultet, Đušina 7, Beograd, Srbija i Crna Gora*
e-mail: hadzi-tonic@tmf.bg.ac.yu

U ovom radu proučavana je mogućnost dobijanja jednofaznih proizvoda polazeći od smeša sledećih sastava: $12Bi_2O_3{\cdot}V_2O_5$ (odnos Bi:V jednak je 12, uzorak „BiV-12”), $12Bi_2O_3{\cdot}0{,}8V_2O_5$ (Bi:V = 15, uzorak „BiV-15”) i $12Bi_2O_3{\cdot}0{,}4V_2O_5$ (Bi:V = 30, uzorak „BiV-30”). Proizvodi su dobijeni visokotemperaturnom reakcijom u čvrstom stanju, a karakterizacija je izvršena rendgenskom difrakcijom, SEM i DT analizom.

Metastabilan γ-Bi_2O_3 može se na sobnoj temperaturi stabilizovati različitim dopantima pa, samim tim, i dodatak V_2O_5 u α-Bi_2O_3, dovodi do njegove stabilizacije. Zagrevanjem uzorka BiV-12 tokom 3 h na 750 °C nastala je smeša γ-Bi_2O_3 [a_γ = 10.2262(3) Å], kao glavne faze, i faze sa strukturom δ-Bi_2O_3, uz tragove α-Bi_2O_3. Nakon istog termičkog tretmana, BiV-15 daje čistu γ-Bi_2O_3 fazu [a_γ = 10,2251(3) Å], dok su kod uzorka BiV-30 dobijene dve izostrukturne γ-Bi_2O_3 faze [$a_{\gamma 1}$ = 10,2310(7), $a_{\gamma 2}$ = 10,260(1) Å] u približno jednakom masenom odnosu.

S obzirom na to da je samo uzorak BiV-15 dao jednu fazu, on je dalje termički tretiran na višim temperaturama. Posle zagrevanja iznad temperature topljenja (919 ºC), pri hlađenju nastaje faza sa strukturom δ-Bi_2O_3. Glavni pikovi na difraktogramu ove faze odgovaraju δ-Bi_2O_3, ali se javlja i nekoliko slabih pikova na malim 2θ uglovima, koji se ne mogu pripisati teseralnoj strukturi. To ukazuje na pojavu romboedarske superstrukture koja u osnovi ima površinski centriranu teseralnu ćeliju. Parametri δ_r-Bi_2O_3 superstrukture su: a = 11,7957(2) i c = 28,298(1) Å (prostorna grupa $R3m$). Detaljno proučavanje difraktograma pokazalo je da pored teseralne i romboedarske δ_r-faze, postoji i mala količina tetragonalne β-Bi_2O_3 faze sa a = 7,7668(3) i c = 5,6089(3) Å.

DT analizom utvrđeno je da se pri zagrevanju proizvoda nastalih od polaznh smeša BiV-12 i BiV-15, prelaz γ-$Bi_2O_3 \rightarrow \delta$-$Bi_2O_3$ odigrava u jednom koraku na 774, odnosno 778 ºC, dok se pri zagrevanju proizvoda nastalih od uzorka BiV-30 ovaj prelaz odvija u dva koraka, na 731 i 760 ºC. Prva temperatura vrlo verovatno odgovara prelazu nedopirane γ-Bi_2O_3 faze, a druga bi se mogla pripisati prelazu γ-Bi_2O_3 faze dopirane vanadijumom. Pri hlađenju prva dva reakciona proizvoda, $\delta \rightarrow \gamma$ prelaz se javlja u intervalu 714 - 690 ºC, dok se kod trećeg proizvoda on opet odvija u dva koraka, na 688 i 684 ºC, jer se δ-Bi_2O_3 verovatno transformiše u dve γ-Bi_2O_3 faze. Prelaz $\delta \rightarrow \gamma$ ne javlja se posle zagrevanja iznad temperature topljenja. Zagrevanjem tako dobijene δ-Bi_2O_3 faze, ona se na 430 ºC transformiše u γ-Bi_2O_3.

EDS analizom utvrđeno je da sadržaj vanadijuma u proizvodu BiV-15 iznosi 1,65(10) % (izračunato 1,42 %), dok u BiV-30 on iznosi 0,84(2) za γ_1- i 0 % za γ_2-fazu.

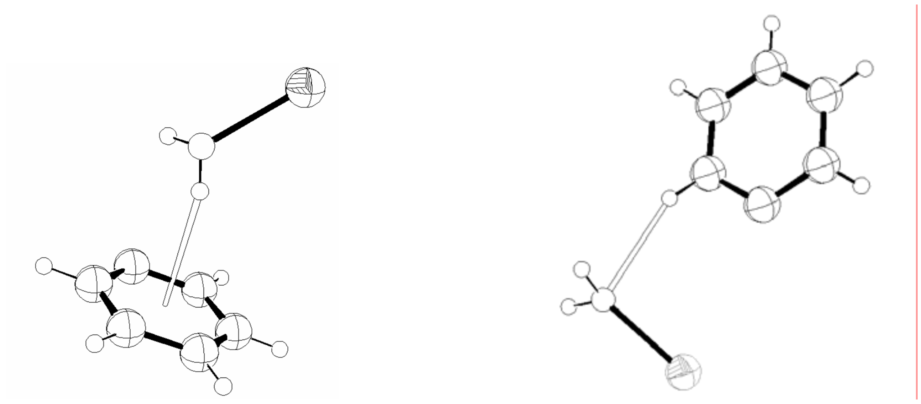
THEORETICAL STUDY OF INTERACTIONS BETWEEN COORDINATED WATER MOLECULE AND PHENYL GROUP

Goran Janjić, **Miloš Milčić, Snežana Zarić**

Department of Chemistry, University of Belgrade, Studentski trg 16, 11000 Belgrade, SCG
e-mail: szaric@chem.bg.ac.yu

Ligands coordinated to metal cation can be involved in noncovalent interactions with aromatic moleculs. These interactions are called metal ligand aromatic cation-π (MLACπ) interactions [1,2]. Water molecule coordinated to a metal can interact with phenyl group producing some of the shortest X-H...π interactions [3].

Analysis of crystal structures obtained from Cambridge Structural Database (CSD) indicate that there are two types of interactions between coordinated water molecule and phenyl group. In the first type of interactions, hydrogen atom donor is coordinated water molecule and hydrogen atom acceptor is π-system of the phenyl group (Figure 1a). These are MLACπ interactions. In the second type of interactions phenyl group is hydrogen atom donor and oxygen atom from coordinated water molecule is hydrogen atom acceptor (Figure 1b). These are C-H···O interactions.


[a] [b]

MLACπ [a] and C-H...O [b] interactions between coordinated water molecule and phenyl group.

[1] S. D. Zarić, *Chem. Phys. Lett.* **311** (1999), , 77.
[2] S. D. Zarić, D. Popović, E. W. Knapp, *Chem. Eur. J.* **6**, (2000), 213.
[3] M. K. Milčić, Z. D. Tomić, S. D. Zarić, *Inorg. Chim. Acta*, **35**7, (2004), 4327.

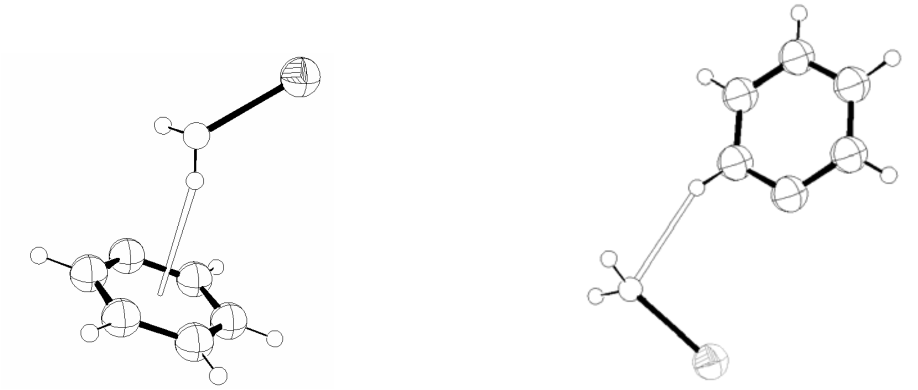
TEORIJSKO PROUČAVANJE INTERAKCIJA KOORDINOVANOG MOLEKULA VODE I FENILNE GRUPE

Goran Janjić, Miloš Milčić, Snežana Zarić

Hemijski fakultet, Studentski trg 16, 11000 Beograd, SCG
e-mail: szaric@chem.bg.ac.yu

Ligandi koordinovani za metal mogu da grade nekovalentne interakcije sa aromatičnim prstenima. Ove interakcije su nazvane metal ligand aromatične katjon-π (MLACπ) interakcije [1,2]. Voda koordinovana za metal gradi neke od najkraćih X-H...π interakcija [3].

Analiza geometrijskih parametara u kristalnim strukturama dobijenim iz Kembridžske banke strukturnih podataka (CSD), ukazuje na postojanje dva tipa interakcija između koordinovanog molekula vode i fenilne grupe. U jednom tipu interakcija, donor vodonikovog atoma je koordinovani molekul vode, a akceptor je π sistem fenilne grupe (slika 1.a), i to su MLACπ interakcije. Kod drugog tipa interakcija donor vodonikovog atoma je fenilna grupa, a akceptor je koordinovani molekul vode (slika 1.b). Ovo su C-H...O interakcije.



[a] [b]

Slika 1. Prikaz MLACπ [a] i C-H...O [b] interakcija izmedju koordinovanog molekula vode i fenilne grupe

[1] S. D. Zarić, Chem. Phys. Lett. (1999), 311, 77.
[2] S. D. Zarić, D. Popović, E. W. Knapp, Chem. Eur. J. (2000), 6, 213.
[3] M. K. Milčić, Z. D. Tomić, S. D. Zarić, Inorg. Chim. Acta, 357, (2004), 4327-4329.

C–H···π INTERACTIONS IN THE METAL-PORPHYRIN COMPLEXES WITH PYRROLE AND SIX-MEMBERED CHELATE RINGS AS THE H ACCEPTORS

Vesna Medaković[a], Miloš Milčić[a], Goran Bogdanović[b], Snežana Zarić[a]

[a]Department of Chemistry, University of Belgrade, Studentski trg 16, 11000 Belgrade, Serbia and Montenegro; [b]Laboratory of Theoretical Physics and Condensed Matter Physics, Vinča Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade, Serbia and Montenegro
e-mail: szaric@chem.bg.ac.yu

Porphyrin molecule and derivatives of porphyrine possess four pyrrole rings with delocalized π-systems. When porphyrin is coordinated to a metal as a tetradentate ligand, additional for six-membered chelated rings with delocalized π-bonds are formed. In our previous study [1], we have shown that these chelate ring π-systems of the coordinated porphyrin can be involved in C–H···π interactions.

The fact that porphyrin possess two different types of rings with delocalized π-bonds, pyrrole and six-membered chelate, prompted us to study and compare C–H···π interactions for both of them. In order to determine preferred positions in porphyrinato ring for C–H···π interactions we have chosen fifteen different points distributed over porphyrin ring and analyzed each of them.

The Cambridge Structural Database (CSD) was screened in order to find C–H···π interactions with five and six-membered chelate rings with delocalized bonds. Statistical analysis shows that there are differences in distributions of the geometrical parameters, depending on the substituents on porphyrinato ring and on the position in the porphyrin ring. In order to determine the interaction energy for C–H···π interactions with five or six-membered ring of coordinated porphyrin, density functional theory (DFT) calculations have been done for the [Ni(por)]–C_2H_2 system where the hydrogen atom of the acetylene interacts with the pyrrole or six-membered chelate ring of porphyrin. To investigate the influence of substituents of porphyrinato ring, DFT calculations have been done on three different model systems: (i) with nonsubstituted porphyrinato ring; (ii) with dimethylporphyrinato ring, where two hydrogen atoms from the fivemembered pyrrole ring were substituted with methyl groups; (iii) with phenylporphyrinato ring, where one hydrogen atom from the six-membered chelate ring were substituted with the phenyl group.

