PLENARY LECTURES
ПЛЕНАРНА ПРЕДАВАЊА

Chirality in Crystals and Molecules

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The objective of the presentation is to provide a succint and stimulating introduction for use in teaching and research to problems of chirality and achirality in crystals and the molecules composing them. As an example of a chiral crystal, the morphology of quartz provides a useful starting point especially in relation to the achiral building units in this compound. It is then useful to study both the classical and modern definitons of (stereochemical) chirality and the impact of this on the symmetry of chiral and achiral crystals and molecules. We then proceed to an analysis of how chiral, both enantiopure and racemic, and achiral molecules may or may not form chiral and achiral crystal structures. This shows two important results: (a) that there are no known achiral crystal structures formed of enantiopure (chiral) molecules and (b) that, perhaps surprisingly but rarely, racemates do form chiral crystal structures. Observation (a) is then analysed from a mathematical standpoint using 'La Coupe du Roi' to find that the underlying cause of (a) is physical and chemical.

The second part of the presentation deals with X-ray diffraction from crystals and the way that the 'absolute structure' of the crystal and the 'absolute configuration' of the molecules may be determined. A most important physical phenomenon to understand is that of twinning by inversion. This is illustrated by the examples of quartz and hexahelicene. This leads to a study of the relation between chirality and non-centrosymmetricity in crystals, and the definition of the three classes of crystal structure: CA centrosymmetric achiral, NC non-centrosymmetric chiral and NA non-centrosymmetric achiral. The physical meaning of these three classes will be stressed hopefully clarify some or all of the common misconceptions for the NA class. After a short presentation of Neumann's principle and diffraction by non-centrosymmetric crystals, the modelling of the latter is dealt with in detail leading to the Flack parameter which quantifies the absolute-structure determination. Following an examination of the conditions on the Flack parameter which allow determination of the absolute structure, and a detailed comparison of the definitions of absolute structure and absolute configuration, we may see the further restrictions which apply for the determination of absolute configuration. We terminate this part with some comments on Friedel's law and its inappropriate use in the teaching of X-ray diffraction by crystals.

The final section, time permitting, deals with the characterization of bulk and crystal by such techniques as optical rotation, circular dichroism, enantioselective chromatography and differential scanning calorimetry. Practical advice on the best practices in experimentation and reporting cover such topics as the use of right-handed axes, intensity data region, use of SHELXL, prior estimates of the standard uncertainty of the Flack parameter, ways to decrease it, partial polar ambiguities, and use of checkCIF/PLATON.

A handout of the most important slides used in the presentation is available on the author's website. The URL and password to access this file will be displayed during the presentation.

CRYSTALLOGRAPHY ON A NANOSCALE, THE NANOSTRUCTURE PROBLEM, AND SOME FIRST STEPS TO SOLVE IT

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A diverse array of complex materials and structures are driving the nanotechnology and molecular biology revolutions. To understand and design these materials, it is essential to perform high precision structural characterization at the nanoscale. Often, even sub Angstrom changes in inter-atomic bond lengths have profound consequences for the chemistry and functionality of these structure-sensitive materials. Crystallographic methods are the gold standard for atomic structure determination, however a broad and growing class of materials and/or nanophase morphologies do not yield to a crystallographic analysis. The scattering is diffuse and Bragg-peaks become broad and overlapped (see Figure for an example). This is "the nanostructure problem" which currently has no robust solution. Diffuse scattering contains much less information, while on the other hand number of degrees of freedom needed to determine the structure model is increasing (in principle it is of the order of the number of atoms in the nanostructure). Recently, the atomic pair distribution function (PDF) analysis based on powder diffraction experiments has been extended to study nanostructured materials. Presentation will give an overview of selected successes on that front both in bulk materials containing nanoinhomogeneities, and in nanostructured materials [1]. Alternative, more broadly applicable, methods which are emerging for these nanostructure problems [2] will be discussed. The complete solution will likely lie in a synthesis of different scattering, imaging and spectroscopic approaches bound up in a coherent computational framework.

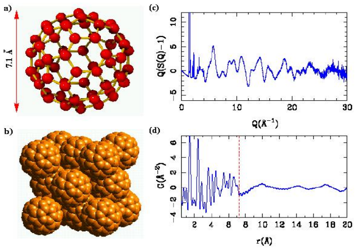

Figure: C_{60} molecule (a) within FCC structure (b), neutron diffraction pattern (c), and corresponding PDF (d). Vertical dashed line at 7.1Å denotes diameter of the C_{60} molecule. Due to the spinning of the molecules in the structure, at higher distances in the PDF only correlations between the molecular centers appear.

[1] E. S. Božin *et al.*, Phys. Rev. Lett., 98 (2007) 137203; H. J. Kim *et al.*, Phys. Rev. B, 75 (2007) 134103; A. Sartbaeva *et al.*, Phys. Rev. Lett., 97 (2006) 065501.
[2] P. Juhas *et al.*, Nature, 440 (2006) 655-658

КРИСТАЛОГРАФИЈА НА НАНОСКАЛИ, НАНОСТРУКТУРНИ ПРОБЛЕМ И ПРВИ КОРАЦИ У ЊЕГОВОМ РЕШАВАЊУ

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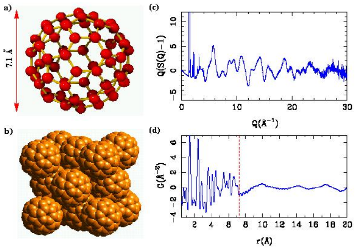
Разнолики низ комплексних материјала и структура покреће револуције у нанотехнологији и молекуларној биологији. Да би се ови материјали боље разумели и дизајнирали, неопходно је извршити високо прецизну структурну карактеризацију на наноскали. Често чак и суб-ангстремске промене међуатомских растојања имају далекосежне последице на хемију и функционалност тих структурно осетљивих материјала. Кристалографски методи су златни стандард у одређивању атомске структуре, међутим широка и растућа класа материјала и/или нанофазних морфологија не подлеже кристалографској анализи. Расејање је дифузно и Брагови пикови постају широки и узајамно се преклапају (видети пример на слици). Ово је “наноструктурни проблем” који је тежак и у овом тренутку нема јасно утврђено решење. Дифузно расејање садржи много мање информација, док се с друге стране број степени слободе потребних да би се одредио модел повећава (у принципу је пропорционалан броју атома који чине наноструктуру). У последње време анализа дистрибуционе функције атомских парова (ПДФ) из експеримената дифракције на праху проширена је на истраживања наноструктурних материјала. Презентација ће дати преглед одабраних успеха на том фронту како у балк материјалима са нано-нехомогеностима, тако и у истраживању наноструктура [1]. Биће говора о шире примењивим алтернативним методима [2] који се појављују као кандидати за решавање поменутог наносруктурног проблема. Потпуно решење ће вероватно бити у комбинованој примени дифракционих, имиџинг, и спектроскопских приступа повезаних у кохерентно компјутерско окружење.



Слика: C_{60} молекул (a) у FCC структури (b), неутронски дифрактограм (c), и одговарајућа ПДФ (d). Вертиклна испрекидана линија на 7.1Å означава дијаметар C_{60} молекула. Због ротација молекула на већим растојањима у ПДФ опстају само корелације између молекулских центара.

[1] E. S. Božin *et al.*, Phys. Rev. Lett., 98 (2007) 137203; H. J. Kim *et al.*, Phys. Rev. B, 75 (2007) 134103; A. Sartbaeva *et al.*, Phys. Rev. Lett., 97 (2006) 065501.
[2] P. Juhas *et al.*, Nature, 440 (2006) 655-658

Crystal *versus* Solution Protein Structures: Solvent-induced Differentiation of Protein-backbone H-bonds

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Protein backbone H-bonds, that are identified from geometrical criteria in crystal structures of proteins, form two broad groups defined by to the spin-spin couplings ($^{h3}J_{NC'}$) measured across H-bonds in solutions by NMR spectroscopy. The H-bonds detected in solution by the $^{h3}J_{NC'}$ couplings show correlation among the H-bond geometrical parameters in solid proteins, and appear supported by the protein dynamics in solution. The H-bonds not directly detected in solution by the $^{h3}J_{NC'}$ couplings populate a more flexible and water-exposed regions of the protein secondary structure.

In a variety of small globular proteins about 80% of the H-bonds identified from application of geometrical criteria in the helices and sheets of the corresponding crystal structures have also been detected in solution via $^{h3}J_{NC'}$ couplings [1-5]. However, both NMR and IR spectroscopic studies have indicated the formation of solvent (water) H-bonds to the protein backbone [6,7] that may weaken intra-protein H-bond networks [8,9]. Theoretical calculations predict significant impact of protein solvation on the H-bond networks at protein backbone [10]. Increased dynamics of the protein backbone in solution [11,12] may also challenge sustenance of H-bonds that appear in the proteins' crystal structure. A recent interpretation of the residual dipolar couplings (RDC) in streptococcal protein-G invoke the possibility that correlated motions affect secondary-structure determined H-bond networks[13]; structural flexibility may occur without much disruption of H-bonds. Such correlated motions are suggested to be rather slow, in the millisecond time regime, and may also be associated with a protein's function [13].

If such correlated dynamics exist, the forces that govern them may influence the conformational state of the protein backbone in crystal structures. We therefore analyzed the crystal structures of six proteins whose H-bond $^{h3}J_{NC'}$ couplings in solution have been reported (crambin, ubiquitin, parvalbumin and intestinal fatty acid binding protein) or are reported here (*apo* and *holo*CaM). Backbone H-bonds seen in the crystal structures of these proteins may be divided into two subsets according to the magnitude of the $^{h3}J_{NC'}$ couplings measured for the proteins in solution. The subset with $| ^{h3}J_{NC'} | > 0.2$ Hz shows correlations among the H-bond geometry parameters, while the other subset with $|^{h3}J_{NC'} | < 0.1$ Hz (or $^{h3}J_{NC'}$ not detected) shows no such correlation (Figure 1). The main feature of the subset with $| ^{h3}J_{NC'} | > 0.2$ Hz (high-*J* subset in further text) is an angle/distance correlation of the H-bond parameters. Accordingly, at shorter H-bond distances the deviation from the linearity at both donor (>N-H) and acceptor (O=C<) gets smaller (Figure 1, top). Such correlation is consistent with the H-bond dipole-dipole attractive force (preference for short, linear H-bonds). It is also consistent with dynamical expansion-contraction of the H-bond network (less orientational pull at the larger distances). The angles at the acceptor end are proportionally larger by ~ 30% in comparison to the donor angles, which agrees with there being a smaller orientation force of a weaker donor-dipole (>N-H).

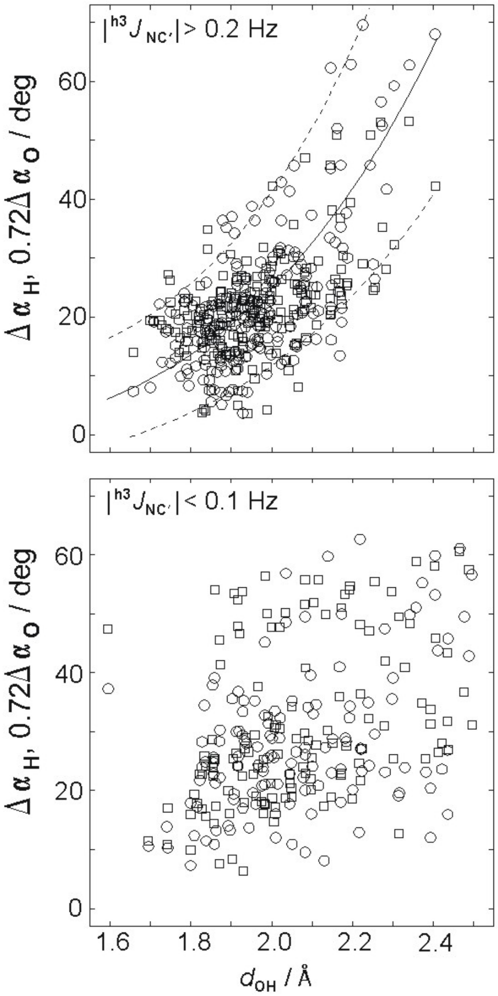

Figure 1. Angle-distance correlation of H-bonds from seven proteins (crambin, ubiquitin, protein G, parvalbumin, IFABP and *apo*- and *holo*- calmodulin) divided into two subsets according to the magnitude of the H-bond couplings ($|^{h3}J_{NC'}| > 0.2$ Hz, top; $|^{h3}J_{NC'}| < 0.1$ Hz, bottom). Distance correlation for the donor angle, $\Delta\alpha_H$ (○), is matched with correlation for the acceptor angle, $\Delta\alpha_O$ (□), upon scaling the latter by 0.75. The full curved line represents the fifth-power distance dependence ($0.8 \cdot d_{OH}^5$), while dashed lines indicate ~90% containment boundaries. The peptide groups involved in the coordination to Ca^{2+} where excluded from the analysis.

The other, low-*J* subset, has many H-bonds with geometries that should give intense $^{h3}J_{NC'}$ couplings but the couplings are undetected in solution presumably due to unfavorable dynamics of the H-bonds. Evidently, if mobility is the only culprit, then the low-*J* subset of H-bonds do not persist in solution on the time scale of the $^{h3}J_{NC'}$ couplings measurements (~ 100 ms). It is unlikely that dynamical rupture of the H-bonds [14] can exist on the time scale needed for disappearance of the *J*-couplings, unless some other H-bonds are formed. A likely mechanism is one that involves bifurcated H-bonds of amide carbonyls with water [6-8,15]. Under dynamical conditions the bifurcated H-bonds can fluctuate in the H-bond donor partner between water and amide proton with little structural stress to the alpha helix [8].

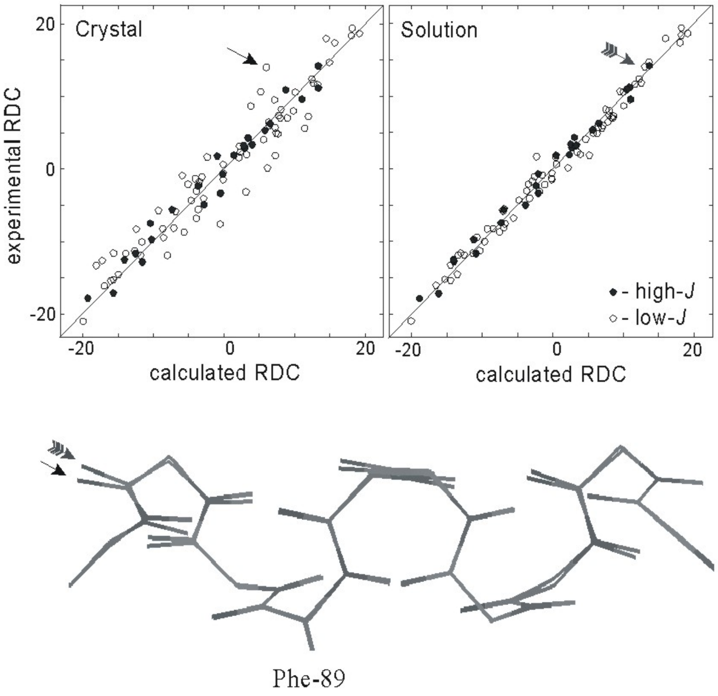

Figure 2. Experimental RDCs of peptide-groups ($\Delta^1 J_{HN}$, $\Delta^1 J_{NC}/0.12$ and $\Delta^1 J_{CCa}/0.20$) in alpha-helices of *holo*CaM C-terminus, in comparison with the calculated values for the corresponding crystal and solution structures. The crystal structure is represented by x-ray high-resolution structure 1exr –model-A [16], while solution structure is modeled from the x-ray structure to satisfy RDCs. The high-*J* and low-*J* data refer to the size of proton donating H-bonds of the peptide groups. Lower insert shows the x-ray and the modeled solution structure of the helix E. Small arrows indicate connection between peptide group orientations and RDC fit for peptide-group in position 91/92. The hydrophobic anchoring residue is indicated.

The proposed dynamics of the low-*J* subset of H-bonds, which involve bifurcated H-bonds to water, should change the average orientation of the respective peptide groups. Such a hypothesis can be tested by analysis of RDCs of the peptide groups in solution. We tested this on *holo*CaM, for which both the high resolution x-ray structure[16] and solution RDCs[17] have been reported. As presented in Figure 2, the solution RDCs of peptide groups can be fitted well to the crystal structure for the high-*J* subset, while major deviations occur for the low-*J* subset. To assess peptide-group orientations in solution, we have allowed changes of their orientations seen in the crystal structure until the solution RDCs were fitted. Notable changes in orientations occurred only for the peptide groups of the low-*J* subset. The majority of these peptide groups adopted orientations consistent with the higher exposure of carbonyl oxygen to water. The flexibility, or conformational mobility, addressed by the *J*-profile of H-bonds should be useful for understanding dynamical heterogeneity within the regular secondary structure motiffs of proteins. In conjunction with data on the angular distribution of peptide groups orientations it furthers our understanding of the correlated dynamics within H-bond networks of proteins

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ORAL PRESENTATIONS
САОПШТЕЊА

STRUCTURAL AND MICROSTRUCTURAL CHARACTERIZATION OF NANO-SIZED $ZnY_{0.15}Fe_{1.85}O_4$

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In this work, $ZnY_{0.15}Fe_{1.85}O_4$ was sinthesized using sol-gel method, and it was thermally treathed at 500 ºC for one hour. X-Ray Powder Diffraction patterns for the initial and thermally treathed samples were collected. The structures were refined using software package FullProf. Space group $Fd\bar{3}m$ was selected for the refinement [1]. The refinement of thermally treated sample was perfomed to the good agreement (R_B=2.82%, R_F=2.32, χ^2=1.23) Microstructural analysis confirmed that the samples contained nano – sized (6.7(5) nm) particles (Fig. 1) and that maximum microstrain was $23(2)\cdot10^{-4}$ (Fig. 2).

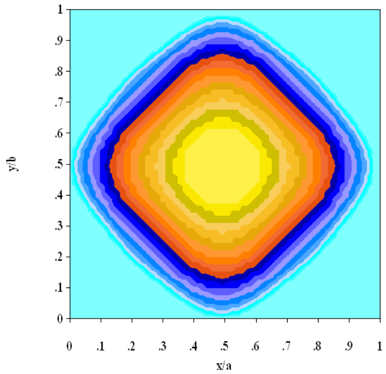

Figure 1. Projection in ab plane of three dimensional body that represents apparent size.

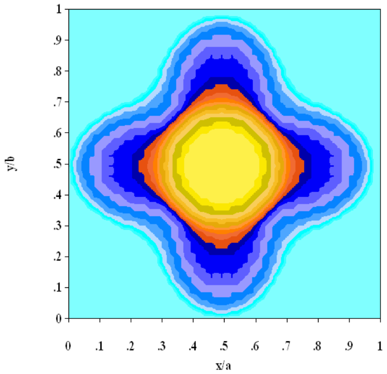

Figure 2. Projection in ab plane of three dimensional body that represents apparent strain.

[1] Ž. Cvejić, S. Rakić, A. Kremenović, B. Antić, Č. Jovalekić, Ph. Collomban, Solid State Sciences 8 (2006) str. 908–915.

STRUKTURNA I MIKROSTRUKTURNA KARAKTERIZACIJA NANOČESTIČNOG $ZnY_{0.15}Fe_{1.85}O_4$

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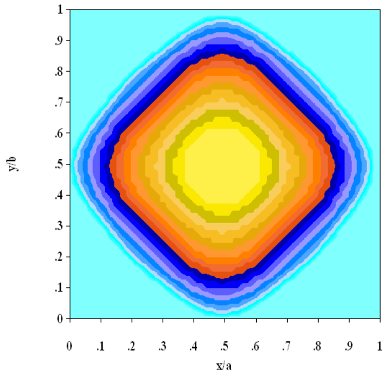
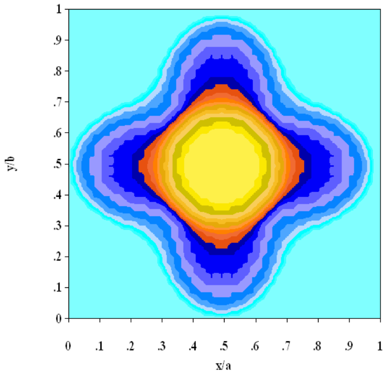
U ovom radu, $ZnY_{0.15}Fe_{1.85}O_4$ je sintetisan sol-gel metodom i žaren je na temperaturi od 500 ºC u trajanju od jednog časa. Polazni i temperaturski tretiran uzorak snimljeni su na rendgenskom difraktometru za prah, a zatim je struktura utačnjavana Ritveldovom metodom korišćenjem programskog paketa FullProf. Struktura je utačnjavana u prostornoj grupi $Fd\bar{3}m$ [1]. Parametri pouzdanosti za utačnjavanje strukture žarenog uzorka su pokazali da je utačnavanje dobro urađeno (R_B=2.82%, R_F=2.32, χ^2=1.23) Mikrostrukturnom analizom je potvrdjeno da su čestice dimenzija 6.7(5) nm (Slika 1) kao i da je veličina mikronaprezanja $23(2)\cdot10^{-4}$ (Slika 2).



Slika 1. Projekcija u ab ravni trodimenzionog tela koje predstavlja veličinu kristalita



Slika 2. Projekcija u ab ravni trodimenzionog tela koje predstavlja mikronaprezanje kristalita

[1] Ž. Cvejić, S. Rakić, A. Kremenović, B. Antić, Č. Jovalekić, Ph. Collomban, Solid State Sciences 8 (2006) str. 908–915.

STACKING VS. CH/π INTERACTIONS BETWEEN CHELATE AND ARIL RINGS IN CRYSTAL STRUCTURES OF SQUARE-PLANAR TRANSITION METAL COMPLEXES

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The crystal structures of square-planar transition-metal complexes from Cambridge Structural Databank (CSD) with close contacts between planar chelate rings and aril rings containing six carbon atoms (C_6-aril) were analyzed. Most of the chelate rings in these structures are fused with aromatic or other π-delocalized chelate rings. The results show that planar chelate rings can be involved in stacking and CH/π interactions with organic aril rings, however, the number of stacking interactions is a few times larger than number of CH/π interactions. The analysis also shows that almost in all cases CH/π interactions are formed only when stacking interactions are prevented by voluminous substituents. Hence, between planar chelate rings and C_6-aril rings stacking interactions are preferred to CH/π interactions.

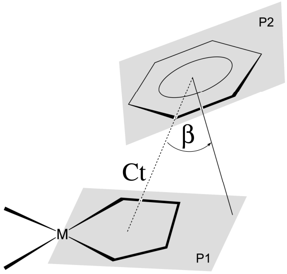

Figure 1. Geometrical parameters describing the interaction of chelate ring of square-planar complexes with the C_6-aril ring.

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STEKING NASUPROT CH/π INTERAKCIJAMA U KRISTALNIM STRUKTURAMA KVADRATNO-PLANARNIH KOMPLEKSA PRELAZNIH METALA

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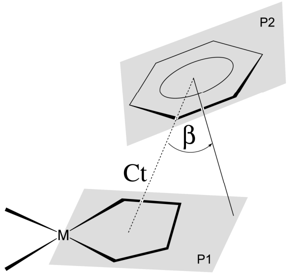
Analizirane su kristalne strukture kvadratno-planarnih kompleksa prelaznih metala iz Kembričke kristalografske banke podataka (CSD) u kojima postoji bliski kontakt između planarnih helatnih prstenova i aril prstenova koji sadrže šest atoma ugljenika (C_6 – aril). Najveći broj helatnih prstenova u ovim strukturama je kondenzovan sa aromatičnim ili drugim π-delokalizovanim helatnim prstenovima. Rezultati ukazuju na to da planarni helatni prstenovi mogu biti uključeni u steking i u CH/π interakcije sa organskim aril prstenovima, međutim, broj steking interakcija je nekoliko puta veći od broja CH/π interakcija. Analize takođe pokazuju da se, gotovo u svim slučajevima, CH/π interakcije formiraju jedino kada je blokirano formiranje steking interakcija voluminoznim supstituentima na helatnom prstenu. Prema tome, steking interakcije između planarnih helatnih prstenova i C_6 – aril prstenova su dominantne u odnosu na CH/π interakcije.



Slika 1. Geometrijski parametri koji opisuju interakcije helanog prstena kvadratno-planarnih kompleksa sa C_6 – aril prstenovima.

[1] D. N. Sredojević, G. A. Bogdanović, Z. D. Tomić, S. D. Zarić, CrystEngComm, (2007), u štampi
[2] Z. D. Tomić, D. Sredojević, S. D. Zarić Cryst. Growth and Design, 6 (2006), 29-31.
[3] D. N. Sredojević, Z. D. Tomić, S. D. Zarić Cent. Eur. J. Chem., 5 (2007), 1-11.
[4] Z. D.Tomić, S. B. Novakovic, S. D. Zarić, Eur. J. Inorg. Chem., (2004), 2215-2218.