[1] V. B. Medaković, M. K. Milčić, G. A. Bogdanović, S. D. Zarić, J. Inorg. Biochem., 98 (2004), 1867–1873

C–H···π INTERAKCIJE U METALOPORFIRINSKIM KOMPLEKSIMA SA PIROLOVIM I ŠESTOČLANIM HELATNIM PRSTENOVIMA KAO AKCEPTORIMA H ATOMA

Vesna Medaković[a], Miloš Milčić[a], Goran Bogdanović[b], Snežana Zarić[a]

[a] *Hemijski fakultet, Univerzitet u Beogradu, Studentski trg 16, 11000 Beograd, SCG*
[b] *Laboratorija za teorijsku fiziku i fiziku kondenzovane materije, Insitut za nuklearne nauke Vinča, P.O. Box 522, 11001 Beograd, SCG*
e-mail: szaric@chem.bg.ac.yu

Molekul porfirina i negovi derivati sadrže četiri pirolova prstena sa delokalizovanim π-vezama. Kada se porfirin koordinuje za metal kao tetradentatni ligand, dodatno se formiraju četiri šestočlana helatna prstena sa delokalizovanim π-vezama. Naša prethodna istraživanja [1] pokazala su da π-sistemi ovih helatnih prstenova koordinovanog porfirina, mogu biti uključeni u C–H···π interakcije.

Zbog činjenice da koordinovani porfirin poseduje dva različita tipa prstenova sa delokalizovanim π-vezama, pirolov i šestočani helatni prsten, proučavane su i poređene C–H···π interakcije za svaki od njih. Da bi odredili preferentne položaje u porfirinskom prstenu za C–H···π interakcije izabrali smo petnaest tačaka raspoređenih na različitim mestima u porfirinskom prstenu i analizirali svaku od njih.

U cilju pronalaženja C–H···π interakcija sa petočlanim i šestočlanim helatnim prstenovima pretražena je Kembridžska baza podataka (CSD). Urađena je statistička analiza koja pokazuje razliku u raspodeli geometrijskih parametara, zavisno od prisustva supstituenata na porfirinskom prstenu i položaja posmatrane tačke u prstenu. Da bi izračunali energiju za C–H···π interakcije sa petočlanim ili šestočlanim helatnim prstenom koordinovanog porfirina, urađeni su DFT proračuni na model sistemu $[Ni(por)]–C_2H_2$ gde atom vodonika iz acetilena interaguje sa pirolovim ili šestočlanim helatnim prstenom. Da bi ispitali uticaj supstituenata na porfirinskom prstenu na ovaj tip interakcija, urađeni su DFT proračuni na tri različita model sistema: (i) sa nesupstituisanim porfirinskim prstenom; (ii) sa dimetilporfirinskim prstenom u kome su dva atoma vodonika iz petočlanog pirolovog prstena zamenjena sa dve metil grupe; (iii) sa fenilporfirinskim prstenom, u kom je jedan atom vodonika iz šestočlanog helatnog prstena zamenjen fenil grupom.

[1] V. B. Medaković, M. K. Milčić, G. A. Bogdanović, S. D. Zarić, J. Inorg. Biochem., 98 (2004), 1867–1873

THE APPLICATION OF X-RAY DIFFRACTION FOR THE IDENTIFICATION OF INCLUSION COMPLEXES OF β-CYCLODEXTRIN

A. Kapor [a], **T. Džomić** [a], **V. Nikolić** [b], **M. Mitrić** [c]

[a] *Department of Physics,Faculty of .Sciences, University of Novi Sad, Trg D.Obradovića 4, 21000 Novi Sad, Serbia and Montenegro,* [b] *Faculty of Technology, University of Niš, Bulevar Oslobođenja 124, 16000 Leskovac, Serbia and Montenegro;* [c] *Institute of Nuclear Sciences „Vinča", POB.522, 11001 Beograd, Serbia and Montenegro*
e-mail: akapor@if.ns.ac.yu

The use of cyclodextrin (CD) in complexing of various drugs has been extensively studied during the last few years [1]. Cyclodextrin is a cyclic oligosaccharide with the possibility of total or partial inclusion in its hydrophobic cavity, with broad variety of guest molecules with which it forms the i*nclusion complex* [2]. β-blockers as atenolol are characterized by their weak solvability in water solutions of the digestion tract, so their inclusion complexes with CD are often produced to obtain better solvable drug [3]. The aim of this paper is to prove the formation of atenolol/β-CD inclusion complex in the solid state by using X-ray Diffraction (XRD) method.

Racemic atenolol (AT) is complexed with β-cyclodextrine (β-CD) and with 2-hydroxipropil-β-cyclodextrin (2-HP-β-CD). Inclusion complexes are formed and their physical mixtures produced. Powder data are recorded at the powder diffractometer Philips PW1050 using CuK$_\alpha$ radiation (λ=1.54178 Å) within the range 2θ=5-65° with step 0.05° and exposition time 5 s.

The results of XRD analysis show the difference of the diffraction spectrum of the inclusion complex of atenolol/β-CD and atenolol/2-HP-β-CD and their physical mixtures. This result indicates that atenolol molecule is built-in into the cavity of β-cyclodextrin and that the diffractograme of the inclusion complex retained the corresponding peaks, i.e. the dimensions and the symmetry of the crystal lattice of the host β-cyclodextrin(PDF-32-1627). In the other complex with a derivative of cyclodextrin (2-HP-β-CD) as the host , higher sample crystallinity was noticed and a good agreement of the diffractogram of the host and inclusion complex. One can notice in the XRD spectrum of the physical mixture besides the host peaks also the peaks of the pure atenolol (PDF 41-1657, 2θ (°)=6.305; 9.476; 20.362; 22.053).

The application of XRD for the confirmation of the inclusion of the molecule of β-blocker in β-cyclodextrine has also some deficiencies since the synthesized sample might be partially amorphous. In this case, the final confirmation of the inclusion can be provided only by the additional analyses in the solid state like NMR and DSC.

[1] K.H.Frömmming, J. Szejtli (Eds.), *Cyclodextrines in Pharmacy*, Kluwer, Dordrecht, (1994), pp.105-115

[2] G.A.Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, (1997), pp 154-181

[3] R. Ficarra, P.Ficarra, M.R-Di Bella, D.Raneri, S.Tommasini, M.L.Calabro, M.C.Gamberini, C.Rustichelli, *Journal of Pharmaceutical and Biomedical Analysis*, 23 (2000) 33-40.

PRIMENA RENDGENSKE DIFRAKCIJE U IDENTIFIKACIJI INKLUZIONIH KOMPLEKSA β-CIKLODEKSTRINA

A. Kapor [a], **T. Džomić** [a], **V. Nikolić** [b], **M. Mitrić** [c]

[a] *Departman za fiziku, PMF, Univerzitet u Novom Sadu, Trg D.Obradovića 4, 21000 Novi Sad, Srbija i Crna Gora;* [b] *Tehnološki fakultet, Univerzitet u Nišu, Bulevar Oslobođenja 124, 16000 Leskovac, Srbija i Crna Gora;* [c] *Institut za nuklearne nauke „ Vinča”, p.pr.522, 11001 Beograd, Srbija i Crna Gora*
e-mail: akapor@if.ns.ac.yu

Korišćenje ciklodekstrina (CD) u kompleksiranju različitih lekova veoma se mnogo izučava poslednjih godina [1]. Ciklodekstrin je ciklični oligosaharid sa mogućnošću potpune ili parcijalne inkluzije u njegovu hidrofobnu šupljinu, sa širokom raznolikošću gostujućeg molekula sa kojima formira *inkluzioni komple*ks [2]. β-blokeri kao atenolol su karakteristični po slaboj rastvorljivosti u vodenim rastvorima probavnog trakta i često se prave njihovi inkluzioni kompleksi sa CD da bi se dobio bolje rastvorljiv lek [3]. Cilj ovog rada je da se dokaže formiranje atenolol/β-CD inkluzinog kompleksa u čvrstom stanju primenom metode rendgenske difrakcije.

Racematski atenolol (AT) je kompleksiran sa β-ciklodekstrinom (β-CD) i sa 2-hidroksipropil-β-ciklodekstrinom (2-HP-β-CD). Formirani su inkluzioni kompleksi i fizičke smeše ovih jedinjenja. Rendgenogrami praha su načinjeni sa difraktometrom za prah Philips PW1050 korišćenjem CuK$_\alpha$ zračenja (λ=1,54178 Å) u intervalu 2θ=5-65° sa korakom 0,05° i vremenom ekspozicije od 5 s.

Rezultati XRD analize pokazuju razliku difrakcionog spektra inkluzionog kompleksa atenolola/β-CD i atenolol/2-HP-β-CD i njihovih fizičkih smeša. Dobijeni rezultat ukazuje na to da se molekul atenolola ugradio u šupljinu β-ciklodekstrina i da je difraktogram inkluzionog kompleksa zadržao odgovarajuće pikove, odnosno približne dimenzije i simetriju kristalne rešetke domaćina β-ciklodekstrina (PDF-32-1627). U drugom kompleksu u kojem je domaćin derivat ciklodekstrina (2-HP-β-CD) uočena je veća kristaličnost uzorka i dobro slaganje difraktograma domaćina i inkluzionog kompleksa. U XRD spektru fizičke smeše može se uočiti osim pikova koji pripadaju domaćinu i pikovi čistog atenolola (PDF 41-1657, 2θ (°)= 6,305; 9,476; 20,362; 22,053).

Primena XRD za potvrđivanje inkluzije molekula β-blokatora u β-ciklodekstrinu ima svoje nedostatke jer dobijeni uzorak može biti sintetisan delimično amorfan. U tom slučaju konačnu potvrdu o inkluziji mogu dati samo dodatne analize u čvrtom stanju kao što su NMR i DSC.

[1] K.H.Frömmming, J.Szejtli (Eds.), *Cyclodextrins in Pharmacy*, Kluwer, Dordrecht, (1994), pp.105-115.
[2] G.A.Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, (1997), pp 154-181.
[3] R. Ficarra, P.Ficarra, M.R-Di Bella, D.Raneri, S.Tommasini, M.L.Calabro, M.C.Gamberini, C.Rustichelli, *Journal of Pharmaceutical and Biomedical Analysis*, 23 (2000) 33-40.

COMPARATIVE ANALYSIS OF HIGH-RESOLUTION X-RAY DIFFRACTION DATA OBTAINED ON DIFFERENT SINGLE CRYSTAL DIFFRACTOMETERS

Goran A. Bogdanović[a], Slađana B. Novaković[a], Aleksandar Kremenović[b], Vukadin M. Leovac[c], Anne Spasojević-de Biré[d]

[a] *”VINČA” Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, P.O.Box 522, 11001 Belgrade, Serbia and Montenegro;* [b]*Faculty of Mining and Geology, Laboratory for Crystallography, University of Belgrade, Đušina 7, 11000 Belgrade, Serbia and Montenegro;* [c]*Institute of Chemistry, Faculty of Sciences, University of Novi Sad, 21000 Novi Sad, Serbia and Montenegro;* [d]*Laboratoire de Structures, Propriétés et Modélisation des Solides, (SPMS), UMR 8580 du CNRS, Ecole Centrale Paris, Grande Voie des Vignes 92295 Châtenay-Malabry Cedex, France.*
e-mail: goranb@vin.bg.ac.yu

As a part of the project organized by the Serbian Crystallographic Society three data sets were collected on single crystal diffractometers from three companies: Oxford Diffraction (Oxford, Xcalibur, Sapphire 3), Rigaku/MSC Inc (Rigaku, R-axis Spider) and Bruker AXS (SMART 1K CCD).