DETERMINATION OF MINERALOGICAL COMPONENTS IN COAL AND FLY ASH BY XRPD ANALYSIS

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Samples of coal from Kolubara basin and fly ash, from Thermal Power Plant „Nikola Tesla" - Obrenovac, were investigated by XRPD analysis. Obtained results indicated the presence of quartz and clay minerals: kaolinite and montmorillonite, in coal samples, while in fly ash samples the present crystalline phases were: quartz, mullite, hematite, feldspar and anhydrite. This work has been done under the participation project "Petrographic, geochemical and physicochemical characteristics of Kolubara basin coal" and investigation of the influence of Thermal Power Plant waste waters on the surrounding surface and ground waters [1]. Nearly 8 million tones of fly ash are disposed annually in Serbia [2]. The problem with fly ash lies in the fact that its disposal requires large area of land and considerable consumption of water, and if not managed well, can cause serious environmental problems. Utilization of fly ash as a secondary raw material has been studied for decades in many areas, such as, cement, glass and ceramic industries as well mining and construction [3-4]. The main purpose of this study was to obtain detail characterization of Kolubara basin coal and fly ash produced through its combustion, which would help gain its better utilization.

[1] A. Dangić, B. Simonović, Petrografske, geohemijske i fizičko-hemijske karakteristike uglja Kolubarskog ugljenog basena.
[2] http://www.eps.co.yu/ekologija/zastita.htm
[3] T. Okuda, Y. Isihara, Y. Aoyagi, Manufacturing a New Type of Compound Cement Using Limestone and Coal Ash as Main Raw Material, Review of 42nd general meeting. Technical session. Tokyo, Cement Association of Japan, (1988), 46-49
[4] P. Kumar, N. Mal, Y. Oumi, K. Yamana, T. Sano, Mesoporous materials prepared using coal fly ash as the silicon and aluminium source, J. Mater. Chem, 11 (2001), 3285- 3290.

ODREĐIVANJE MINERALNIH PRIMESA U UGLJU I PEPELU METODOM RENDGENSKE DIFRAKTOMETRIJE PRAHA

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Tri uzorka uglja, sa bušotina različitih dubina površinskog kopa Kolubara, i šest uzoraka pepela, sa dva bloka Termolelektrane "Nikola Tesla", ispitivana su metodom rendgenske difraktometrije praha. Iz evidentiranih kristalnih faza, u uzorcima uglja identifikovano je prisustvo faza kvarca i minerala gline: kaolinita i montmorionita, dok je u uzorcima pepela utvrđeno prisustvo kristalnih faza kvarca, anhidrita, feldspata, mulita i hematita.

Rad je urađen u okviru studije „ Petrografske, geohemijske i fizičkohemijske karakteristike uglja Kolubarskog ugljenog basena" [1] i programa ispitivanja uticaja otpadnih voda Termolelektrane "Nikola Tesla" na površinske i podzemne vode u okruženju. U Srbiji se godišnje deponuje 7-8 miliona tona pepela iz termoelektrana, koji ne samo da opterećuje prostor oko njih, vec pod uticajem atmosfere (vetra i kiše) zagađuje životnu sredinu, kao leteći pepeo ili zagađuje površinske i podzemne vodotokove [2]. U svetu se sve više istražuju načini da se pepeo koristi kao sekundarna sirovina i upotrebi u građevinarstvu u industriji cementa ili u sintezi silikatnih materijala [3-4]. Cilj ovog istraživanja je da se izvrši potpuna karakterizacija uglja iz Kolubarskog basena i pepela dobijenog njegovim sagorevanjem, što bi pomoglo njihovom boljem korišcenju.

[1] A. Dangić, B. Simonović, Petrografske, geohemijske i fizičko-hemijske karakteristike uglja Kolubarskog ugljenog basena.
[2] http://www.eps.co.yu/ekologija/zastita.htm
[3] T. Okuda, Y. Isihara, Y. Aoyagi, Manufacturing a New Type of Compound Cement Using Limestone and Coal Ash as Main Raw Material, Review of 42nd general meeting. Technical session. Tokyo, Cement Association of Japan, (1988), 46-49
[4] P. Kumar, N. Mal, Y. Oumi, K. Yamana, T. Sano, Mesoporous materials prepared using coal fly ash as the silicon and aluminium source, J. Mater. Chem, 11 (2001), 3285- 3290.

VESZELYITE FROM THE LOCALITY ZDRAVO VRELO NEAR KREŠEVO (BOSNIA AND HERZEGOVINA): ITS MINERALOGICAL CHARACTERIZATION AND ABSOLUTE CRYSTAL STRUCTURE

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Veszelyite from the locality Zdravo Vrelo, near Kreševo (Bosnia and Herzegovina) appears as isometric blue to dark green crystals of 1-2 mm diameter. The mineral generally occurs in baryte veins, where it is associated with tetrahedrite, pyrite, coveline, malachite and other minerals. This paragenesis belongs to low-temperature hydrothermal activities in which veszelyite was formed in the oxidation zone [1].

The chemical composition of veszelyite was determined by electron microprobe analysis as $(Cu_{1.76}Zn_{0.24})_2Zn(PO_4)(OH)_3{\cdot}2(H_2O)$. Thermogravimetric and differential thermal analyses (TG/DTA) were performed also to clarify the water content of veszelyite.

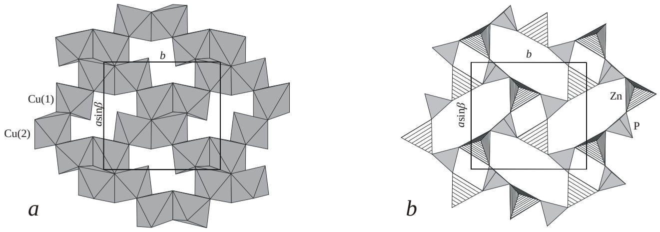

Figure 1. *a*) octahedral and *b*) tetrahedral sheets in the structure of veszelyite.

The investigated veszelyite crystal is monoclinic, space group $P2_1/a$ (14), $Z = 4$, $a = 9.814(1)$ Å, $b = 10.222(1)$ Å, $c = 7.5006(9)$ Å and $\beta = 103.210(9)$ º. These data are in good agreement with previous investigations [2]. The crystal structure was solved by direct methods and refined by least-squares techniques to residuals of $R_1 = 0.051$ (calculated for the 1932 unique observed reflections ($I > 2\sigma I$)), and $wR_2 = 0.083$ for all data collected at ambient temperature with a two-circle Stoe IPDS-II diffractometer. Both Cu(1) and Cu(2) atoms have a tetragonally distorted octahedral coordination. The octahedra form 8-membered rings by sharing common edges (Fig. 1*a*). The $ZnO_3(OH)$ and PO_4 groups are nearly regular tetrahedra with average Zn–O and P–O distances of 1.943 and 1.539 Å, respectively. They are also forming 8-membered rings (Fig. 1*b*). The octahedral and tetrahedral rings are linked into sheets which regularly alternate along the *c* axes. Hydrogen positions in the structure were determined from a second data set collected at –100 ºC.

[1] Janjić, S., Đorđević, D., Jovanović, R., Bugarski, P., *Geol. Glas.*, **17** (1973), 181-192.
[2] Ghose, S., Leo, S. R., and Wan, C., *Am. Mineral*., **59**, (1974), 573-581.

ВЕСЕЛИТ ИЗ ЛОКАЛНОСТИ ЗДРАВО ВРЕЛО ПОРЕД КРЕШЕВА (БОСНА И ХЕРЦЕГОВИНА): МИНЕРАЛОШКА КАРАКТЕРИЗАЦИЈА И АПСОЛУТНА КРИСТАЛНА СТРУКТУРА

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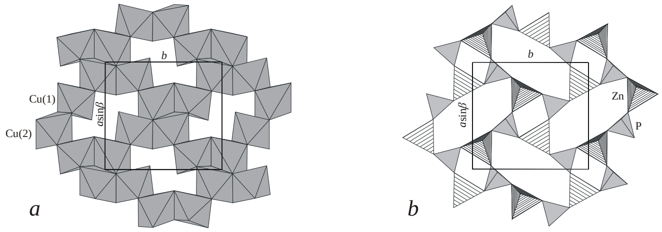
Веселит из локалности Здраво Врело покрај Крешева (Босна и Херцеговина) појављује се у плавим до тамно зеленим кристалима пречника 1-2 mm. Минерал се обично јавља у баритским жицама где је асоциран са тетраедритом, пиритом, ковелином, малахитом и другим минералима. Парагенеза припада нискотемпературним активностима у којима је веселит формиран у оксидационој зони [1].

Хемијски састав веселита одређен је електронском микросондом као $(Cu_{1.76}Zn_{0.24})_2Zn(PO_4)(OH)_3\cdot2(H_2O)$. Садржај воде у веселиту утврђен је термогравиметријским и диференцијално-термичким (TG/DTA) испитивањима.



Слика 1. *а*) октаедарски и *б*) тетраедарски слој у структури веселита.

Испитивани кристал веселита је моноклиничан, просторна група $P2_1/a$ (14), $Z = 4$, $a = 9{,}814(1)$ Å, $b = 10{,}222(1)$ Å, $c = 7{,}5006(9)$ Å и $\beta = 103{,}210(9)$ °. Ови подаци су у добром слагању са претходним испитивањима [2]. Кристална структура је решена директним методама и утачњена до фактора слагања $R_1 = 0{,}051$ (за 1932 симетријски независне рефлексије ($I > 2\sigma I$)), и $wR_2 = 0{,}083$ за све податке прикупљене на двокружном дифрактометру Stoe IPDS-II на собној температури. Координациони полиедри атома Cu(1) и Cu(2) су у облику тетрагонално деформисаних октаедара. Октаедри граде осмочлане прстенове преко заједничких ивица (Сл. 1*а*). Групе $ZnO_3(OH)$ и PO_4 су готово правилни тетраедри средњих растојања Zn–O и P–O од 1,943 и 1,539 Å. Они исто тако граде осмочлане прстенове (Сл. 1*б*). Октаедарски и тетраедарски прстенови повезани су у слојеве који се правилно смењују дуж *c*-осе. Положаји водоника у структури одређени су из другог сета података прикупљеног на –100 ºC.

[1] Janjić, S., Đorđević, D., Jovanović, R., Bugarski, P., *Geol. Glas.*, **17** (1973), 181-192.
[2] Ghose, S., Leo, S. R., and Wan, C., *Am. Mineral*., **59**, (1974), 573-581.

Microstructural parameters of nanosized $Zn_{0.1}Ni_{0.9}O$ annealed at different temperatures

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A mixture of crystalline ZnO and NiO powders was used as starting material to produce $Zn_{0.1}Ni_{0.9}O$. Mechanochemical treatment was performed in a planetary ball mill for 20 hours. As-prepared sample was annealed at temperatures 500°C for three and twenty four hours, 700°C for three hours and 950°C for three hours. X-ray powder diffraction data were collected in transmission mode on a Stoe STADI MP automated X-ray powder diffractometer using Cu$K\alpha_1$ radiation, Ge monochromator and linear PSD counter.

The collected XRPD data were refined by the Rietveld method [1]. The X-ray line broadening analysis was used to follow crystallite size and microstrain changes with annealing. The X-ray line broadening was analyzed through the refinement of regular TCH-pV function parameters (isotropic effects) or through the refinement of symmetrized cubic harmonics (anisotropic size effects) and coefficients of Stephens form for anisotropic strain broadenning [2, 3]. The method used for sample preparation is a well established technique to produce nanomaterials with usually anisotropic microstrain. Therefore, we assumed that X-ray line broadening anisotropy is influenced by both size and strain effects. However, the deviations from calculated average maximum strains are small indicating negligible anisotropy of X-ray line broadening provoked by the strain effect. The refined average apparent crystallite size and maximum strain are in the ranges 15 – 60 nm and $4.5 \cdot 10^{-3}$ – $2.5 \cdot 10^{-3}$, respectively.

[1] H. M. Rietveld, J. Appl.Cryst., 2 (1969), 65.
[2] V. Honkimäki, P. Surotti, Effects of instrument function, crystallite size and strain on reflection profiles in: Snyder R. L.; Fiala J.; Bunge H. J. (Eds) Defect and Microstructure Analysis by Diffraction; IUCr book series; Oxford University Press Inc.: New York (1999).
[3] P. W. Stephens, J. Appl. Cryst., 32 (1999), 281.

Mikrostrukturni parametri nanočestičnog $Zn_{0,1}Ni_{0,9}O$ odgrejanog na različitim temperaturama

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Uzorak $Zn_{0.1}Ni_{0.9}O$ dobijen je mehanohemijskim postupkom. Mešavina ZnO i NiO u molskom odnosu 1:9 mlevena je u planetarnom mlinu u trajanju od 20 h. Dobijeni uzorak je grejan u tajanju od tri časa na temperaturama: 500°C, 700°C i 950°C. Na temperaturi od 500°C odgrevanje je izvršeno i u trajanju od dvadeset četiri časa. Difraktogrami praha su snimljeni neposredno po sintezi i nakon odgrevanja. Snimanje je izvršeno u transmisionoj geometriji na uređaju Stoe STADI MP koristeći Cu$K\alpha1$ zračenje, Ge monohromator i PSD brojač.