Main goal of this project was to reach relevant conclusions about capability of tested instruments for application in experimental charge density studies. For this purpose it was necessary to prepare excellent single crystals and to collect high-resolution low-temperature diffraction data with high redundancy and the highest possible quality. Very good single crystals of (Benzoylacetone 3-methylisothiosemicarbazonato(2-)-O,N^1,N^4)(pyridine-N)nickel(II) [1] were provided by prof. Leovac and preliminary tested on a Enraf-Nonius CAD-4 diffractometer in the Vinča Intitute of Nuclear Sciences.

Data from tested diffractometers (Oxford, Rigaku and Bruker) are compared using different crystallographic criteria. Therefore we would like to inform our crystallographic community believing that the results of this analysis could be useful for a future purchase of a new area detector diffractometer in our country.

[1] G. A. Bogdanović, A. Spasojević-de Bire, V. M. Leovac and V. Češljević; *Acta Cryst.* C55 (1999) 1656-1658.

KOMPARATIVNA ANALIZA PODATAKA VISOKE REZOLUCIJE DOBIJENIH DIFRAKCIJOM RENDGENSKOG ZRAČENJA NA TRI RAZLIČITA DIFRAKTOMETRA ZA MONOKRISTALE

Goran A. Bogdanović[a], Slađana B. Novaković[a], Aleksandar Kremenović[b], Vukadin M. Leovac[c], Anne Spasojević-de Biré[d]

[a]Institut za nuklearne nauke „VINČA“, Laboratorija za teorijsku fiziku i fiziku kondenzovane materije, p.p. 522, 11001 Beograd, Srbija i Crna Gora; [b]Rudarsko-geološki fakultet, Laboratorija za kristalografiju, Univerzitet u Beogradu, Đušina 7, 11000 Beograd, Srbija i Crna Gora; [c] Prirodno-matematički fakultet, Univerzitet u Novom Sadu, Trg Dositeja Obradovića 3, 21000 Novi Sad, Srbija i Crna Gora; [d]Laboratoire de Structures, Propriétés et Modélisation des Solides, (SPMS), UMR 8580 du CNRS, Ecole Centrale Paris, Grande Voie des Vignes 92295 Châtenay-Malabry Cedex, France.
e-mail: goranb@vin.bg.ac.yu

Kao deo projekta organizovanog od Srpskog kristalografskog društva prikupljene su tri grupe podataka na difraktometrima za monokristale od tri različita proizvođača: Oxford Diffraction (Oxford, Xcalibur, Sapphire 3), Rigaku/MSC Inc (Rigaku, R-axis Spider) and Bruker AXS (SMART 1K CCD).

Najvažniji cilj ovog projekta bio je testiranje navedenih instrumenata na mogućnost njihove primene u eksperimentalnom određivanju gustine naelektrisanja u kristalnim strukturama. Za ovakvu namenu bilo je neophodno pripremiti monokristale odličnog kvaliteta i uraditi prikupljanje difrakcionih podataka sa puno ekvivalentnih refleksija dobijenih difrakcijom rendgenskog zračenja na niskoj temperaturi. Profesor Leovac je obezbedio monokristale (3-metilizotiosemikarbazon-benzoilacetonato(2-)-O,N^1,N^4)(piridin-N)nikla(II) [1] veoma dobrog kvaliteta i oni su preliminarno testirani na difraktometru Enraf-Nonius CAD-4 u Institutu za nuklearne nauke „VINČA“.

Podaci za sva tri testirana difraktometra (Oxford, Rigaku i Bruker) analizirani su njihovim međusobnim poređenjem uz korišćenje različitih kristalografskih kriterijuma. Verujući da rezultati ove analize mogu biti od koristi za buduću nabavku novog difraktometra za monokristale u našoj zemlji, mi želimo da na ovaj način informišemo naše kolege kristalografe.

[1] G. A. Bogdanović, A. Spasojević-de Bire, V. M. Leovac and V. Češljević; *Acta Cryst.* C55 (1999) 1656-1658.

NON-CONVENTIONAL INTERACTIONS IN PROTEINS WITH THE HEME GROUP

S. Stojanović[a], V. B. Medaković[a], G. Predović[b], S. D. Zarić[a]

[a]*Department of Chemistry, University of Belgrade, Studentski trg 16, 11000 Belgrade, SCG*
[b]*The Faculty of Mathematics, University of Belgrade, Studentski trg 16, 11000 Belgrade, SCG*
e-mail: szaric@chem.bg.ac.yu

Hydrogen bonds, salt bridges and hydrophobic interactions are considered to be the major determinants of structural stability of proteins. However, recent studies showed that weaker interactions such as N-H···π, O-H···π, C-H···π, and C-H···O also play a role in protein stability. Non-conventional interactions have also influence on orientations of imdazoles coordinated to the heme [1,2].

For this study, the Protein Data Bank (PDB) Select October 2004 list of non-redundant protein chains (25% threshold version, 2485 protein chains and 388067 amino acid residues) was used to examine systematically the occurrence and the role of X-H···π-interactions in heme-protein structures. The following criteria were employed to assemble the set: (1) no theoretical model structures and no NMR structures were accepted, (2) only crystal structures with a resolution of 3.0 Å or better and a crystallographic R-factor of 25.0% or lower were accepted, (3) crystal structures containing porphyrin were accepted.

The significant number of interactions with π system of five-membered pyrrole rings and with π system of six-membered chelate rings were founded to satisfy selection criteria. H-atom donors can be C^{α}-H, C_{ali}-H, C_{aro}-H and N-H. The number of C-H···π-interactions is much larger than the number of N-H···π-interactions. The list of C_{ali}-H with five-membered rings contains more hydrophobic residues, which is probably due to the fact that these interactions are, on average, closer to the interior of the protein. Analysis of average distances for C_{ali} and C_{aro} of C-H···π interactions indicate that C_{ali} makes interactions with shorter distances. Another interesting observation is the possibility of C-H(porphyrin) donor groups to exhibit an interaction between five-membered rings from another porphyrine group in proteins and its own side-chain groups (involving hydrogen atoms from methyl and propionyl groups). Amino acids involving in X-H···π-interactions shows significant conservation score. The number of these interactions as well as conservation of amino acids indicates importance of X-H···π-interactions in heme-protein stability.

[1] S. D. Zarić, D. M. Popović, E. W. Knapp, Biochemistry 40 (2001), 7914–7928
[2] V. B. Medaković, S. D. Zarić, Inorg. Chim. Acta 349 (2003), 1–5

NEKONVENCIONALNE INTERAKCIJE U PROTEINIMA KOJI SADRŽE HEM

S. Stojanović[a], V. B. Medaković[a], G. Predović[b], S. D. Zarić[a]

[a]*Hemijski fakultet, Univerzitet u Beogradu, Studentski trg 16, 11000 Beograd, SCG*
[b]*Matematički fakultet, Univerzitet u Beogradu, Studentski trg 16, 11000 Beograd, SCG*
e-mail: szaric@chem.bg.ac.yu

Vodonične veze, soni mostovi i hidrofobne interakcije smatraju se glavnim faktorom stabilnosti strukture proteina. Međutim, nedavna ispitivanja pokazuju da slabije interakcije, kao što su N-H···π, O-H···π, C-H···π i C-H···O, takođe učestvuju u stabilnosti proteina. Nekonvencionalne interakcije utiču i na orijentacije imidazola koordinovanih za hem [1,2].
Za ispitivanje pojave i uloge X-H···π-interakcija u hem-proteinskim strukturama korišćena je proteinska baza podataka (PDB Select) iz oktobra 2004. godine, ne-redundantna lista (verzija 25%) koja sadrži 2485 proteinskih lanaca i 388067 aminokiselinskih ostataka. Primenjeni su sledeći kriterijumi za sastavljanje skupa: (1) nisu prihvaćeni teorijski modeli i NMR strukture, (2) samo su prihvaćene kristalne strukture sa rezolucijom 3.0 Å ili boljom i kristalografskim R-faktorom 25.0% ili nižim, (3) obuhvaćene su kristalne strukture koje sadrže porfirinski prsten.
Pronađen je značajan broj interakcija sa π sistemom petočlanih pirolovih prstena i sa π sistemom šestočlanih helatnih prstena koji zadovoljavaju geometrijske kriterijume za X-H···π-interakcije. H-atom kao donor može biti C^{α}-H, C_{ali}-H, C_{aro}-H i N-H. Broj C-H···π-interakcija je znatno veći od N-H···π-interakcija. Lista interakcija C_{ali}-H sa petočlanim prstenima sadrži više hidrofobnih ostataka, verovatno zbog činjenice da su ove interakcije, u proseku, bliže unutrašnjosti proteina. Analiza srednje distance za C_{ali} i C_{aro} C-H···π interakcije pokazuje da C_{ali} gradi interakcije sa kraćim distancama. Interesantno zapažanje je mogućnost da metil grupe i propionat grupe, koje su vezane za jedan porfirinski prsten, interaguju sa petočlanim prstenima drugih porfirina u istom proteinu. Aminokiseline koje učestvuju u X-H···π-interakcijama sa porfirinskim prstenom pokazuju značajnu konzervativnost. Broj ovih interakcija, kao i konzervativnost aminokiselina ukazuju na značaj X-H···π-interakcija u stabilnosti hem-proteina.

[1] S. D. Zarić, D. M. Popović, E. W. Knapp, Biochemistry 40 (2001), 7914–7928
[2] V. B. Medaković, S. D. Zarić, Inorg. Chim. Acta 349 (2003), 1–5

CRYSTAL STRUCTURE OF A NEW NICKEL(II) COMPLEX WITH 2-HYDROXY-1-NAPHTHALDEHYDE S-METHYLISOTHIOSEMICARBAZONE

B. M. Drašković[a], **G. A. Bogdanović**[a], **V. M. Leovac**[b]

[a] *'Vinča' Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, PO Box 522, 11001 Belgrade, Serbia and Montenegro;*
[b] *Department of Chemistry, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia and Montenegro;*
e-mail: bodraskovic@vin.bg.ac.yu

Square-planar complex, [Ni(L-H)Py](NO_3), (L = 2-hydroxy-1-naphthaldehyde S-methylisothiosemicarbazone) was obtained from 1:1 molar ratio of $Ni(NO_3)_2 \cdot 6H_2O$ and ligand L in warm methanol solution. After complete dissolution of ligand, pyridine was added.

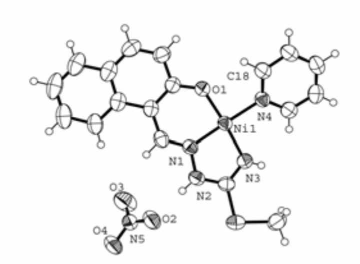


Figure 1. A view of the molecular structure of [Ni(L-H)Py](NO_3), with the non-hydrogen atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

[Ni(L-H)Py](NO_3) complex crystallizes with two independent molecules in the asymmetric unit. The independent molecules have very similar geometrical parameters, but they distinguish only in the orientation of coordinated pyridine. The result of X-ray analysis indicate that the crystal structure of [Ni(L-H)Py](NO_3) complex (Figure 1.) consists of complex cation $[Ni(L\text{-}H)Py]^+$ and of nitrate anion $(NO_3)^-$. Tridentate ONN ligand L is coordinated as a monoanion of 2-hydroxy-1-naphthaldehyde S-methylisothiosemicarbazone, forming two condensed chelate rings (five-membered and six-membered).

In the crystal packing exist numerous hydrogen bonds of N-H···O and C-H···O type. There is only one intramolecular hydrogen bond, C18-H···O1, while the other hydrogen bonds are with participation of the O atoms from nitrate anion, as a proton acceptor. Analising the existence of other noncovalent interactions, we have also found the π···π interactions, which occur between five-membered chelate ring and naphthalene ring, and between six-membered chelate rings of symmetry equivalence.

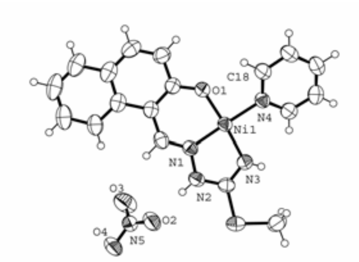
Crystallographic data: formula $C_{18}H_{17}N_5NiO_4S$, triclinic, space group $P\bar{1}$, a = 8.255(3), b = 14.151(2), c = 17.540(3) Å, α = 70.580(10), β = 84.01(2), γ = 83.00(2)°, V = 1913.52 Å^3, μ(Mo $K\alpha$) = 1.160 mm^{-1}, Mo $K\alpha$ radiation, Enraf-Nonius CAD-4 diffractometer, Gaussian absorption correction. Structure was solved using the SHELXS97 program and was refined by SHELXL97 to a residual R-factor of 3.75 % for 6417 reflections with $I > 2\sigma(I)$.

KRISTALNA STRUKTURA NOVOG NIKAL(II) KOMPLEKSA SA S-METILIZOTIOSEMIKARBAZONOM 2-HIDROKSI-1-NAFTALDEHIDA

B. M. Drašković[a], **G. A. Bogdanović**[a], **V. M. Leovac**[b]

[a]*Institut za nuklearne nauke "Vinča", Laboratorija za teorijsku fiziku i fiziku kondenzovane materije, p. p. 522, 11001 Beograd, Srbija i Crna Gora;*
[b]*Departman za hemiju, Prirodno-matematički fakultet, Univerzitet u Novom Sadu, Trg Dositeja Obradovića 3, 21000 Novi Sad, Srbija i Crna Gora;*
e-mail: bodraskovic@vin.bg.ac.yu

Kvadratno-planarni kompleks, [Ni(L-H)Py](NO_3), (L = S-metilizotiosemikarbazon 2-hidroksi-1-naftaldehida) je dobijen reakcijom toplog metanolnog rastvora $Ni(NO_3)_2\cdot 6H_2O$ i liganda L u molskom odnosu 1:1. Nakon potpunog rastvaranja liganda, toplom rastvoru je dodat piridin.



Slika 1. Prikaz molekulske strukture [Ni(L-H)Py](NO_3) sa oznakama nekih nevodoničnih atoma. Anizotropni termalni elipsoidi su prikazani sa 50 % stepenom verovatnoće.

[Ni(L-H)Py](NO_3) kompleks kristališe sa dva nezavisna molekula u asimetričnoj jedinici. Nezavisni molekuli imaju slične geometrijske parametre i razlikuju se samo u orijentaciji koordinovanog piridina. Rezultati rendgenske strukturne analize su pokazali da se kristalna struktura [Ni(L-H)Py](NO_3) kompleksa (Slika 1.) sastoji od kompleksnog katjona $[Ni(L\text{-}H)Py]^+$ i anjona $(NO_3)^-$. L ligand se u kompleksu [Ni(L-H)Py](NO_3) koordinuje tridentatno (ONN), kao monoanjon S-metilizotiosemikarbazon 2-hidroksi-1-naftaldehida, gradeći dva kondenzovana helatna prstena (petočlani i šestočlani).

U kristalnom pakovanju su prisutne brojne vodonične veze N-H···O i C-H···O tipa. Postoji samo jedna intramolekulska C18-H···O1 vodonična veza, dok su sve ostale vodonične veze sa učešćem atoma O iz nitratnog jona kao akceptora vodonika. Analizirajući prisutnost drugih nekovalentnih interakcija nađene su i $\pi\cdots\pi$ interakcije, koje postoje između petočlanog helatnog prstena i naftalenskog prstena, kao i između šestočlanih helatnih prstenova molekula u simetrijski ekvivalentnim položajima.

Kristalografski podaci: $C_{18}H_{17}N_5NiO_4S$, triklinični kristalni sistem, prostorna grupa $P\bar{1}$, a = 8.255(3), b = 14.151(2), c = 17.540(3) Å, α = 70.580(10), β = 84.01(2), γ = 83.00(2)°, V = 1913.52 Å^3, μ(Mo $K\alpha$) = 1.160 mm^{-1}, Mo $K\alpha$ zračenje, Enraf-Nonius CAD-4 difraktometar, korekcija za absorpciju: Gausovska. Struktura je rešena pomoću programa SHELXS97 i utačnjena progrmom SHELXL97 do finalnog R-faktora od 3,75 % za 6417 refleksija sa I>2σ(I).

CRYSTAL STRYCTURE OF Sr-FELDSPARS OBTAINED FROM FAU ZEOLITE BY ION-EXCHANGE

B. Nedić [a], **V. Dondur** [a], **A. Kremenović** [b], **R. Dimitrijević** [b]

[a] *Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, Belgrade*
[b] *Faculty for Mining and Geology, University of Belgrade, Đušina 7, Belgrade*
e-mail: bojananedic@sezampro.yu

Synthetic feldspar phases are materials with interesting electric, dielectric and thermal properties. Sr- and Ba- feldspars are intensively investigated. These phases could be synthesized from oxides, by sol – gel procedures, or by thermal transformations of Sr- and Ba- exchanged zeolites. Thermally induced phase transformation of Sr- and Ba-zeolites leads to pure Sr- and Ba- feldspars.

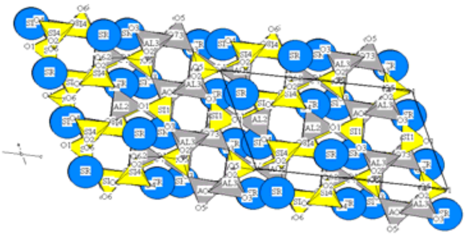


Figure 1: Sr-feldspar structure obtained at 1500ºC

XRPD spectra of Sr-feldspar samples, obtained by thermal treatment of Sr-FAU zeolite at various temperatures (1100 ºC, 1200 ºC and 1500 ºC), have been recorded on powder diffractometer and the structures have been refined by Rietveld method. Structural models have been calculated in the space group I2/c (No. 13). During the thermal treatment of the sample, after the transition through an amorphous phase, two crystal phases appear: Sr-hexacelsian [1] and Sr-feldspar [2]. The refinement shows that the amount of Sr-feldspar in the mixture increases with the temperature. At 1500 ºC, only Sr-feldspar is present in the sample. Crystal structure of Sr-feldspar obtained at 1500 ºC is shown in the figure 1. The structure model is refined to the good agreement (value of Bragg R-factor is around 7%, and value of χ^2 is around 9). The Sr-feldspars structures are characterized with vacancies in the position occupied by the Sr^{2+} ion.

[1] A. Kremenović, P. Norby, R. Dimitrijević, V. Dondur, *Solid State Ionics*, **101**, (1997), 611-618

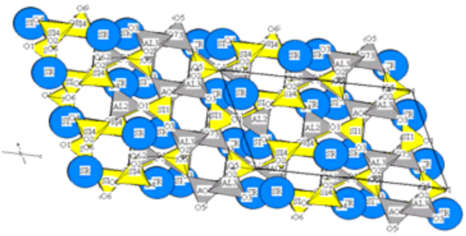
[2] P. Benna, E. Bruno, *American Mineralogist*, **86**, (2001), 690-696

KRISTALNA STRUKTURA Sr-FELDSPATA DOBIJENIH JONSKOM IZMENOM IZ FAU ZEOLITA

B. Nedić [a], **V. Dondur** [a], **A. Kremenović** [b], **R. Dimitrijević** [b]

[a]*Fakultet za fizičku hemiju, Univerzitet u Beogradu, Studentski trg 12-16, Beograd*
[b]*Rudarsko – geološki fakultet, Univerzitet u Beogradu, Đušina 7, Beograd*
e-mail: bojananedic@sezampro.yu

Feldspatske faze dobijene različitim sintetičkim metodama su materijali sa veoma interesantnim električnim, dielektričnim i termalnim osobinama. Među najzanimljivije faze ovog tipa mogu se ubrojiti Sr- i Ba- feldspati. Oni mogu biti dobijeni sintezom iz oksidnih faza, sol – gel sintezom, kao i drugim metodama. Ukoliko se krene od zeolita određene strukture i stehiometrije, može se jonskom izmenom ugraditi Sr^{2+} jon. Ako se zatim dobijeni zeolit termalno tretira, ovako dobijene faze mogu biti izuzetne čistoće.



Slika 1. Struktura Sr-feldspata dobijenog žarenjem na 1500ºC

Uzorci Sr-feldspata, dobijeni termalnom obradom Sr-FAU zeolita na različitim temperaturama (1100 ºC, 1200 ºC i 1500 ºC), snimljeni su na rendgenskom difraktometru za prah i strukture su utačnjavane primenom Ritveldove metode. Strukturni modeli su utačnjavani u prostornoj grupi I2/c (br. 13). U toku zagrevanja uzorka, nakon amorfizacije zeolita, rekristališu dve faze: Sr-heksacelzijan [1] i Sr-feldspat [2]. Utačnjavanje je pokazalo da se sa porastom temperature žarenja, povećava procentni udeo Sr-feldspata u smeši. Na temperaturi 1500 ºC u uzorku je prisutan samo Sr-feldspat. Na slici 1 prikazana je kristalna struktura Sr-feldspata dobijenog na temperaturi od 1500 ºC. Pokazatelji pouzdanosti utačnjavanja su dobri (vrednost Bragovog R-faktora je 7 %, a vrednost χ^2 je 9). Struktura Sr-feldspata (sl. 1) okarakterisana je vakancijama koje se nalaze u položaju Sr^{2+} jona.

[1] A. Kremenović, P. Norby, R. Dimitrijević, V. Dondur, *Solid State Ionics*, **101**, (1997), 611-618

[2] P. Benna, E. Bruno, *American Mineralogist*, **86**, (2001), 690-696

SYNTHESIS AND CRYSTAL STRUCTURE OF 6α,7α-EPOXY-17-OXA-D-HOMO-1,4-ANDROSTADIEN -3,16-DION

O. Klisurić[a], D. Lazar[a], S. Stanković[a], E. Đurendić[a], M. Zaviš[a], K. Penov-Gaši[a], S. Novaković[b], G. Bogdanović[b]

[a]*Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia and Montenegro*
[b]*"Vinča", Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, PO Box 522, 11001 Belgrade, Serbia and Montenegro*
e-mail: olivia@uns.ns.ac.yu

In order to study androgenic vs. antiandrogenic activity, new compound 6α,7α-epoxy-17-oksa-D-homo-1,4-androstadien-3,16-dion was synthesized in several synthetic steps, starting from dehydroepyandrosterone.

The compound crystallizes in the monoclinic system, space group $P2_1$, with the unit cell parameters a=7.418(3), b=10.018(19), c=11.157(4)Å, β=103.97(5)° and Z=2, D_x=1.30 Mgm^{-3}, μ=0.09 mm^{-1}, MoK_α radiation.

The crystal structure was solved by direct methods on the basis of 1501 independent reflections using SHELXS-86 [1] and refined by SHELXL-97 [1]. The final R factor is 0.0498 for 900 reflections with I>2σ(I).