Podaci su korišteni za utačnjavanje strukturnih parametara Rietveld–ovom metodom [1] pomoću programa Fullprof. U cilju praćenja veličine kristalita i mikronaprezanja u zavisnosti od temperature odgrevanja analizirano je širenja difrakcionih linija. Rezultati su dobijeni utačnjavanjem parametara TCH-pV funkcije (izotropni slučaj) ili utačnjavanjem kubnih harmonika (anizotropna veličina) i koeficijenata Stephens-ovog izraza za opisivanje anizotropnog mikronaprezanja [2, 3]. Poznato je da se mehanohemijskim postupkom dobijaju nanomaterijali kod kojih je mikronaprezanje najčešće anizotropno. Stoga je pretpostavljeno da je širenje difrakcionih linja posledica kako anizotropne veličine tako i anizotropnog mikronaprezanja. Međutim, ustanovljeno je da je anizotropija mikronaprezanja zanemarljivo mala. Utačnjene srednje vrednosti dimenzije kristalita i mikronaprezanja nalaze se u intervalima 15 – 60 nm, odnosno $4{,}5\cdot10^{-3} – 2{,}5\cdot10^{-3}$.

[1] H. M. Rietveld, J. Appl.Cryst., 2 (1969), 65.
[2] V. Honkimäki, P. Surotti, Effects of instrument function, crystallite size and strain on reflection profiles in: Snyder R. L.; Fiala J.; Bunge H. J. (Eds) Defect and Microstructure Analysis by Diffraction; IUCr book series; Oxford University Press Inc.: New York (1999).
[3] P. W. Stephens, J. Appl. Cryst., 32 (1999), 281.

Effect of yttrium doping on the structure of $Ca_{1-x}Y_xMnO_3$ ($0 \leq x \leq 1$)

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The doped manganites with general formula $Ca_{1-x}A_xMnO_3$, in which the A is a trivalent rare earth ion exhibit colossal magnetoresistance phenomena and acceptable levels of electrical conductivity for cathode materials used for solid oxide fuel cells operation [1].

In order to estimate the theoretical stability of the perovskite structure, Goldschmidt tolerance factors, (G_t) and global instability indices, (*GII*) were calculated for $Ca_{1-x}Y_xMnO_3$ (x = 0, 0.25, 0.5, 0.75, 1) using the software SPuDS (Structure Prediction Diagnostic Software) [2]. According to these two parameters the formation of perovskites was investigated for the solid solution series $Ca_{1-x}Y_xMnO_3$ ($0 \leq x \leq 1$). In order to confirm these results, nanopowders with the following nominal compositions were synthesized using a modified glycine-nitrate procedure [3]: $CaMnO_3$, $Ca_{0.95}Y_{0.05}MnO_3$, $Ca_{0.85}Y_{0.15}MnO_3$, $Ca_{0.75}Y_{0.25}MnO_3$, $Ca_{0.5}Y_{0.5}MnO_3$, $Ca_{0.25}Y_{0.75}MnO_3$ and $YMnO_3$. After calcination at 800 ºC for 2 hours, the samples were characterized by X-ray powder diffraction. Rietveld refinements of the X-ray diffraction patterns were carried out using the program FullProf [4].

Except $YMnO_3$, all phases are orthorhombic (space group *Pnma*) adopting the perovskite structure type. Hexagonal $YMnO_3$ (space group $P6_3cm$), on the other hand, is isomorphous with $LuMnO_3$ at atmospheric pressures [5].

The influence of the different amounts of Y on the unit cell parameters, the unit cell volume as well as the interatomic distances and angles was analyzed. The effect of doping on the magnitude of the octahedral tilting was determined, since space group *Pnma* belongs to the $a^-b^+c^-$ tilt system [6]. Bond-valence calculations for all samples were performed as well, since the incorporation of Y in the structure of $CaMnO_3$ provokes the reduction of equivalent amounts of Mn^{4+} to Mn^{3+} [7].

[1] B. Raveau, A. Maignan, C. Martin, M. Hervieu: *J. Phys.: Condens. Mat.*, **11**, (1999), 9221-9238.
[2] M. W. Lufaso, P. M. Woodward: *Acta Cryst.*, B **57 (**2001), 725-738.
[3] S. Bošković, B. Matović, M. Vlajić, V. Krstić, *Ceram. Int.* Vol. **33,** (2007), 89-93.
[4] J. Rodriguez-Carvajal, Collected Abstract of Powder Diffraction Meeting, Toulouse (1990) 127.
[5] M. N. Iliev, M. V. Abrashev, H. G. Lee, V. N. Popov, Y. Y. Sun, C. Thomsen, R. L. Meng, C. W. Chu, *Phys. Rev. B*, **57**, (1998), 2872-2877.
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[7] O. Agüero, A. G. Leyva, P. König, D. Vega, G. Polla, H. Aliaga, M. T. Causa, *Phys. B* **320,** (2002), 47-50.

Uticaj dopiranja itrijumom na strukturu $Ca_{1-x}Y_xMnO_3$ ($0 \leq x \leq 1$)

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[a]*Institut za nuklearne nauke "Vinča", Laboratorija za materijale, p. pr. 522, 11001 Beograd, Srbija;* [b]*Rudarsko-geološki fakultet, Laboratorija za kristalografiju, Univerzitet u Beogradu, p. pr. 162, 11001 Beograd, Srbija;* [c]*Institut za mineralogiju i petrografiju, Univerzitet u Insbruku, Innrain 52, A-6020, Insbruk, Austrija*
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Dopirani manganiti opšte formule $Ca_{1-x}A_xMnO_3$, gde je A trovalentna retka zemlja imaju osobine kolosalne magnetne otpornosti i prihvatljiv nivo električne provodnosti za primenu u gorivnim ćelijama [1].

Da bi se procenila teoretska stabilnost perovskitske strukture korišćenjem softvera SPuDS (dijagnostički softver za predviđanje strukture) izračunati su Goldšmitov faktor tolerancije, (G_t) i globalni indeks nestabilnosti, (*GIN*) za $Ca_{1-x}Y_xMnO_3$ (x = 0, 0,25, 0,5, 0,75, 1) [2]. Na osnovu ova dva parametra analizirana je mogućnost formiranja perovskitskog tipa strukture kod $Ca_{1-x}Y_xMnO_3$ ($0 \leq x \leq 1$). Da bi se proverili dobijeni rezultati, sintetizovani su nanoprahovi sledećih nominalnih sastava: $CaMnO_3$, $Ca_{0,95}Y_{0,05}MnO_3$, $Ca_{0,85}Y_{0,15}MnO_3$, $Ca_{0,75}Y_{0,25}MnO_3$, $Ca_{0,5}Y_{0,5}MnO_3$, $Ca_{0,25}Y_{0,75}MnO_3$ i $YMnO_3$, korišćenjem modifikovane glicin-nitratne metode [3]. Nakon kalcinisanja na 800 °C / 2 h, prahovi su okarakterisani metodom rendgenske difrakcije na polikristalnim uzorcima. Ritveldova analiza difrakcionih podataka urađena je pomoću programa FullProf [4].

Sve faze, osim $YMnO_3$, su rombične (prostorna grupa *Pnma*) sa perovskitskim tipom strukture. Heksagonalni $YMnO_3$ (prostorna grupa $P6_3cm$) je na atmosferskom pritisku izomorfan sa $LuMnO_3$ [5].

Ispitivan je uticaj različitog sadržaja Y na parametre jedinične ćelije, zapreminu jedinične ćelije, međuatomska rastojanja i uglove. Određen je uticaj dopiranja na intenzitet naginjanja oktaedara, s obzirom da prostorna grupa *Pnma* pripada $a^-b^+c^-$ sistemu naginjanja oktaedara [6]. Izračunate su i valence veza za sve ispitivane uzorke pošto ulazak Y u strukturu $CaMnO_3$ dovodi do redukcije jednake količine Mn^{4+} u Mn^{3+} [7].

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Crystal data for some minerals of Vršac mountains

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Bannatian Plain ends on the south-east by Vršac Mountains, consists of an augengneisses and granites, which ends on the east by micashistes. The augens of gneisses are Karlsbad twins of felspars (albites and ortoclasses). In these rocks is possible find pegmatites consisting felspars, quartz, micas (muscovites and biotites) and tourmaline. In this paper is presented the type of this mineral based on the unit cell. In east part of Vršac Mountains it impossible to fid mineralization as pyrite, magnetite and geikielite. The unit cell for these minerals are measured and presented in this paper.

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Кристалографски подаци за
неке минерале Вршачких планина

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Банатска равница завршава се на југоистоку наглим израњањем планина са којих доминира поглед на далеко, јер у близини не постоје никаква брда која би ометала поглед. Брда се састоје углавном од окцастих гнајсева и гранита, који на истоку постепено прелазе у микашисте. Окца гнајсева су у ствари кристали карлсбадских близанаца албита и ортокласа. Ове стене, а поготову микашисти су понегде пробијене пегматитима, који садрже осим кварца и фелдспата, минерале лискунске групе (мусковита, илита, серицита...), још и турмалин. За овај последњи минерал измерена је јединична ћелија како би се утврдила врста турмалина. У источним деловима може се наићи и на пиритску минерализацију као и гејкилит.

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[3] Bukurov, B., (1951), Vršačke planine, Matica srpska, Novi Sad
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DIOXOVANADIUM(V) COMPLEX WITH PYRIDOXAL-SEMICARBAZONE. SYNTHESIS AND STRUCTURAL STUDIES OF COMPLEX

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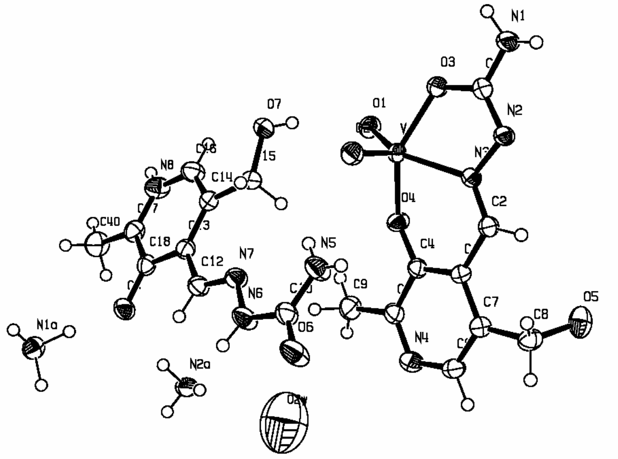
Orange single crystals of the compound $C_{18}H_{30}N_{10}O_9V$, were prepared by the reaction of MeOH and NH_3 solution of NH_4VO_3 and $H_2L{\cdot}H_2O$ in mole ratio 1:1 The single crystal X-ray analysis of the complex has shown a distorted square-pyramidal structure established by the tridentate ONO ligand and one atom from the VO_2 group in the basis of the pyramid and with the other oxygen atom from the same group in the apex. The compound crystallizes in the P-1,space group with a = 8.50(8)Å, b = 10.876(11) Å, c = 13.810(14)Å, ά = 95.4(3)°,β = 100.01(2)°, γ = 100.11(2)°, V = 1228(12) Å^3. X-ray diffraction data were recorded on an Philips diffractometer with graphite monochromated Mo-Kα radiation (λ=0.7107Å). Anisotropic refinement of all non-hydrogen atoms converged to R=0.0716 for 5586 independent reflections and 463 parameters.


N1
O3
O1
N2
V
N3
O7
C16
15
N8
C14
O4
C2
C40
C18
C4
N5
N7
C12
N6
C9
C7
O5
C8
O6
N4
N1a
N2a
O2W

DIOKSOVANADIJUM(V) KOMPLEKS SA SMIKARBAZONOM PIRIDOKSALA.
SINTEZA I STRUKTURA KOMPLEKSA

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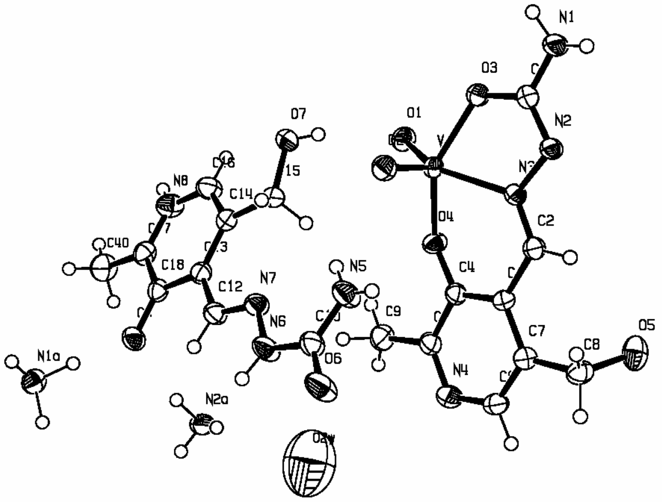
Naranđasti monokristali kompleksnog jedinjenja, formule $C_{18}H_{30}N_{10}O_9V$, dobijeni su reakcijom metanolno-amonijačnog rastvora NH_4VO_3 i liganda semicarbazona piridoksala u molskom odnosu 1: 1. Rentgenostrukturna analiza ovog kompleksa je pokazala da dobijeni monokristal ima deformisanu kvadratno-piramidalnu strukturu sa tridentatnim ONO ligandom i jednim atomom kiseonika iz VO_2 grupe u osnovi piramide i drugim atomom kiseonika iz iste grupe u njenom vrhu. Jedinjenje kristališe u P-1, sa a = 8.50(8)Å, b = 10.876(11) Å, c = 13.810(14)Å, ά = 95.4(3)°,β = 100.01(2)°, γ = 100.11(2)°, V = 1228(12) Å^3. Analiza je rađena na Philipsovom difraktometru sa grafitnim monohromatom Mo-Kα zračenjem
(λ=0.7107Å). Anizotropno utačnjavanje za sve nevodonične atoma daje R=0.0716 za 5586 analiziranih refleksija i 463 parametra.