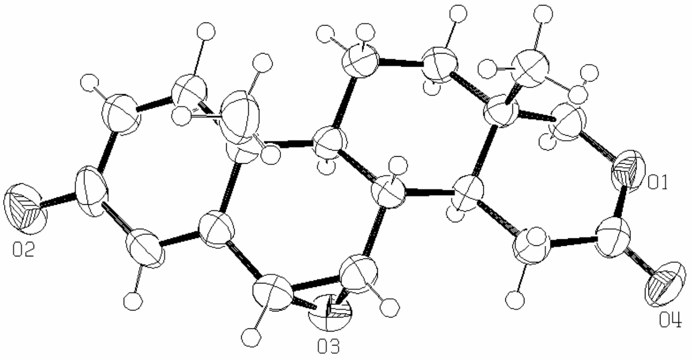


Figure 1. A view of the molecular structure of $C_{19}O_4H_{22}$

[1] SHELX97 - Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

SINTEZA I KRISTALNA STRUKTURA 6α,7α-EPOKSI-17-OKSA-D-HOMO-1,4-ANDROSTADIEN -3,16-DIONA

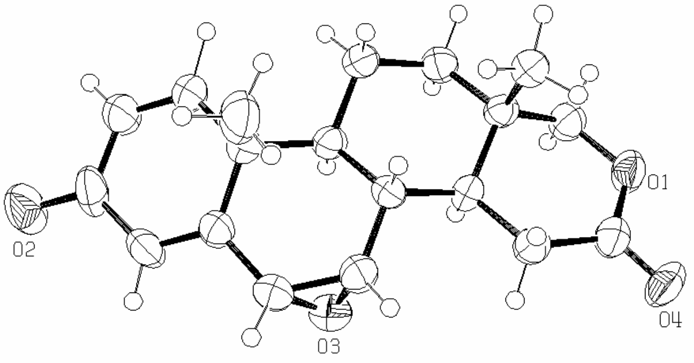
O. Klisurić[a], D. Lazar[a], S. Stanković[a], E. Đurendić[a], M. Zaviš[a], K. Penov-Gaši[a], S. Novaković[b], G. Bogdanović[b]

[a]*Prirodno-matematički fakultet, Univerzitet u Novom Sadu, Trg Dositeja Obradovića 4, 21000 Novi Sad, Srbija i Crna Gora*
[b]*Institut za nuklearne nauke "Vinča", laboratorija za teorijsku fiziku i fiziku kondezovane materije, P. P. 522, 11001 Beograd, Srbija i Crna Gora*
e-mail: olivia@uns.ns.ac.yu

U cilju ispitivanja androgene odnosno antiandrogene aktivnosti, polazeći od dehidroepiandrosterona, sintetizaovano je u više sintetskih faza novo jedinjenje: 6α,7α-epoksi-17-oksa-D-homo-1,4-androstadien-3,16-dion.

Jedinjenje kristališe u monokliničnom kristalografskom sistemu, prostorna grupa $P2_1$, sa parametrima elementarne ćelije a=7,418(3), b=10,018(19), c=11,157(4)Å, β=103,97(5)° i Z=2, D_x=1,30 Mgm^{-3}, μ=0,09 mm^{-1}, MoK_α zračenje.

Struktura kristala je rešena primenom direktnih metoda na bazi 1501 nezavisnih refleksa pomoću SHELXS-86 [1] i utačnjena pomoću SHELXL-97 [1]. Konačna vrednost R faktora je 0,0498 za 900 refleksa sa I>4σ(I).



Slika 1. Prikaz molekulske strukture $C_{19}\,O_4\,H_{22}$

[1] SHELX97 - Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

INTERPRETATION OF THE WEAK INTERMOLECULAR INTERACTIONS ON THE BASIS OF THE EXPERIMENTAL CHARGE DENSITY ANALYSIS: C-H…S INTERACTIONS IN SALICYLADEHYDE THIOSEMICARBAZONE

S.B. Novaković[a], G.A. Bogdanović[a], A. Spasojević-de Biré[b], N.E.Ghermani[b]

[a] *"VINČA" Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, PO Box 522, 11001 Belgrade, Serbia and Montenegro*
[b] *Laboratory SPMS, UMR 8580 CNRS – Ecole Centrale Paris, 92295 Châtenay-Malabry, France*
e-mail: snovak@vin.bg.ac.yu

The thiourea derivates have often been found among the therapeutic agents[1] or other biologically interacting molecules such as insecticides and pesticides. In a majority of cases, the biological activities of these compounds are attributed to the particularities of the sulfur atom in their thioureide fragment ($-NH-C(=S)-NH_2$). It is well known that in these kinds of compounds, the resonance effect which includes free electron pairs of both nitrogen atoms and C=S bond considerably increase the negative charge on a sulfur atom and its acceptor ability in the hydrogen bonding proces[2]. Thioureido fragment is also a part of the thiosemicarbazide derivates and theirs transition metal complexes. A high resolution low temperature X-ray experiment combined with the multipole refinement[3] has been used for the determination of the charge density distribution in salicylaldehyde tiosemcarbazone. In this crystal structure, sulfur atom is engaged as an acceptor in several hydrogen bonding interactions of N-H...S and C-H...S types. The electron density of the sulfur's lone pairs has the shape of torus which is symmetrically distributed around the sulfur atom. It has been found that one of the C-H...S interactions induce stronger polarization of the electron density within the sulfur's torus than the corresponding N-H..S hydrogen bond.

[1] O.J. D'Cruz & F.M. Uckun *Mol. Hum. Reprod*; 2005 11(10):767-777 B. Phetsuksiri et al. *J. Biol.Chem*. 278 (2003) 53121-53130.
[2] F.H. Allen et al. *Acta Cryst. B53* (1997) 680-695.
[3] Hansen, N. K. & Coppens, P. *Acta Crystallogr*. A34 (1978) 909-921.

INTERPRETACIJA SLABIH INTERMOLEKULSKIH INTERAKCIJA NA OSNOVU REZULTATA EKSPERIMENTALNE GUSTINE NAELEKTRISANJA: C-H…S INTERAKCIJE U TIOSEMIKARBAZONU SALICILALDEHIDA

S.B. Novaković[a], G.A. Bogdanović[a], A. Spasojević-de Biré[b], N.E.Ghermani[b]

[a] Institut za nuklearne nauke "VINČA", Laboratorija za torijsku fiziku i kondenzovane materije, P. P. 522, 11001 Beograd, Srbija i Crna Gora;
[b] Laboratory SPMS, UMR 8580 CNRS – Ecole Centrale Paris, 92295 Châtenay-Malabry, Francuska.
e-mail: snovak@vin.bg.ac.yu

Derivati tiouree su često prisutni kao terapeutski agensi[1] ili druge vrste bilološki aktivnih molekula kao što su neke grupe insekticida i pesticida. U velikom broju slučajeva, biološka aktivnost ovih jedinjenja je uslovljena specifičnim osobinama atoma sumpora iz tioureido fragmenta (-NH-C(=S)-NH_2). Poznato je da rezonancioni efekt u ovom fragmentu, koji uključuje slobodne elektronske parove oba atoma azota i C=S vezu značajno povećava negativno naelektrisanje na atomu sumpora a time i njegove akceptorske sposobnosti u vodoničnim vezama[2]. Tioureido fragment je takodje sastavni deo derivata tiosemikarbazida i njihovih kompleksa sa prelaznim metalima. Primenom niskotemperaturnog eksperimenta difrakcije rendgenskog zračenja visoke rezolucije u kombinaciji sa multipol-utačnjavanjem[3] odredjena je raspodela elektronske gustine u tiosemikarbazonu salicilaldehida. U ovoj kristalnoj strukturi, atom sumpora je angažovan kao akceptor u nekoliko vodoničnih interakcija N-H...S i C-H...S tipa dok je elektronska gustina njegovih slobodnih elektronskih parova simetrično rasporedjena oko C-S veze i ima oblik torusa. Utvrđeno je da jedna od C-H...S interakcija uslovljava jaču polarizaciju valentne elektronske gustine atoma sumpora nego što je to slučaj sa N-H...S vodoničnom vezom.

[1] O.J. D'Cruz & F.M. Uckun *Mol. Hum. Reprod*; 2005 11(10):767-777 B. Phetsuksiri et al. *J. Biol.Chem*. 278 (2003) 53121-53130.
[2] F.H. Allen et al. *Acta Cryst. B53* (1997) 680-695.
[3] Hansen, N. K. & Coppens, P. *Acta Crystallogr*. A34 (1978) 909-921.

THE MINERALOGICAL AND CRYSTALLOGRAPHIC CHARACTERIZATION OF THE ANALCIME TUFF FROM THE "JOVIĆI" DEPOSIT, BOSNIA AND HERZEGOVINA

J. Stojanovic[a], A. Radosavljevic-Mihajlovic[b], and J. Dukic[b]

[a] *Institute for Technology of Nuclear and Other Raw Mineral Materials, Applied Mineralogy Unit, Fransche d'Eperey 86, 11000 Belgrade -P.O. Box 390, Serbia;*
[b] *Institute of Nuclear Sciences "Vinca", Laboratory for Materials, P. O. Box 522, 11001 Belgrade, Serbia.*
e/mail: j.stojanovic@itnms.ac.yu

The mineralogical and crystallographic properties of zeolitic tuff from "Jovići" deposit (Bosnia and Herzegovina) have been investigated. Samples rich in natural analcime were characterized by DT (Differential Thermal) and TG (Thermo-Gravimetric), SEM (Scanning Electron Microscopy) and XRPD (X-Ray Powder Diffraction) analyses. The Rietveld method was used for quantitative phase determination. The criterion used to assign mass losses was following: analcime exibits a continuous mass loss up to 400 ^{o}C of about 5.5 wt%. The chemical data (EDS analyses) for analcime are following (average on four analyses): Si=26.43 %; Al=11.84 %; O=51.07 %; Na=9.55 %; K=0.31 %; Mg=0.15 %; Σ=99.35 %. The R value (Si/(Si+Al) ratio) is 0.69 and Na/(Na+Ca) ratio is 1.

Analcime, biotite, sanidine and quartz were the only minerals determined by XRPD in the analcime tuff sample. The quantitative Rietveld analyses were performed by using the FULLPROF software. Quantitative volume fractions (%) are as follows: analcime 44.79(0.9), sanidine 33.20(0.6), biotite 20.99(0.9), and quartz 1.02(0.1). The analcime tuff sample was refined on cubic (*Ia-3d*), tetragonal ($I4_1/acd$) and orthorhombic (*Ibca*) analcime unit-cell parameters. Tetragonal unit-cell parameters of analcime yielded the best refinement agreement factors (R_w=22.0, R_p=24.2, R_{exp}=10.0, R_B=5.99, R_F=5.95). Refined tetragonal unit-cell parameters for analcime are a=13.7097(3), c=13.6953(4) Å, V=2574.112(7) Å^3.