N1
O3
O1
V
N2
N3
O7
C16
N8
C14
15
C40
C18
C12
N7
N5
O4
C4
C2
N6
C9
C7
C8
O5
O6
N4
N1a
N2a
O2w

THE BEGINING OF THE TEACHING MINERALOGY IN VOJVODINA

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There is no a determined moment of the beginning of mineralogy teaching in Vojvodina. The first printed matter about minerals in this area is originated from Zaharija Orfelin (1726-1785) [1]. The author in his book on popular way presented the minerals and rocks. The text is transmitted mainly from Richter's text-book, edited in 1776. Another popular like text-book is „Фусїка" by Atanasia Stoikovich (1773-1832) [2]. This text-book is on studious way explained minerals, rocks and stones. The book is written on Russian-orthodox language. The mineralogy was taught as teaching subject in Sremski Karlovci in the Serbian Orthodox high school, by fomous professor Andreas Wolny (1759-1824). He was born and studied in Schemnitz, where was founded the first Academy of Mining, in Hungarian Kingdom. Wolny taught Mineralogy in I *Pro classe Praeparandorum,* where taught: salts, sulphur, metals, ores and rocks. In the II class *Pro Gramatica* he taught saltpeter, iron (II) sulfate, asbestos, calcedon, achat, gold silver etc. He made together with his pupils a collection of minerals. In the Serbian Orthodox high school in Novi Sad the best knownt professor of mineralogy, physics and chemistry was Stevan Milovanov (1855-1946) who edited also his text-book in Novi Sad [3]. The Milovanov's collection of minerals was saved also in Girls' school in Novi Sad where 4 pieces were donated by Đorđe Natošević (1821-1887), also fomous professor of natural sciences. The first scientific paper from mineralogy was included in the *„Програм Српске велике гимназије карловачке*" for the 1892/93 [4]. The author is Stevan Popović and he described the microscopic investigation of the homogenicity of minerals and chrystals which might include gases, liquides and solid materials as (ad)mixture and he studyied polymorphism also. In XIX century in Vojvodina were used text-books and scientific papers on Serbian language and also materials from German, English, Russian and Hungarian language.

In this paper bibliographic and archival methods of investigation were used. We could conclude that in the XIX century mineralogy was an important subject of study and research in Vojvodina.

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POČECI NASTAVE MINERALOGIJE U VOJVODINI

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Sam početak nastave mineralogije nije tačno određen u Vojvodini. Prvi štampani materijal u ovom regionu o mineralima potiče od Zaharije Orfelina (1726-1785) [1]. Autor u svojoj knjizi na popularan način predstavlja minerale i stene. Tekst je delom preuzet iz Rihterovog udžbenika iz 1776. Drugo popularno delo, nalik na udžbenik je „Фусїка" od Atanasije Stoikoviča (1773-1832) [2]. Ovaj udžbenik na studiozan način objašnjava minerale, stene i kamenje. Knjiga je pisana na Rusko-crkvenoslovenskom jeziku. Mineralogija kao nastavni predmet prvi je predavao čuveni profesor Velike srpske pravoslavne gimnazije u Sremskim Karlovcima Andrija Volni (*Andreas Wolny*, 1759-1827). On je rođen i školovao se u Šemnicu, gde je osnovana prva Rudarska akademija u Kraljevini Ugarske. Volni je predavao mineralogiju u I *Pro classe Praeparandorumu*, a predavao je o solima, sumporu, metalima, rudama i stenama. U II razredu *Pro Gramatica* predavao je o šalitri, zelenoj galici, azbestu, kalcedonu, ahatu, zlatu, srebru i drugo. On je zajedno sa svojim učenicima sačinio zbirku minerala. U Velikoj srpskoj pravoslavnoj gimnaziji u Novom Sadu najpoznatiji profesor mineralogije, fizike i hemije bio je Stevan Milovanov (1855-1946), koje je prvi objavio Udžbenik iz mineralogije u Novom Sadu [3]. Zbirka minerala Stevana Milovanova je sačuvana u *Višoj devojačkoj školi u Novom Sadu*, gde 4 minerala potiče od poznatog profesora prirodnih nauka Đorđa Natoševića (1821-1887). Prvi naučni rad iz mineralogije je bio uključen u *„Програм Српске велике гимназије карловачке"* za 1892/93 [4]. Autor je Stevan Popović i on opisuje mikroskopsko ispitivanje homogenosti minerala i kristala u kojima primese mogu da budu gasovi, tečnosti i čvrste metrije. On je proučavao i polimorfiju. U XIX veku u Vojvodini u upotrebi su bili udžbenici i naučni radovi na srpskom jeziku, kao i na nemačkom, engleskom, ruskom i mađarskom jeziku.

U ovom radu su korišćene bibliografske i arhivske metode istraživanja. Možemo da zaključimao da u XIX veku mineralogija je bila važan predmet proučavanja i istraživanja u Vojvodini.

[1] Zaharija Orfelin, 1783, *O postanku sveta,* VEČNI KALENDAR, Kurzbeck, Viena, (Fototipsko izdanje Matica Srpska, Novi Sad) str. 106-287.

[2] Аѳанасіа Стойкович, 1803, Фусіка, Треша часшъ. Писменїе Кралевского Унїверсішеша, Въ Будимъ, сшр. 197-223.

[3] Стеван Милованов, 1895, Минералогија, петрографија и геологија са основима хемије, Браћа Бајић, Нови Сад.

[4] Стеван Поповић, 1893, *Страна тела у минералима и њихова важност,* ПРОГРАМ, Српске велике гимназије карловачке, за школску годину 1892/93, Година XLI. Књига XXXIV. Књиж. и Штамп. А. Пајевића, Нови Сад, „Научни радови професора карловачке гимназије", I, 1991, Уредник Пешикан, В., Сремски Карловци, стр. 535-547.

Crystal structure of a garnet with composition $(Fe_{1.72}Ca_{1.04}Mg_{0.19}Mn_{0.05})_3Al_2Si_3O_{12}$

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Minerals of the garnet group have a complex chemical composition which can be attributed to garnets great ability to make solid solutions. The general formula for the most of the natural garnets is $X_3Y_2Z_3O_{12}$, where X = Mg^{2+}, Fe^{2+}, Ca^{2+}, Mn^{2+}, Zn^{2+}, Y^{2+}, Na^{+}, *etc*., Y = Al^{3+}, Cr^{3+}, Fe^{3+}, Ti^{3+}, Ti^{4+}, V^{3+}, Fe^{2+}, Zr^{4+}, Sn^{4+}, *etc*. and Z = Si^{4+}, Al^{3+}, Ti^{4+}, Fe^{2+}, Fe^{3+}, P^{3+}, *etc*. They crystallize in space group $Ia\bar{3}d$. Single-crystal X-ray data of $(Fe_{1.72}Ca_{1.04}Mg_{0.19}Mn_{0.05})_3Al_2Si_3O_{12}$ were collected with a Stoe IPDS-II imaging plate diffractometer (Mo$K\alpha$ radiation, 293 K, $2\theta_{max}$ = 57.26 °). The structure was refined by SHELXL97 incorporated in the WinGX system using the atom parameters reported by Novak and Gibbs [1] as starting values. The refinement (19 parameters) of the cubic structure (a = 11.6306(6) Å, V = 1573.28 Å^3, Z = 8) yielded R_1 = 0.0247 and wR_2 = 0.0714 for 174 unique reflections with $I \geq 2\sigma(I)$ and a goodness-of-fit S = 1.393. A relatively long X—O (X=Fe^{2+}) distance suggested partial occupancy of the X site by larger cations. To determine the cation species on the X site in more detail, an electron microprobe analysis was performed on a JEOL 8100 microprobe, which also proved the homogeniety of the crystals. The analyses from the four points gave the following structural formula: $(Fe_{1.86}Ca_{0.88}Mg_{0.19}Mn_{0.05})_{2.98}Al_{1.93}Si_{3.06}O_{12}$. Further refinement was carried out keeping the occupation factors of Mg and Mn fixed according to the chemical analysis. The calculations finally resulted in a structural formula $(Fe_{1.72}Ca_{1.04}Mg_{0.19}Mn_{0.05})_3Al_2Si_3O_{12}$, which is very similar to the one obtained from the microprobe analysis. The derived contents of the different garnet end-members are as follows: almandine (57.3 %), grossular (34.7 %), pyrope (6.3 %) and spessartine (1.7 %).

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Кристална структура граната $(Fe_{1,72}Ca_{1,04}Mg_{0,19}Mn_{0,05})_3Al_2Si_3O_{12}$

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Минерали групе граната имају сложен хемијски састав што је последица могућности грађења чврстих раствора. Општа формула минерала ове групе је $X_3Y_2Z_3O_{12}$, где је X = Mg^{2+}, Fe^{2+}, Ca^{2+}, Mn^{2+}, Zn^{2+}, Y^{2+}, Na^{+}, итд., Y = Al^{3+}, Cr^{3+}, Fe^{3+}, Ti^{3+}, Ti^{4+}, V^{3+}, Fe^{2+}, Zr^{4+}, Sn^{4+}, итд. и Z = Si^{4+}, Al^{3+}, Ti^{4+}, Fe^{2+}, Fe^{3+}, P^{3+}, итд. Гранати кристалишу у просторној групи $Ia\bar{3}d$. Дифракциони подаци за $(Fe_{1,72}Ca_{1,04}Mg_{0,19}Mn_{0,05})_3Al_2Si_3O_{12}$ прикупљени су на дифрактометру за монокристал Stoe IPDS-II са IP детектором (Mo$K\alpha$ зрачење, 293 K, $2\theta_{max}$ = 57,26 °). Структура граната утачњена је коришћењем програмског пакета WinGX. Тесерална структура граната (a = 11,6306(6) Å, V = 1573,28 Å^3, Z = 8) утачњена је (19 параметара) до следећих R-вредности: R_1 = 0,0247, wR_2 = 0,0714 за 174 независне рефлексије које су истовремено и рефлексије код којих је $I \geq 2\sigma(I)$; S=1,393. Утачњавање структурног модела започето је са атомским параметрима које су дали Новак и Гибс [1]. На основу дужине везе X—O (X = Fe^{2+}) закључено је да је у положају X присутан и катјон са већим јонским радијусом. Да би се утврдило који су катјони присутни кориштена је микросонда JEOL 8100, која је утврдила хомогеност кристала. Анализом података добијених са четири тачке прерачуната је структурна формула: $(Fe_{1,86}Ca_{0,88}Mg_{0,19}Mn_{0,05})_{2,98}Al_{1,93}Si_{3,06}O_{12}$. У даљем утачњавању структуре фактори заузећа за Mg и Mn били су фиксирани на вредности добијене из хемијске анализе. На основу фактора заузећа прерачуната је структурна формула: $(Fe_{1,72}Ca_{1,04}Mg_{0,19}Mn_{0,05})_3Al_2Si_3O_{12}$, која је веома слична формули добијеној хемијском анализом. На основу добијених формула прерачуната је заступљеност минералних компоненти у узорку: алмандин (57,3 %), гросулар (34,7 %), пироп (6,3 %) и спесартин (1,7 %).

[1] Novak, G. A. and Gibbs, G. V., *Am. Mineral.* 56, (1971), 791-825.

EFFECTS OF A-SITE DOPING ON THE LOCAL STRUCTURE OF Pb-BASED RELAXOR FERROELECTRICS

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Relaxors represent a special class of ferroelectric materials. Their main features are extremely high dielectric constant, broad diffuse phase transition near the dielectric constant maximum and a strong frequency dependence of the dielectric constant as a function of temperature. Due to their excellent dielectric properties, strong electrostriction and large electro-optic coefficients relaxors are of significant interest for various technological applications. The relaxor properties result from the existing nano-scale structural inhomogeneities, i.e., strong deviations of the local structure from the average structure.

Pb-based perovskite-type complex oxides of the general formula ABO_3 are best known materials with relaxor-ferroelectric properties. The perovskite structure enables ion substitutions on both A- and B-sites. Variations in the chemical composition influence the nano-domain structure and thus allow enhancement of the desired relaxor properties.

Here we present our results on the structure of Ba- and La- doped $PbSc_{0.5}Ta_{0.5}O_3$ and $PbSc_{0.5}Nb_{0.5}O_3$. The structural changes caused by the doping were studied by complementary application of single-crystal X-ray diffraction and polarized Raman spectroscopy.

The results show that the incorporation of a three-valent cation in the A-site leads to a tetragonal modification of the unit cell and enhancement of some of the local structural distortions existing in the stoichiometric compound.

The loading of stereochemically non-active ions causes lattice distortions and changes in the local symmetry. Our results indicate fragmentation of the ferroic clusters in the host matrix by breaking the pattern of Pb^{2+} off-centre shifts and generation of new ferroic species. The latter depend on the valency of the A-site extra cation.

EFEKTI DOPIRANJA A-POZICIJA NA LOKALNU STRUKTURU OLOVNIH RELAKSORKSIH FEROELEKTRIKA

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Relaksori predstavljaju posebnu klasu feroelektričnih materijala. Osnovna odlika su im ekstremno visoke vrednosti dielektrične konstante, široki difuzni fazni prelaz u blizini maksimuma dielektrične konstante i jaka povezanost dielektrične konstante sa frekvencom u funkciji temperature. Zahvaljujući odličnim dielektričnim osobinama, jakoj elektrostrikciji i visokim elektro-optičkim koeficijentima, relaksori su od posebnog značaja za različite tehnološke primene. Relaksorske osobine su rezultat postojeće nehomogenosti na nano-metarskoj skali veličina, kao npr. znatne devijacije lokalne strukture od celokupne strukture.

Kompleksni oksidi Pb-perovskitskog tipa, osnovne formule ABO_3 su najpoznatiji materijali sa osobinama relaksorkih feroelektrika. Perovskitska struktura omogućava jonsku substituciju i na A- i na B-pozicijama. Varijacija hemijskog sastava utiče na strukturu na nanometarskoj skali i time se poboljšavaju poželjne relaksorske osobine.

Prezentujemo rezlutate ispitivanja struktura Ba- and La- dopiranih $PbSc_{0.5}Ta_{0.5}O_3$ and $PbSc_{0.5}Nb_{0.5}O_3$. Strukturne promene uzrokovane dopiranjem su proučavane komplementarnom primenom monokristalne rendgenske difrakcije i polarizovane ramanske spektroskopije sa monokristala.

Rezultati ukazuju na tetragonalnu modifikaciju jedinične ćelije i umnožavanja lokalnih strukturnih distorzija koje se zatiču još kod stehiometrijskih uzoraka.

Unošenje stereohemijski neaktivnih jona dovodi do poremećaja strukturne rešetke i promene u lokalnoj simetriji. Naši rezultati ukazuju na fragmentaciju feroičnih klastera u matriksu-domaćinu usled razbijanja periodičnosti decentriranih Pb^{2+} pomeraja i stvaranje novih feroičnih vrsta, posebno zavisnih od valence katjona u A-pozicijama.

CRYSTAL STRUCTURE OF $Mg1_{0.7}Mg2_{6}(OH)_{3}(H_{0.2}V1O_{4})_{3}(HV2O_{4})$ AND ISOTYPIC COMPOUNDS

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During work aimed at crystal structural investigation of the compounds in the AO–BO–X_2O_5–H_2O system (A^{2+} = Sr, Cd, Ba; B^{2+} = Mg, Mn, Fe, Co, Ni, Cu, Zn; X^{5+} = As, V), the new magnesium vanadate $Mg1_{0.7}Mg2_{6}(OH)_{3}(H_{0.2}V1O_{4})_{3}(HV2O_{4})$ was obtained [space group $P6_3mc$, a = 12.9096(2), c = 5.0755(1) Å, V = 732.55(2) Å^3, Z = 1] using hydrothermal synthesis. Its crystal structure was refined with single-crystal X-ray diffraction data [CCD area detector, Mo$K\alpha$ radiation, 298 K, $2\theta_{\max}$ = 60°], starting from the structural model of isotypic $Ni1_{1-x}Ni2_{6}(OH)_{3}(H_{2x/3}As1O_{4})_{3}(HAs2O_{4})$ [1]. The refinement (68 free parameters) yielded R_1 = 0.0208, wR_2 = 0.0483 for 349 unique reflections; for 326 observed reflections with $F_o^2 \geq 4\sigma(F_o^2)$ R_1 = 0.0187. The Flack parameter x was 0.08(5). The already known cobalt and nickel arsenate analogues [1] were structurally re-examined in order to discuss the role of hydrogens in the structure.

The structures of investigated compounds are very similar to that of the mineral dumortierite. They consist of two parts: the first part is made up of a partly occupied chain of face-sharing $M1O_6$-octahedra, and the second one is based on a 3D octahedral framework having the topology of the zeolite cancrinite. The main part of a 3D framework is the double [001] chain consisting of $M2O_6$-octahedra, which share edges and, within the (001), one face. The M2-based double chains are interconnected through O atoms in a 3D framework, where two type of [001] channels similar to those in cancrinite are formed. The first larger channel is filled with the M1-based octahedral chain and the second with $HX2O_4$-tetrahedra.

The Mg1 site contains a significant number of vacancies. The distance along [001] between adjacent Mg1 sites (c/2 = 2.5377 Å) is too short to allow full occupancy of the Mg1 site, which also shows a very large displacement parameter along [001] (U_{33} = 4.1(4) Å^2). This suggests a local displacement of the Mg1 cation from its average position, probably to an adjacent empty Mg1 site. The Mg2 site is fully occupied. The partial substitution of $V1O_4$ with $HV1O_4$ is necessary to achieve charge neutrality. In all investigated structures a fully occupied OH^- is linked to the double chains. Despite a significant disorder of O (U_{11} = U_{22} = 6.7(5), U_{33} = 5.(8) Å^2) the position of the H atom belonging to the $HV2O_4$-group could be identified. The H atom responsible for the partially protonation of the $V1O_4$-tetrahedra occupies these sites only at the M1 vacancies.

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[1] R.W. Hughes, L.A. Gerrard, D.J. Price, M.T. Weller, *Inorg. Chem.*, **42** (2003), 4160-4164.

КРИСТАЛНА СТРУКТУРА $Mg1_{0,7}Mg2_6(OH)_3(H_{0,2}V1O_4)_3(HV2O_4)$ И ИЗОСТРУКТУРНИХ СУПСТАНЦИ

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У току кристалохемијских испитивања система $AO–BO–X_2O_5–H_2O$ (A^{2+} = Sr, Cd, Ba; B^{2+} = Mg, Mn, Fe, Co, Ni, Cu, Zn; X^{5+} = As, V), методом хидротермалне синтезе добијен је нови магнезијумски ванадат: $Mg1_{0.7}Mg2_6(OH)_3(H_{0.2}V1O_4)_3(HV2O_4)$ [просторна група $P6_3mc$, a = 12,9096(2), c = 5,0755(1) Å, V = 732,55(2) Å^3, Z = 1]. Његова структура утачњена је коришћењем података добијених рендгенском дифракцијом на монокристалу [CCD детектор, Mo$K\alpha$ зрачење, 298 K, $2\theta_{\max}$ = 60°], почевши од координата изоструктурног $Ni1_{1-x}Ni2_6(OH)_3(H_{2x/3}As1O_4)_3(HAs2O_4)$ [1]. Утачњавање 68 слободних параметра дало је следеће R вредности: R_1 = 0,0208, wR_2 = 0,0483 за 349 независних рефлексија и R_1 = 0,0187 за 326 рефлексије са $F_o^2 \geq 4\sigma(F_o^2)$. Флаков параметар x је 0,08(5). Већ познати изоструктурни арсенати кобалта и никла, поново су утачњавани због прецизнијег одређивања положаја водоника у структури.

Структуре испитиваних једињења сличне су структури минерала думортијерита. Оне се састоје из две целине. Прва је изграђена од пљоснима повезаних ланаца $M1O_6$-октаедара, где је $M1$ положај само делимично заузет $M1$-катјонима, док се друга састоји од тродимензионалне (3D) мреже октаедара који имају топологију зеолита канкринита. Основни део те мреже састоји се од двоструких ланаца $M2O_6$-октаедара који се пружају дуж [001] и имају заједничке ивице, а у (001)-равни и једну заједничку пљосан. Ови ланци су преко заједничких кисеоника повезани у 3D мрежу и дуж c-осе формирају два типа канала сличних онима код канкринита. Први, већи канали, попуњени су $M1$-октаедарским ланцима, док су други попуњени $HX2O_4$-тетраедрима.

Положај Mg1 садржи значајан број ваканција. Растојање дуж [001] између два суседна Mg1 атома (c/2 = 2,5377 Å) сувише је кратко да омогући потпуно заузеће Mg1 положаја, па је параметар померања атома Mg1 дуж [001] велики (U_{33} = 4,1(4) Å^2). То указује на локалну неуређеност Mg1 и његово померање са очекиване позиције ка суседном, непопуњеном Mg1 положају. Положај Mg2 је попуњен. Делимична замена $V1O_4$ са $HV1O_4$ неопходна је ради баланса наелектрисања. Код свих сличних структура OH^--група, која 100 % попуњава свој положај, везана је за дупле ланце. Упркос великој неуређености кисеоника [U_{11}=U_{22}=6,7(5), U_{33}=5,8(8) Å^2], водоник из $HV2O_4$-групе успешно је лоциран. Водоник који делимично протонује $V1O_4$-тетраедре присутан је само кад је Mg1-положај упражњен.

[1] R.W. Hughes, L.A. Gerrard, D.J. Price, M.T. Weller, *Inorg. Chem.*, **42** (2003), 4160-4164.

LOW TEMPERATURE HIGH RESOLUTION X-RAY DIFFRACTION DATA FOR 4-METHYL-3-THIOSEMICARBAZIDE

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Continuing the investigation on the electronic properties of the thiosemicarbazide based compounds [1] we have collected the high resolution low temperature diffraction data for 4-methyl-3-thiosemicarbazide. Here we present the crystal structure of this compound based on the high resolution data set. This preliminary analysis should serve as an indicator of the quality of the data for the following charge density study.

The single crystal X-ray analysis revealed that an asymmetric unit in the crystal structure of the analyzed compound contains two crystallographically independent molecules. The molecules show only small differences in bond distances and angles, but they have dissimilar network of intermolecular hydrogen bonds. Both molecules form numerous interactions of N−H···S, N−H···N and C−H···N type. The molecules B form dimers through N3b−H3b···N1b interactions and further *via* intermolecular N1b−H11b···S1b interactions form a chain of dimers.

Preliminary electron density maps were determined for both independent molecules. These maps clearly indicate that the maxima of charge density are localized in the region of C−N, N−N and C−S bonds. Also, maxima exist in the vicinity of the N1, N2 and S1 atoms corresponding to their free electron pairs. The following step is a multipole refinement.

The X-ray diffraction data were collected at 100.0(1) K on a Bruker-SMART three axis diffractometer equipped with a SMART 1000 CCD area detector using monochromated Mo $K\alpha$ radiation (wavelength $\lambda = 0.71073$ Å) in the range $0<\theta<51.4^{\circ}$. The total number of the reflections collected was 115688 with the average measurement multiplicity of 10.2. The data sorting and averaging led to a 10361 unique reflections with final $R_{int} = 2.31$ %.

Crystallographic data: formula $C_4H_{14}N_6S_2$, monoclinic crystal system, space group $P2_1/c$, $a = 5.9666(2)$, $b = 8.7396(6)$, $c = 19.1354(2)$ Å, $\beta = 92.854(2)^{\circ}$, $V = 996.59(8)$ Å^3. Structure was solved using the SHELXS97 program and was refined by SHELXL97 to a residual R-factor of 2.78 % for 7506 reflections with $I>3\sigma(I)$ and 165 refined parameters.

[1] S. B. Novaković, B. Fraisse, G. A. Bogdanović, A. Spasojević-de Biré, Crystal Growth Design, 7 (2007), 191-195.