МИНЕРАЛОШКА И КРИСТАЛОГРАФСКА КАРАКТЕРИЗАЦИЈА АНАЛЦИМСКОГ ТУФА СА ЛОКАЛИТЕТА „ЈОВИЋИ“, БОСНА И ХЕРЦЕГОВИНА

Ј. Стојановић[a], А. Радосављевић-Михајловић[б], Ј. Дукић[б]

[a] *Институт за технологију нуклеарних и других минералних сировина, Лабораторија за минералошка испитивања, Франше д‘Епере 86, 11000 Београд, Србија;*
[б] *Институт за нуклеарне науке "Винча", Лабораторија за материјале, 11001 Београд, Србија.*
e-mail: j.stojanovic@itnms.ac.yu

У овом раду дати су резултати кристалографских испитивања аналцимског туфа са локалитета „Јовићи“, Босна и Херцеговина. Узорци богати аналцимом анализирани су диференцијално-термичком (DT), термо-гравиметријском (TG), скенирајуће-елекронском (SEM) и рендген-дифракционом (XRPD) методом. Квантитативна минералошка анализа је извршена помоћу Ритвелдове (Rietveld) методе. Диференцијално-термичка и термо-гравиметријска анализа је показала да код аналцима постоји константан губитак масе до око 400 ^{o}C. Укупан губитак масе је око 5,5 % (тежинских). Просек четири хемијске анализе (SEM-EDS) аналцима је следећи: Si=26.43 %; Al=11.84 %; O=51.07 %; Na=9.55 %; K=0.31 %; Mg=0.15 %; Σ=99.35 %. Однос мрежних катјона (Si/(Si+Al)) је R=0,69, док је однос ванмрежних катјона (Na/(Na+Ca)) 1.

Аналцим, биотит, санидин и кварц су минерали који су одређени квалитативном рендгенском анализом праха. Квантитативна минералошка анализа је урађена помоћу рачунарског програма FULLPROF. Квантитативни однос минерала (%) је следећи: аналцим 44.79(0.9), санидин 33.20(0.6), биотит 20.99(0.9), и кварц 1.02(0.1). Тетрагонални параметри јединичне ћелије аналцима су дали најбоље факторе слагања (R_w=22,0, R_p=24,2, R_{exp}=10,0, R_B=5,99, R_F=5,95). Утачњени параметри јединичне ћелије ($I4_1/acd$) су следећи: a=13,7097(3), c=13,6953(4) Å, V=2574,112(7) Å^3.

STRUCTURE AND MICROSTRUCTURE OF $\mathrm{CA_{1-X}Y_XMNO_3}$ AND $\mathrm{CA_2MN_3O_8}$

J. Dukić[a], **Lj. Karanović**[b], **A. Kremenović**[b], **S. Bošković**[a] **and B. Matović**[a]

[a]*Institute of Nuclear Sciences "Vinča", Laboratory for Materials, P. O. Box 522, 11001 Belgrade, Serbia and Montenegro;* [b]*Faculty of Mining and Geology, Laboratory for Crystallography, University of Belgrade, P. O. Box 162, 11001 Belgrade, Serbia and Montenegro.*
e-mail: jelena@vin.bg.ac.yu

Four mixtures of $\mathrm{Ca_{1-x}Y_xMnO_3}$ with x equal 0, 0.1, 0.2, and 0.3 were synthesized by modified glycine nitrate procedure [1]. According to X-ray powder diffraction results the obtained nanopowders consist of perovskite-type structure as a main phase, and small amount of $\mathrm{Ca_2Mn_3O_8}$. Rietveld refinement of X-ray diffraction patterns and calculation of the contents of both phases in investigated samples were carried out using the program FullProf [2].

Refined orthorhombic cell dimensions of perovskite-type compounds $\mathrm{Ca_{1-x}Y_xMnO_3}$ (space group *Pnma*, $Z = 4$) are: $a = 5.2808(5)$, $b = 7.4575(4)$, $c = 5.2776(6)$ Å, $V = 207.84(3)$ Å^3 in sample with x = 0, $a = 5.3052(4)$, $b = 7.4708(6)$, $c = 5.2801(5)$ Å, $V = 209.28(3)$ Å^3 in sample with x = 0.1, $a = 5.283(1)$, $b = 7.5227(4)$, $c = 5.292(1)$ Å, $V = 210.31(6)$ Å^3 in sample with x = 0.2 and $a = 5.314(1)$, $b = 7.4614(8)$, $c = 5.302(1)$ Å, $V = 210.23(7)$ Å^3 in sample with x = 0.3.

The secondary phase, $\mathrm{Ca_2Mn_3O_8}$, is the first reported example of a compound possessing prismatically coordinated $\mathrm{Ca^{2+}}$ ions [3]. The refined lattice parameters of $\mathrm{Ca_2Mn_3O_8}$ (space group *C2/m*, $Z = 2$) are $a = 11.032(1)$, $b = 5.8457(7)$, $c = 4.9442(7)$ Å, $\beta = 109.841(9)$ °, $V = 299.92(6)$ Å^3 in sample with x = 0 and $a = 11.004(6)$, $b = 5.865(3)$, $c = 4.942(3)$ Å, $\beta = 110.15(4)$ °, $V = 299.4(3)$ Å^3 in sample with x = 1. Quantitative analysis shows that the amount of $\mathrm{Ca_2Mn_3O_8}$ decreases with increasing concentration of Y. In undoped $\mathrm{CaMnO_3}$ sample the amount of $\mathrm{Ca_2Mn_3O_8}$ is ~ 28%, and in sample with x = 0.3 it is below 1%. The influence of Y on unit cell parameters and atomic positions was analyzed. Microstructure size-strain analysis was performed for all samples.

[1] S. Bošković, B. Matović, M. Vlajić, V. Krstić, *Ceram. Int.*, Article in Press.
[2] J. Rodriguez-Carvajal, Collected Abstract of Powder Diffraction Meeting, Toulouse (1990) 127.
[3] G. B. Ansell, M. A. Modrick, *Acta. Cryst.*, B **38** (1982), 1795-1797.

STRUKTURA I MIKROSTRUKTURA $CA_{1-X}Y_XMNO_3$ I $CA_2MN_3O_8$

J. Dukić[a], Lj. Karanović[b], A. Kremenović[b], S. Bošković[a] and B. Matović[a]

[a]Institut za nuklearne nauke "Vinča", Laboratorija za materijale, p. pr. 522, 11001 Beograd, Srbija i Crna Gora; [b]Rudarsko-geološki fakultet, Laboratorija za kristalografiju, Univerzitet u Beogradu, p. pr. 162, 11001 Beograd, Srbija i Crna Gora.
e-mail: jelena@vin.bg.ac.yu

Modifikovanom glicin-nitrat metodom sintetizovane su četiri mešavine $Ca_{1-x}Y_xMnO_3$ pri čemu x ima vrednosti 0, 0,1, 0,2, i 0,3 [1]. Prema rezultatima rendgenske difrakcije dobijeni nanoprahovi kao dominantnu sadrže fazu sa perovskitskom strukturom i malu količinu $Ca_2Mn_3O_8$. Na ispitivanim uzorcima urađena je Ritveldova analiza korišćenjem programa FullProf [2] i izračunat sadržaj obe faze.

Utačnjavanjem su dobijeni sledeći parametri za rombičnu jediničnu ćeliju kod faze sa perovskitskom strukturom, $Ca_{1-x}Y_xMnO_3$ (prostorna grupa *Pnma*, $Z = 4$): $a = 5{,}2808(5)$, $b = 7{,}4575(4)$, $c = 5{,}2776(6)$ Å, $V = 207{,}84(3)$ Å^3 u uzorku sa $x = 0$, $a = 5{,}3052(4)$, $b = 7{,}4708(6)$, $c = 5{,}2801(5)$ Å, $V = 209{,}28(3)$ Å^3 u uzorku sa $x = 0{,}1$, $a = 5{,}283(1)$, $b = 7{,}5227(4)$, $c = 5{,}292(1)$ Å, $V = 210{,}31(6)$ Å^3 u uzorku sa $x = 0{,}2$ i $a = 5{,}314(1)$, $b = 7{,}4614(8)$, $c = 5{,}302(1)$ Å, $V = 210{,}23(7)$ Å^3 u uzorku sa $x = 0{,}3$.

Sekundarna faza, $Ca_2Mn_3O_8$, je prvo jedinjenje kod kojeg je pronađena prizmatska koordinacija Ca^{2+} jona [3]. Utačnjeni parametri jedinične ćelije za $Ca_2Mn_3O_8$ (prostorna grupa *C2/m*, $Z = 2$) su: $a = 11{,}032(1)$, $b = 5{,}8457(7)$, $c = 4{,}9442(7)$ Å, $\beta = 109{,}841(9)$ °, $V = 299{,}92(6)$ Å^3 u uzorku sa $x = 0$ i $a = 11{,}004(6)$, $b = 5{,}865(3)$, $c = 4{,}942(3)$ Å, $\beta = 110{,}15(4)$ °, $V = 299{,}4(3)$ Å^3 u uzorku sa $x = 1$. Kvantitativna analiza pokazuje da se količina $Ca_2Mn_3O_8$ smanjuje sa povećanjem koncentracije Y. U nedopiranom $CaMnO_3$ uzorku maseni udeo $Ca_2Mn_3O_8$ je ~ 28%, a u uzorku sa $x = 0{,}3$ ispod 1%. Analiziran je uticaj Y na parametre jedinične ćelije i položaje atoma. Za sve uzorke je urađena analiza mikrostrukturnih parametara, veličine kristalita i mikronaprezanja.

[1] S. Bošković, B. Matović, M. Vlajić, V. Krstić, *Ceram. Int.*, Article In Press.
[2] J. Rodriguez-Carvajal, Collected Abstract of Powder Diffraction Meeting, Toulouse (1990) 127.
[3] G. B. Ansell, M. A. Modrick, *Acta. Cryst.*, B **38** (1982), 1795-1797.

MECHANOCHEMICAL SYNTHESIS OF TIO_X WITH X<2

I. Živanović[a], **D. Poleti**[a], **Lj. Karanović**[b], **M. Zdujić**[c], **Č. Jovalekić**[d]

[a] *Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia and Montenegro*
[b] *Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia and Montenegro*
[c] *Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, 11000 Belgrade, Knez Mihailova 35, 11000 Belgrade, Serbia and Montenegro*
[d] *Centre for Multidisciplinary Studies, University of Belgrade, Kneza Višeslava 1a, 11000 Belgrade, Serbia and Montenegro*
e-mail: ivana@tmf.bg.ac.yu

Between Ti and TiO_2 there is extended series of oxides with lower Ti oxidation states. Some of them are of great interest due to high conductivity comparable to graphite and more corrosion resistance than conventional electrode materials. The oxides with a general formula Ti_nO_{2n-1} and $4 \leq n \leq 10$ (or TiO_x, $1{,}75 \leq x \leq 1{,}90$) are known as Magnéli phases. They are related to the TiO_2, rutile structure, which contains a distorted hexagonal close packing (hcp) of O^{2-} ions with Ti^{4+} cations occupying every other octahedral site. The TiO_6 octahedra form the infinite edge-sharing chains, which are further linked together by corner-sharing. In Magnéli phases as n decreases, the number of occupied octahedra increases. As a result the rutil-like chains are interrupted at every nth octahedron making a share plane where the octahedra share faces in addition to edges and corners. Another group of oxides with $x \leq 1$ also exists. It can be derived from hcp of Ti atoms with partial (Ti_6O, Ti_3O, Ti_2O) or full (TiO) occupancy of octahedral sites by O^{2-} ions. In all cases, either direct Ti–Ti contacts or interactions between neighbouring Ti atoms belonging to the face-sharing octahedra are responsible for the metallic conductivity.

So far these oxides were prepared in a very inconvenient way by partial reduction of TiO_2 at about 1700 °C in a hydrogen atmosphere. The aim of this work is the mechanochemical synthesis of TiO_x in a planetary ball mill starting from appropriate mixtures of Ti and TiO_2. The mixtures were milled for different milling times (0.5, 1, 2 and 5 h) using hardened-steel or zirconia vials and balls in an air atmosphere. The products are characterized by X-ray powder diffraction and TG/DT analysis.