НИСКОТЕМПЕРАТУРНИ ПОДАЦИ ВИСОКЕ РЕЗОЛУЦИЈЕ 4-МЕТИЛ-3-ТИОСЕМИКАРБАЗИДА ДОБИЈЕНИ ДИФРАКЦИЈОМ РЕНДГЕНСКОГ ЗРАЧЕЊА

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Настављајући истраживања, која се односе на електронска својстава једињења тиосемикарбазида [1], дифракцијом рендгенског зрачења са монокристала сакупљени су нискотемпературни подаци високе резолуције за 4-метил-3-тиосемикарбазид. У овом раду ћемо описати кристалну структуру овог једињења на основу сета података високе резолуције. Ова прелиминарна анализа требало би да послужи и као индикатор квалитета података за будуће проучавање електронске густине наведеног једињења.

Анализа кристалне структуре открива да у асиметричној јединици постоје два кристалографски независна молекула истог састава. Независни молекули показују веома малу разлику у дужинама веза, као и у угловима између веза, међутим они граде различите интермолекулске водоничне везе N−H···S, N−H···N и C−H···N типа. За разлику од молекула А молекули Б формирају димере преко интермолекулских N3b−H3b···N1b интеракција, а даље преко N1b−H11b···S1b интеракција граде ланац састављен од димера.

Прелиминарне мапе електронске густине одређене су за оба независна молекула. Ове мапе јасно указују да су максимуми електронске густине локализовани у простору хемијских веза C−N, N−N и C−S, као и у околини атома N1, N2 и S1 што одговара положају њихових слободних електронских парова. Следећи корак је мултипол-утачњавање.

Експериментални подаци су сакупљени на 100,0(1) K на Bruker-SMART дифрактометру са три осе опремљеним са SMART 1000 CCD површинским детектором, користећи монохроматско Mo $K\alpha$ рендгенско зрачење (λ = 0,71073 Å) у опсегу $0<\theta<51,4^\circ$. Укупан број сакупљених рефлексија је био 115688 са средњим мултиплицитетом измерених рефлексија од 10,2. Сортирањем и усредњавањем података добија се 10361 јединствена рефлексија са крајњим R_{int} = 2,31 %.

Кристалографски подаци: формула $C_4H_{14}N_6S_2$, моноклинични кристални систем, просторна група $P2_1/c$, a = 5,9666(2) Å, b = 8,7396(6) Å, c = 19,1354(2) Å, β = 92,854(2)°, V = 996,59(8) Å^3. Структура је решена коришћењем SHELXS97 програма и утачњена са SHELXL97 до крајњег R-фактора од 2,78 % за 7506 рефлексија са $I>3\sigma(I)$ и 165 утачњаваних параметара.

[1] S. B. Novaković, B. Fraisse, G. A. Bogdanović, A. Spasojević-de Biré, Crystal Growth Design, 7 (2007), 191-195.

HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURE OF CADMIUM ARSENATE WITH THE APATITE-TYPE STRUCTURE

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From a mixture of $Cd(OH)_2$, Cu powder, $3As_2O_5\cdot 5H_2O$, and distilled water, transparent prismatic single crystals of $Cd_5(AsO_4)_{3-x}(HAsO_4)_xCl_{0.61}(OH)_{0.39-x-(y/2)}O_{x+(y/2)}\square_{y/2}$ were obtained under hydrothermal conditions (Teflon-lined steel autoclave, 493 K, 3 days). The compound is hexagonal (space group $P6_3/m$) with $a = 9.971(1)$, $c = 6.514(1)$ Å, $V = 560.9(1)$ Å^3, $Z = 2$, and adopts apatite structure type. The refinement was made starting from the structural model of $Cd_5(AsO_4)_3Cl_{1-2x-y}O_x\square_x(OH)_y$ [1] and using single-crystal X-ray data (CCD area detector, Mo$K\alpha$ radiation, 298 K, $2\theta_{max} = 60$ °). For 417 unique reflections and 41 free parameters, the refinement yielded $R_1 = 0.0173$ and $wR_2 = 0.0354$, and for 413 observed reflections with $I > 2\sigma(I)$, $R_1 = 0.0170$. The qualitative EDX analysis confirmed the presence of Cd, As and Cl (Cl originated from impurities), while polarized single-crystal IR spectra proved the existence of OH^- stretching vibrations at 3420 cm^{-1} when recorded parallel to the c-axis.

Considering only the crystallographic sites where the Cd^{2+}, Cl^- and O^{2-} ions are located, the structural formula can be written as $Cd1_2Cd2_3(AsO1O2O3_2)_3(Cl,O4)$. Coordination polyhedron of Cd1 can be described as a deformed trigonal prism $Cd1O1_3O2_3$, with two bases formed by $O1_3$- and $O2_3$-triangles twisted to each other by an angle of $\varphi = 14.1$ °. Three additional O3 atoms at longer distances are capping the prism faces. The coordination geometry of the Cd2 site is a distorted $Cd2O2O3_4(Cl,O4)$ octahedron. O1 atom, usually coordinated to this cation position in apatites, is at very long distance (3.371(3) Å) and contributes to the bond valence by only 2 %. In the channels extending along c-axis the Cl (61(1)%) and O4 (39(1) %) atoms occupy the same 2a (0,0,¼) position giving the formula $Cd_5(AsO_4)_3Cl_{0.61}(OH)_{0.39}$.

However, the longest distance in AsO_4-tetrahedron (As–O2 = 1.706(4) Å), together with IR spectral data, suggested that AsO_4^{3-} is partly protonated. Since it was not possible to locate H atoms, the most probable formula is $Cd_5(AsO_4)_{3-x}(HAsO_4)_xCl_{0.61}(OH)_{0.39-x}O_x$.

Additionally, there is also a minor possibility for the vacancy formation at 2a site ($2OH^- \leftrightarrow O^{2-} + \square$), which was found in similar structure [1]. Thus, the formula of the investigated compound could also be: $Cd_5(AsO_4)_{3-x}(HAsO_4)_xCl_{0.61}(OH)_{0.39-x-(y/2)}O_{x+(y/2)}\square_{y/2}$.

The financial support of the Austrian Science Foundation (FWF) (Grant T300-N19) is gratefully acknowledged.

[1] C.D. Johnson, J. Feldman, D.E. Macphee, F. Worrall, J.M.S. Skakle, *Dalton Transactions*, **21** (2004) 3611-3615.

ХИДРОТЕРМАЛНА СИНТЕЗА И КРИСТАЛНА СТРУКТУРА КАДМИЈУМ-АРСЕНАТА СА СТРУКТУРОМ АПАТИТА

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Из смеше $Cd(OH)_2$, Cu-прах, $3As_2O_5 \cdot 5H_2O$ и дестиловане воде, под хидротермалним условима (тефлонски суд, челични аутоклав, 493 K, 3 дана) добијени су провидни призматични кристали хемијског састава $Cd_5(AsO_4)_{3-x}(HAsO_4)_xCl_{0.61}(OH)_{0.39-x-(y/2)}O_{x+(y/2)}\square_{y/2}$. Кадмијум-арсенат је хексагоналан, просторна група $P6_3/m$, $a = 9{,}971\ (1)$, $c = 6{,}514\ (1)$ Å, $V = 560{,}9\ (1)$ Å^3, $Z = 2$ и има структуру апатита. Дифракциони подаци прикупљени су на монокристалу [Mo$K\alpha$ рендгенско зрачење, CCD детектор, 298 K, $2\theta_{max} = 60$ °] и утачњена је структура полазећи од модела $Cd_5(AsO_4)_3Cl_{1-2x-y}O_x\square_x(OH)_y$ [1]. Утачњавањем 41 параметра добијени су следећи параметри слагања: $R_1 = 0{,}0173$, $wR_2 = 0{,}0354$ за 417 независних рефлексија и $R_1 = 0{,}0170$ за 413 рефлексије са $I > 2\sigma(I)$. Квалитативна SEM (EDX) анализа потврдила је присуство кадмијума, арсена и хлора. Порекло хлора је из нечистоћа хемикалија. Присуство OH^- групе у структури доказано је ИЦ-спектроскопијом. Траке карактеристичне за OH^- групу измерене су на 3420 cm^{-1} при оријентацији кристала паралелно *c*-оси.

Узимајући у обзир кристалографске положаје Cd^{2+}, Cl^- и O^{2-} јона, формула овог једињења може да се напише као $Cd1_2Cd2_3[AsO1O2O3_2]_3(Cl,O4H)$. Координациони полиедар око Cd1 јесте деформисана тригонална призма-$Cd1O1_3O2_3$. Основу призме чине $O1_3$- и $O2_3$- троуглови (угао ротације између троуглова $\varphi = 14{,}1^{\circ}$). Преостале три, нешто дуже Cd1—O3 везе, представљају круне на пљоснима призме. Атом Cd2 је у координацији 6 у форми деформисаног $Cd2O2O3_4(Cl,O4H4)$-октаедра. Кисеоник O1, који је обично у координационој сфери Cd2, налази се на великом растојању (3,371(3) Å), а његов допринос укупној валенци везе је свега 2 %. У каналима дуж *c*-осе Cl (60(1) %) и O4 (39(1) %) заузимају исти 2*a* (0,0,¼) положај у $(Cd_5(AsO_4)_3Cl_{0.61}(OH)_{0.39})$. Најдужа As—O веза (As—O2 = 1,706(4) Å) указује да су AsO_4-тетраедри делимично протоновани. Пошто није било могуће утврдити положај и заступљеност овог водоника, највероватнија формула испитиваног једињења јесте $Cd_5(AsO_4)_{3-x}(HAsO_4)_xCl_{0.61}(OH)_{0.39-x}O_x$. Осим тога, постоји мала могућност и за формирање ваканција у положају 2*a* ($2OH^- \leftrightarrow O^{2-} + \square$), која је утврђена у сличној структури [1]. Према томе, могуће је да је хемијска формула испитиваног кристала $Cd_5(AsO_4)_{3-x}(HAsO_4)_xCl_{0.61}(OH)_{0.39-x-(y/2)}O_{x+(y/2)}\square_{y/2}$.

[1] C.D. Johnson, J. Feldman, D.E. Macphee, F. Worrall, J.M.S. Skakle, *Dalton Transactions*, **21** (2004) 3611-3615.

SYNTHESIS AND CRYSTAL STRUCTURE OF TWO ANDROSTENE DERIVATIVES

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Starting from dehydroepiandrosterone, new steroid compounds, 17-picolinylidene-androst-4-ene-3-one (1) and 17β-hydroxy-17α-picolyl-androst-4-ene-3-one (2) were synthesized in several steps, as potent inhibitors of enzyme aromatase, that is responsible for catalyzing the conversion of androgens to estrogens in the last step of estrogen biosynthesis.

The compound **1** crystallizes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters a=7.274(4), b=11.857(5), c=23.92(7)Å, and Z=4, D_x=1.16 Mgm^{-3}, μ=0.07 mm^{-1}, MoK_{α} radiation.

The compound **2** also crystallizes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters a=7.021(4), b=8.964(4), c=33.74(7)Å, and Z=4, D_x=1.18 Mgm^{-3}, μ=0.073 mm^{-1}, MoK_{α} radiation.

The crystal structures were solved by direct methods on the basis of 2328 independent reflections for compound **1** and 2421 reflections for compound **2** using SHELXS-86 [1] and refined by SHELXL-97 [1]. The final R factors were 0.056 for compound **1** and 0.047 for compound **2**.

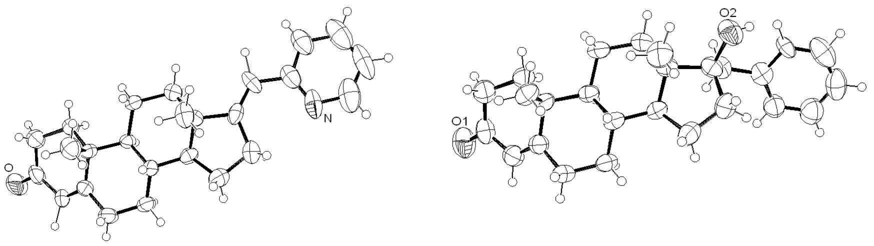

Figure 1. A view of the molecular structure of compound **1** (left) and compound **2** (right)

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[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 DVA DERIVATA ANDROSTENA

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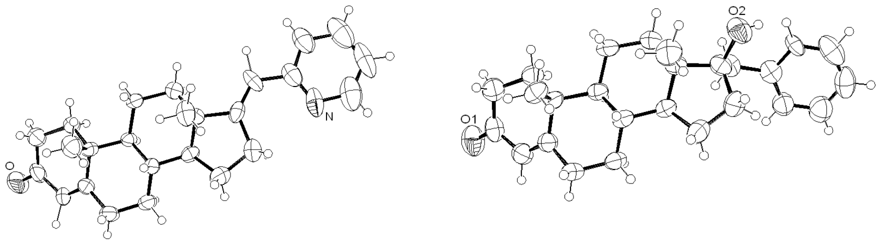
Polazeći od dehidroepiandrosterona, dva nova steroidna jedinjenja, 17-pikolinilidene-4-androsten-3-on (1) i 17β-hidroksi-17α-pikolil-4-androsten-3-on (2) su sintetizovana u više koraka kao potencijalni inhibitori enzima aromataze, koji je odgovoran za katalizaciju konverzije androgena u estrogene, u poslednjem koraku steroidogeneze.