In hardened-steel medium, after 0.5 h of milling only a mixture of reactants was obtained, while after 1 h the maxima of TiO phase, besides the maxima of Ti and TiO_2, became visible. After 2 h of milling a single-phase TiO of very low crystallinity was obtained. The milling during 5 h caused a significant Fe contamination (about 40 mass.%) due to vials and balls debris. In zirconia vials the mechanochemical reaction is faster since almost pure TiO phase was obtained already after 1 h of milling. So far attempts to prepare Ti_nO_{2n-1} compounds, like T_4O_7, were not successful.

The results of TG/DT analysis indicated that the mechanochemically prepared TiO samples very likely are not quite stoichiometric and still contain some Ti^{y+} ions with $y>2$. This is shown by heating a sample up to 1200 °C in an air atmosphere, since the experimental mass gain (18.3 %) was smaller than the value expected for TiO → TiO_2 oxidation (25.0 %).

MEHANOHEMIJSKA SINTEZA TIO$_X$, GDE JE X<2

I. Živanović[a], **D. Poleti**[a], **Lj. Karanović**[b], **M. Zdujić**[c], **Č. Jovalekić**[d]

[a] *Tehnološko-metalurški fakultet, Karnegijeva 4, 11000 Beograd, Srbija i Crna Gora*
[b] *Rudarsko-geološki fakultet, Đušina 7, 11000 Beograd, Srbija i Crna Gora*
[c] *Institut tehničkih nauka srpske akademije nauka i umetnosti, Knez Mihailova 35, 11000 Beograd, Srbija i Crna Gora*
[d] *Centar za multidisciplinarne studije, Kneza Višeslava 1a, 11000 Beograd, Srbija i Crna Gora*
e-mail: ivana@tmf.bg.ac.yu

Između Ti i TiO_2 postoji brojna serija oksida sa nižim oksidacionim stanjima Ti. Neki od tih oksida su posebno interesantni zbog svoje visoke provodnosti, poredive sa grafitnom, kao i zbog toga što su otporniji na koroziju od većine poznatih elektrodnih materijala. Jedna grupa oksida opšte formule Ti_nO_{2n-1} sa $4 \leq n \leq 10$ (ili TiO_x, $1,75 < x < 1,90$) naziva se Manjelijevim fazama. Njihova struktura se izvodi iz strukture rutila, TiO_2, koja predstavlja deformisano heksagonalno najgušće pakovanje (hcp) O^{2-}-jona, gde katjoni Ti^{4+} popunjavaju svaku drugu oktaedarsku šupljinu. Povezivanjem preko zajedničkih ivica TiO_6 oktaedri formiraju beskonačno duge lance, koji su međusobno povezani preko rogljeva. Kako se vrednost n smanjuje, broj popunjenih oktaedarskih šupljina u Manjelijevim fazama se povećava, tako da se lanci oktaedara posle svakog n-tog oktaedra modifikuju povezivanjem preko zajedničkih pljosni. Postoji i druga grupa oksida sa $x \leq 1$, čija se struktura može izvesti iz hcp atoma Ti, pri čemu joni O^{2-} delimično (Ti_6O, Ti_3O, Ti_2O) ili potpuno (TiO) popunjavaju oktaedarske šupljine. U svakom slučaju direktne Ti–Ti veze, ili interakcije između susednih atoma Ti iz oktaedara sa zajedničkim pljosnima, dovode do provodnosti metalnog tipa.

Do sada su opisani oksidi dobijani veoma neudobnim postupkom – redukcijom TiO_2 u atmosferi vodonika na temperaturama većim od 1700 °C. Cilj ovog rada jeste mehanohemijsko dobijanje TiO_x u planetarnom mlinu polazeći od odgovarajućih smeša Ti i TiO_2. Smeše su mlevene u posudama od čelika i ZrO_2 sa odgovarajućim kuglicama u atmosferi vazduha. Vremena mlevenja su bila različita (0,5, 1, 2 i 5 h), a dobijeni uzorci su okarakterisani rendgenskom difrakcijom i TG/DT analizom.

Nakon mlevenja od 0.5 h u čeličnim posudama dobijena je samo smeša polaznih komponenata, dok su se posle mlevenja od 1 h pored pikova Ti i TiO_2 pojavili i pikovi TiO. Mlevenjem u trajanju od 2 h dobijena je samo TiO faza niskog kristaliniteta. Petočasovno mlevenje dovelo je do značajnog zaprljanja sistema gvožđem (oko 40 mass.%) usled otiranja posuda i kuglica. Mehanohemijska reakcija u ZrO_2 posudama odigrava se većom brzinom, jer je već nakon 1 h dobijen skoro monofazni TiO kao proizvod. Pokušaji da se dobiju oksidi tipa Ti_nO_{2n-1}, kao što je Ti_4O_7, za sada nisu bili uspešni.

Rezultati TG/DT analize ukazali su da mehanohemijski dobijeni uzorci TiO nisu stehiometrijski, već sadrže i Ti^{y+}-jone sa $y>2$. Naime, zagrevanjem uzoraka do 1200 °C u vazduhu zapažen je manji porast mase (18,3 %) nego što je bilo očekivano za reakciju oksidacije $TiO \rightarrow TiO_2$ (25,0 %).

SYNTHESIS AND CRYSTAL STRUCTURE OF 4β,5β-EPOXY-17-OXA-D-HOMO-ANDROSTA -3,16-DIONA

D. Lazar[a], **O. Klisurić**[a], **S. Stanković**[a], **E. Đurendić**[a], **M. Zaviš**[a], **K. Penov-Gaši**[a], **S. Novaković**[b], **G. Bogdanović**[b]

[a]*Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 4, 21000 Novi Sad, Serbia and Montenegro*
[b]*"Vinča", Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter Physics, PO Box 522, 11001 Belgrade, Serbia and Montenegro*
e-mail: olivia@uns.ns.ac.yu

In order to study androgenic vs. antiandrogenic activity, new compound, 4β,5β-epoxy-17-oxa-D-homo-androsta-3,16-dion, was synthesized in several synthetic steps, starting from dehydroepyandrosterone.

The compound crystallizes in the monoclinic system, space group $P2_1$, with the unit cell parameters a=7.555(4), b=10.510(4), c=10.189(6)Å, β=92.43(5)° and Z=2, D_x=1.31 Mgm^{-3}, μ=0.09 mm^{-1}, MoK_α radiation.

The crystal structure was solved by direct methods on the basis of 1674 independent reflections using SHELXS-86 [1] and refined by SHELXL-97 [1]. The final R factor is 0.0447 for 994 reflections with I>2σ(I).

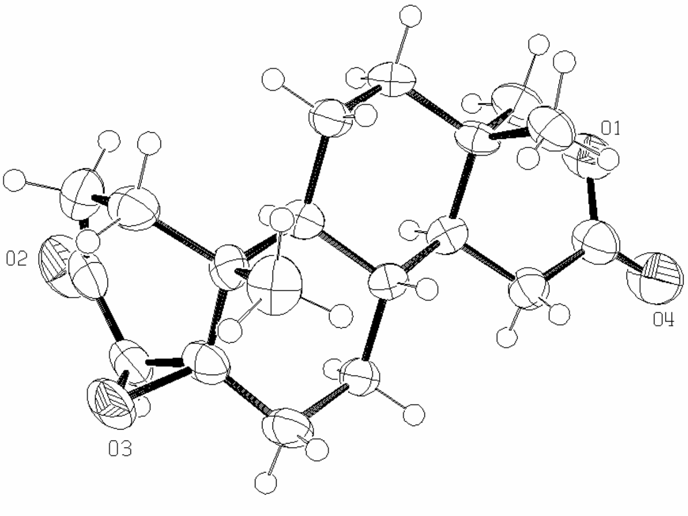


Figure 1. A view of the molecular structure of $C_{19}O_4H_{26}$

[1] SHELX97 - Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

SINTEZA I KRISTALNA STRUKTURA 4β,5β-EPOKSI-17-OKSA-D-HOMO-ANDROSTA -3,16-DIONA

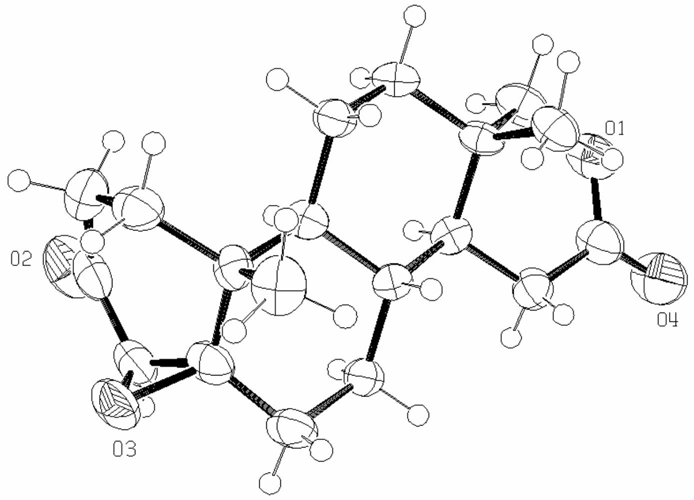
D. Lazar[a], O. Klisurić[a], S. Stanković[a], E. Đurendić[a], M. Zaviš[a], K. Penov-Gaši[a], S. Novaković[b], G. Bogdanović[b]

[a]*Prirodno-matematički fakultet, Univerzitet u Novom Sadu, Trg Dositeja Obradovića 4, 21000 Novi Sad, Srbija i Crna Gora*
[b]*Institut za nuklearne nauke "Vinča", laboratorija za teorijsku fiziku i fiziku kondezovane materije, P. P. 522, 11001 Beograd, Srbija i Crna Gora*
e-mail: olivia@uns.ns.ac.yu

U cilju ispitivanja androgene odnosno antiandrogene aktivnosti, polazeći od dehidroepiandrosterona, sintetizaovano je u više sintetskih faza novo jedinjenje: 4β,5β-epoksi-17-oksa-D-homo-androsta-3,16-dion.

Jedinjenje kristališe u monokliničnom kristalografskom sistemu, prostorna grupa $P2_1$, sa parametrima elementarne ćelije a=7,555(4), b=10,510(4), c=10,189(6)Å, β=92,43(5)° i Z=2, D_x=1,31 Mgm^{-3}, μ=0,09 mm^{-1}, MoK_α zračenje.

Struktura kristala je rešena primenom direktnih metoda na bazi 1674 nezavisnih refleksa pomoću SHELXS-86 [1] i utačnjena pomoću SHELXL-97 [1]. Konačna vrednost R faktora je 0,0447 za 994 refleksa sa I>4σ(I).



Slika 1. Prikaz molekulske strukture $C_{19}O_4H_{26}$

[1] SHELX97 - Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

METAL-DEPENDENT CAPACITY FOR CH/π INTERACTIONS OF ACETYLACETONATO CHELATES

Miloš K. Milčić[a], Vesna B. Medaković[a], Dušan N. Sredojević[a], Nenad O. Juranić[b] and Snežana d. Zarić[a]

[a]*Departmen of Chemistry, University of Belgrade, Studentski Trg16, 11000 Belgrade, Serbia and Montenegro,*
[b]*Departmen of Biochemistry and Molecular Biology, Mayo College of Medicine, Mayo Clinic and Foundation, Rochester, Minnesota, 55905.*
e-mail: szaric@chem.bg.ac.yu

The noncovalent interactions of π-system have been extensively studied in recent year. The cation-π interactions is considered an important non-covalent bonding force in a wide range of molecular systems. It was shown that this type of interactions can also exist when the cation is a transition metal complex. Cation-π interactions between ligands coordinated to a metal cation and aromatic groups, so-called metal ligand arometic cation-π (MLAC-π) interactions, have been found in crystal structures of metalloproteins from the Protein Data Bank[1], and in crystal structures of transition metal complexes from Cambridge Structural Database[2].

By coordination to metal atoms, the acetylacetonato ligand (acac) makes a planar chelate ring with the delocalized bonds. The acetylacetonato ligand has negative charge, but a partial positive charge is transferred from a metal cation to the ligand by coordination. Hence, the acac chelate can make CH/π interactions with phenyl ring in two ways: as the hydrogen atom donor or acceptor[3]. The extent and nature of electron delocalization in the chelate ring can influence CH/π interactions. The analyses of crystal structures show that interactions with the acetylacetonato ligand acting as H-atom donor depend on the metal in an acetylacetonato chelate ring: the chelate rings with soft metals make stronger interactions. The same trend was not observed in the interactions where the acetylacetonato chelate ring acts as the hydrogen atom acceptor.

By searching Cambrdige Structural Database (CSD), we found a large number of structures where an acetylacetonato ligand (CH and CH_3 groups) is involved in interactions with a phenyl ring as a hydrogen atom donors. We found 32 interactions with CH group and 584 interactions with CH_3 groups. In case of CH/π interactions with chelate acetylacetonato ring as H-atom acceptor, we found 41 intermolecular and 30 intramolecular interactions.

[1] S. D. Zarić, D. Popović, E. W. Knapp *Chem-Eur. J.* **6** (2000) 3935-3942.
[2] M. K. Milčić, S. D. Zarić *Eur. J. Inorg. Chem.* (2001) 2143-2150.
[3] M. K. Milčić, V. B. Medaković, D. N. Sredojević, N. O. Juranić and S. D. Zarić *Inorg. Chem* **20** (2006), in press

SPOSOBNOST ACETILACETONATO HELATA ZA CH/π INTERAKCIJA U ZAVISNOSTI OD METALA

Miloš K. Milčić[a], Vesna B. Medaković[a], Dušan N. Sredojević[a], Nenad O. Juranić[b] i Snežana d. Zarić[a]

[a]Departman za Hemiju, Univerziteta u Beogradu, Studentski Trg16, 11000 Beograd, Srbjia i Crna Gora
[b]Departmen of Biochemistry and Molecular Biology, Mayo College of Medicine, Mayo Clinic and Foundation, Rochester, Minnesota, 55905.
e-mail: szaric@chem.bg.ac.yu

Nekovalentne interakcije π-sistema su intenzivno proučavane poslednjih godina. Katjon-π interakcije se smatraju važnim nekovalentnim vezivnim silama i proučavane su u mnogim molekulskim sistemima. Pokazano je da ovaj tip interakcija može takođe postojati kada je katjon kompleks prelaznih metala. Katjon-π interakcije između liganada koordinovanih za metalni katjon i aromatičnih grupa, takozvane metal ligand aromatične katjon-π (MLAC-π) interakcije, su pronađene u kristalnim strukturama metaloproteina iz Proteinske banke podataka[1], i u kristalnim strukturama kompleksa prelaznih metala iz Kembridžske banke podataka[2].

Koordinujući se za atome metala, acetilacetonato ligand (acac) gradi planarne helatne prstenove sa delokalizovanim vezama. Acetilacetonato ligand poseduje negativno naelektrisanje, ali koordinacijom za metal parcijalno pozitivno naelektrisanje se prenosi sa metala na ligand. Prema tome, acac helati mogu graditi CH/π interakcije sa fenil grupom na dva načina: kao donori vodonikovog atoma ili kao akceptori[3]. Stepen i priroda elektronske delokalizacije u helatnom prstenu mogu da utiču na CH/π interakcije. Analiza kristalnih struktura pokazuje da interakcije sa acetilacetonato ligandima kao donorima vodonika zavisi od metala u acetilacetonato helatnom prstenu: helatni prstenovi sa mekim metalima grade jače interakcije. Isti trend nije primećen kod interakcija gde se acetilacetonato helatni prsten ponaša kao akceptor vodonikovog atoma.

Pretragom Kembridžske banke podataka (CSD), pronašli smo veliki broj struktura gde je acetilacetonato ligand (CH i CH_3 grupe) uključen u interakcije sa fenil grupom kao donor vodonikovog atoma. Pronađene su 32 interakcije sa CH-grupom i 584 sa CH_3-grupom. U slučaju CH/π interakcija sa acetilacetonato helatnim prstenom kao akceptorom H-atoma, pronašli smo 41 intermolekulsku i 30 intramolekulskih interakcija.

[1] S. D. Zarić, D. Popović, E. W. Knapp *Chem-Eur. J.* **6** (2000) 3935-3942.
[2] M. K. Milčić, S. D. Zarić *Eur. J. Inorg. Chem.* (2001) 2143-2150.
[3] M. K. Milčić, V. B. Medaković, D. N. Sredojević, N. O. Juranić and S. D. Zarić *Inorg. Chem* **20** (2006), u štampi.

IN MEMORIAM

Akademik Bela Ribar
(1930-2006)

22.marta 2006. godine iznenada je preminuo naš profesor, Dr Bela Ribar.
Dr Bela Ribar je rođen 5. septembra 1930 godine u Debeljači. Gimnaziju je završio u Zrenjaninu 1949 godine. 1955. godine je diplomirao na PMF u Beogradu na odseku za fiziku. Posle kratkog rada kao profesor fizike u gimnaziji 1958. odlazi na PMF u Sarajevo gde započinje svoju akademsku karijeru. Kao stipendista Švajcarskog nacionalnog fonda, u periodu od 1966 do 1969 godine boravi na Univerzitetu u Bernu na Odeljenju za kristalografiju, gde je maja 1969. godine odbranio doktorsku disertaciju. Od septembra 1970. godine prelazi na PMF u Novom Sadu, gde je izabran za docenta a septembra 1980. za redovnog profesora na predmetu Elektromagnetizam i Optika za studente II godine fizike.

1987. godine izabran je za dopisnog člana VANU, a 2000. za redovnog člana SANU. 2003-4. je jedan od inicijatora za reosnivanje VANU, gde je 2004. godine izabran za redovnog člana. 3.maja 2004. godine izabran je za spoljnjeg člana Mađarske akademije nauka.

Akademik profesor dr Bela Ribar objavio je oko 200 naučnih radova iz oblasti Kristalografije i rendgenske strukturne analize kristala, od kojih je većina objavljena u vodećim Međunarodnim časopisima. Dr Bela Ribar je dao značajan naučni doprinos proučavanju kristalnih struktura niza neorganskih i organskih supstanci i minerala i u tom području spada u red veoma uspešnih i produktivnih istraživača. Svojim radom je obezbedio visoku naučnu reputaciju među istraživaćima na polju Rendgenske kristalografije pre svega u našoj zemlji ali i u inostranstvu.

Široko naučno područje u kojem se citiraju radovi dr Bele Ribara dokazuju da je problematika koju je istraživao izvanredno aktuelna i pre svega interdisciplinarnog karaktera. Prema Science Citation Indexu do kraja 2001. godine rezultati njegovih istraživanja citiraju se više od 1000 puta u naučnim časopisima, knjigama, monografijama, udžbenicima, priručnicima i disertacijama, i to u širokoj lepezi različitih područja, fundamentalnih istraživanja.

Tokom 25 godina delovanja u Novom Sadu, profesor Bela Ribar je učinio veoma mnogo za razvoj strukturne kristalografije u Vojvodini. Osnivač je Laboratorije za Strukturnu analizi kristala u okviru Instituta za fiziku PMF u Novom Sadu čiji je rukovodilac bio sve do penzionisanja. Svoje znanje i iskustvo je uz ogroman entuzijazam nesebično prenosio na svoje saradnike, koji su pod njegovim neposrednim rukovodstvom odbranili magistarske i doktorske disertacije i uz njega postali i sami istaknuti istraživači.

Kao izvanredan nastavnik i pedagog pokazao je nesebično zalaganje na popularizaciji fizike i kristalografije kako u zemlji tako i u inostranstvu. Pod njegovim rukovodstvom diplomske radove je uradilo tridesetak studenata fizike.

Sa svojom istraživačkom ekipom ostvario je intenzivnu i plodnu međunarodno saradnju. Zahvaljujući naučnoj reputaciji koju je stekao u inostranstvu, na osnovu njegove preporuke više mladih naučnih radnika iz naše zemlje je dobilo švajcarske stipendije. Plodnu međunarodnu saradnju dr Bele Ribara ilustruje i činjenica da je znatan broj naučnih publikacija ostvareno sa istraživačima iz drugih zemalja.

Dr Bela Ribar je bio jedan od osnivača i aktivnih članova Jugoslovenskog centra za kristalografiju. Bio je i prvi predsednik Srpskog kristalografskog društva osnovanog 1991 godine, koje je zahvaljujući njegovoj naučnoj reputaciji 1992 godine primljeno u Evropsku kristalografsku asocijaciju a 1993 i u Internacionalnu uniju za kristalografiju.

Niz godina je bio recenzent internacionalnih časopisa Acta Crystallographica, Journal of Solid State Chemistry i član redakcionog odbora Glasnika Jugoslovenskog centra za kriatlografiju, kao i član organizacionog odbora više domačih i međunarodnih konferencija na kojima je učestvovao sa 120 referata.

Za svoje zasluge akademik prof.dr Bela Ribar je dobio niz odlikovanja i priznanja.

Njegovi saradnici iz Laboratorije za strukturnu analizu kristala, Instituta za fiziku Prirodno-matematičkog fakulteta u Novom Sadu.

IN MEMORIAM

Academic Bela Ribar
(1930-2006)

Professor Bela Ribar died suddenly on March 22th 2006 in Novi Sad, Serbia and Montenegro. He was born on September 5th 1930 in Debeljača (Yugoslavia). He graduated in 1955 at the the Department of Physics, Faculty of Sciences in Belgrade. After a short period of high school teaching, he started his academic career at the Faculty of Sciences in Sarajevo in 1958. Being a grantee of the Swiss National Fund, he spent three years at the Crystallography Department of the Bern University, where he obtained his Ph.D. degree in 1969. He joined the Faculty of Sciences in Novi Sad (1970), where he shall become the full professor in 1980 and teach until his retirement. In 1987 he became the member of the Academy of Sciences and Arts of Vojvodina (VANU), in 2000 the permanent member of the Serbian Academy of Sciences and Arts (SANU). In May 2004, he became also the foreign member of the Hungarian Academy of Sciences (MTA).

Professor dr Bela Ribar published over 200 papers in the field of Crystallography and X-ray diffraction crystal structure analysis, most of them in the leading international journals. Dr Bela Ribar made a significant scientific contributions by studying the crystal structure of a series of inorganic and organic substances and minerals.The broad scientific field where the results of Prof. Ribar are cited, proves that his scope of problems was always actual and dominantly of interdisciplinary character. According to Science Citation Index his results were cited over 1000 times in various scientific publications of different branches of fundamental research.

During 25 years of activity in Novi Sad, professor Bela Ribar has done a lot for the development of the structural crystallography in the region of Vojvodina. He was the founder and the Head of the Laboratory for the Crystal Structure Analysis within the Institute of Physics of the Faculty of Sciences. He shared his knowledge and experience with great enthusiasm with his colaborators, who prepared their M.Sc.and Ph.D.Theses under his supervision and became prominent researchers themselves.He and his research team realized an intensive and fruitful international cooperation.

Dr Bela Ribar was one of the founders and active members of the Yugoslav Center for Crystallography. He was also the first president of the Serbian Crystallographic Society founded in 1991.He served for many years as the referee of the international journals Acta Crystallographica, Journal of Solid State Chemistry and the member of the Editorial Board of the publication of the Yugoslav Center for Crystallography.