Jedinjenje **1** kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije a=7,274(4), b=11,857(5), c=23.92(7)Å, i Z=4, D_x=1.16 Mgm^{-3}, μ=0.07 mm^{-1}, MoK$_\alpha$ zračenje.

Jedinjenje **2**, takođe, kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije a=7,021(4), b=8,964(4), c=33,74(7)Å, and Z=4, D_x=1.18 Mgm^{-3}, μ=0.073 mm^{-1}, MoK$_\alpha$ zračenje.

Strukture kristala su rešene primenom direktnih metoda na bazi 2328 nezavisnih refleksija za jedinjenje **1** i 2421 refleksija za jedinjenje **2** pomoću SHELXS-86 [1] i utačnjena pomoću SHELXL-97 [1]. Konačna vrednost R faktora je 0,056 za jedinjenje **1** i 0,047 za jedinjenje **2**.



Slika 1. Prikaz molekulske strukture jedinjenja **1** (levo) i jedinjenja **2** (desno).

[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.

LOW TEMPERATURE HIGH RESOLUTION X-RAY DIFFRACTION DATA FOR Co(III) COMPLEX WITH FAMOTIDINE LIGAND

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Famotidine is a widely used anti-ulcer drug which belongs to the class of the histamine receptor antagonists [1]. Although the famotidine molecule displays several potential donor atoms a little is known about its coordination abilities. Up to now only two crystal structures of the metal complexes of famotidine have been reported, the title complex [Co(fam)(en)]Cl·H_2O (fam = famotidine, en = ethylenediamine) [2] and the square-planar complex $[Cu(H_2fam)](ClO_4)_2$ [3]. In these structures the ligand shows different ways of coordination demonstrating the structural flexibility. The biological investigations have shown that the title compound exhibits considerable antibacterial and antifungal activity which is higher in comparison with the drug alone [2].

The crystal structure of the title compound based on the room temperature X-ray diffraction data has already been reported [2]. Here we present the structural features of the same compound based on the accurate high resolution data as an introduction to the following investigation of its electronic properties. The preliminary results show that the low temperature single crystal data are of very high quality and that can be used for the multipole refinement and the charge density analysis of Co(III) complex with famotidine.

Experimental details: The data were collected at 100.0(1) K on a Bruker-SMART diffractometer equipped with a SMART 1000 CCD area detector using monochromated Mo $K\alpha$ X-ray radiation (λ = 0.71073 Å). Maximal resolution $(\sin\theta/\lambda)_{max} = 1.10$ Å^{-1}. The total number of the reflections collected was 86400. The data sorting and averaging led to 19124 unique reflections with a final R_{int} = 2.02 %.

Crystallographic data: formula $C_{10}H_{23}ClCoN_9O_3S_3$, triclinic crystal system, space group P-1, a = 9.0922(1), b = 9.2850(1), c = 12.3436(2) Å, α = 86.058(1), β = 77.715(2), γ = 73.977(1)°, V = 978.59(8) Å^3. Structure was solved using the SHELXS97 program and refined by SHELXL97 to a residual R-factor of 2.22 % for 15436 reflections with $I > 3\sigma(I)$ and 336 refined parameters.

[1] J. Overgaard and D. E. Hibbs Acta Cryst. A60 (2004) 480-487;
[2] Đ. U. Miodragović, G. A. Bogdanović, Z. M. Miodragović, M.Đ. Radulović, S. B. Novaković, G.N. Kaluđerović, H. Kozłowski, J. Inorg. Biochem. 100 (2006) 1568–1574;
[3] M. Kubiak, A. Duda, M.L. Ganadu, H. Kozłowski, J. Chem. Soc., Dalton Trans. (1996) 1905–1908.

NISKOTEMPERATURNI PODACI VISOKE REZOLUCIJE DOBIJENI DIFRAKCIJOM RENDGENSKOG ZRAČENJA ZA KOMPLEKS Co(III) SA FAMOTIDINOM

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Famotidin je široko primenjivani antiulkusni lek koji pripada klasi antagonista histamina [1]. Iako famotidin ima nekoliko potencijalnih donornih atoma, malo se zna o njegovim kompleksirajućim sposobnostima. Do sada su opisana dva kompleksa metala sa famotidinom, naslovljeni kompleks [Co(fam)(en)]Cl·H_2O (fam = famotidin, en = etilendiamin) [2] i kvadratno-planarni kompleks [Cu(H_2fam)]$(ClO_4)_2$ [3]. U ovim kristalnim strukturama ligand pokazuje raličite načine koordinacije što ukazuje na njegovu strukturnu fleksibilnost. Biološka ispitivanja su pokazala da naslovljeni Co(III) kompleks pokazuje značajnu antibakterijsku i antifungalnu aktivnost koja je veća u poređenju sa aktivnošću nekoordinovanog leka [2].

Kristalna struktura naslovljenog jedinjenja je određena na osnovu podataka dobijenih eksperimentom na sobnoj temperaturi [2]. Ovde ćemo prezentovati strukturna svojstva istog jedinjenja koja su određena na osnovu niskotemperaturnih podataka visoke rezolucije. Ova analiza predstavlja uvod u predstojeće ispitivanje elektronskih svojstava naslovljenog Co(III) kompleksa. Preliminarni rezultati pokazuju da su podaci dobijeni difrakcijom rendgenskog zračenja visoke rezolucije visokokvalitetni i da se mogu koristiti za dalje multipol-utačnjavanje i analizu raspodele gustine naelektrisanja u kompleksu Co(III) sa famotidinom.

Eksperimentalni detalji: Podaci su prikupljani na difraktometru Bruker-SMART opremljenim SMART 1000 CCD detektorom, na temperaturi od 100.0(1) K. Korišćeno je monohromatsko Mo $K\alpha$ zračenje (λ = 0,71073 Å). Maksimalna ostvarena rezolucija $(\sin\theta/\lambda)_{max}$ = 1,10 $Å^{-1}$. Prikupljeno je ukupno 86400 refleksija. Usrednjavanjem podataka dobijeno je 19124 nezavisnih refleksija (R_{int} = 2,02 %). Kristalografski podaci: formula $C_{10}H_{23}ClCoN_9O_3S_3$, triklinični sistem, prostorna grupa P-1, a = 9,0922(1), b = 9,2850(1), c = 12,3436(2) Å, α = 86,058(1)°, β = 77,715(2), γ = 73,977(1)°, V = 978,59(8) $Å^3$. Struktura je rešena SHELXS97 programom i utačnjena programom SHELXL97 do finalnog R = 2,22 % za 15436 refleksija (I>3σ(I)) i 336 utačnjavanih parametara.

[1] J. Overgaard and D. E. Hibbs Acta Cryst. A60 (2004) 480-487; [2] Đ. U. Miodragović, G. A. Bogdanović, Z. M. Miodragović, M. Đ. Radulović, S. B. Novaković, G. N. Kaluđerović, H. Kozłowski, J. Inorg. Biochem. 100 (2006) 1568–1574; [3] M. Kubiak, A. Duda, M. L. Ganadu, H. Kozłowski, J. Chem. Soc., Dalton Trans. (1996) 1905–1908.

Structural characterization of mechanochemically prepared TiO

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Titanium monoxide belongs to the class of highly nonstoichiometric interstitial phases and exists in a wide composition range, from $\mathrm{TiO}_{0.80}$ to $\mathrm{TiO}_{1.25}$. Even among highly nonstoichiometric compounds TiO_y is unique in the sense that it contains a large amount of both, metal and non-metal vacancies. To adequately describe the defect structure of titanium monoxide, its formula should take into account Ti and O vacancies: $\mathrm{Ti}_x\mathrm{O}_z = \mathrm{TiO}_y$, or $\mathrm{Ti}_x\blacksquare_{1-x}\mathrm{O}_z\square_{1-z} = \mathrm{TiO}_y$, where $y = z/x$, while $\square$ and $\blacksquare$ designate O and Ti vacancies, respectively. The distribution of atoms and vacancies over the crystal lattice of titanium monoxide can be disordered and ordered, depending on the oxygen content and thermal treatment. In a disordered phase, with the cubic NaCl structure, atoms and structural vacancies are randomly distributed over the crystal lattice sites. Ordering is accompanied by the reduction to the monoclinic symmetry, but the effect of ordering on thermodynamic properties of titanium monoxide has not been studied in detail yet.

In conventional synthetic procedures, TiO_y samples usually consist of two phases and contains both, ordered and disordered phase. Also, the colour of conventionally synthesized materials vary from yellowish silvery over golden yellow to dark golden yellow. In this work TiO_y samples were prepared from Ti metal and TiO_2 (rutile) powders by solid state reaction in a planetary ball mill. The mixtures of reactants, with Ti:TiO_2 molar ratios equal to 1:1, 1.10:1 and 1.25:1, were milled for 2 hours using hardened-steel vials and balls in an air or argon atmosphere. The synthesized samples were further annealed (sealed quartz ampoules) in a vacuum or argon atmosphere for 24 hours at temperature range 600–1100 °C. The products were characterized by X-ray powder diffraction (XRPD) and TG/DT/DSC analysis, optical and scanning electron microscopy. The approximate average crystallite size of milled samples was calculated using the Scherrer formula.

After milling, XRPD analysis confirmed formation of disordered cubic titanium monoxide of low crystallinity and nanometer crystallite size in all cases. After annealing at different temperatures the crystallinity increased and disordered structure remained, except in the case of the 1.25:1 reactants ratio, where the maxima of an ordered monoclinic titanium monoxide were observed at 900 °C. Optical microscopy showed a wide range of colours (intensive blue, violet, golden yellow, brown and silver grey) what probably can be attributed to the nonstoichiometry and iron contamination, because the EDS analysis revealed an average iron content of about 2.5 wt.%.

The cubic to monoclinic and *vice versa* TiO_y phase transitions were investigated by DSC analysis in an argon atmosphere. No expected phase transitions were observed up to 1300 ºC.

Strukturna karakterizacija mehanohemijski dobijenog TiO

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Titan-monoksid, sa kubnom NaCl strukturom, predstavlja školski primer nestehiomerijskih oksida. Svi oksidi u opsegu od $TiO_{0,80}$ do $TiO_{1,25}$ smatraju se monoksidima. Čak i među tipičnim predstavnicima nestehiometrijskih jedinjenja TiO_y je jedinstven, jer u kristalnoj strukturi istovremeno postoje defekti prouzrokovani vakancijama na mestima predviđenim i za anjone i za katjone. Da bi defektna struktura titan-monoksida bila pravilno predstavljena prilikom pisanja hemijske formule potrebno je uvrstiti i šupljine: $Ti_xO_z = TiO_y$, ili $Ti_x\blacksquare_{1-x}O_z\square_{1-z} = TiO_y$, gde je $y = z/x$, dok □ i ■ označavaju redom šupljine O i Ti. U zavisnosti od sadržaja kiseonika i termičkog tretmana raspored atoma i šupljina u kristalnoj rešetki titan-monoksida može biti uređen i neuređen. U neuređenoj kubnoj fazi, atomi i strukturne šupljine su nasumice raspoređeni unutar kristalne rešetke. Uređivanje strukture praćeno je sniženjem simetrije do monoklinične, ali uticaj uređivanja na termodinamičke osobine titan-monoksida još uvek nije detaljno ispitan.

Konvencionalno dobijeni uzorci titan-monoksida obično su dvofazni i sastoje se od uređene i neuređene faze. Boja ovako pripremljenih uzoraka varira od srebrnastožute do različitih nijansi zlatnožute. U ovom radu uzorci TiO_y dobijeni su u planetarnom mlinu mehanohemijskom reakcijom u čvrstom stanju između Ti i TiO_2 (rutil). Smeše reaktanata, sa molskim odnosima Ti:TiO_2 jednakim 1:1, 1,10:1 i 1,25:1, mlevene su 2 h u posudama od specijalnog čelika sa odgovarajućim kuglicama u atmosferi vazduha ili argona. Ovako mleveni uzorci zagrevani su (zatopljene kvarcne ampule) u vakuumu ili atmosferi argona 24 h na temperaturama od 600 do 1100 °C. Proizvodi su okarakterisani rendgenskom difrakcijom, TG/DT/DSC-analizom, optičkom i skenirajućom elektronskom mikroskopijom. Prosečna veličina kristalita mlevenih uzoraka izračunata je na osnovu Šererove jednačine.

Rendgenskom difrakcijom potvrđeno je da se tokom mlevenja u svim slučajevima formira neuređena faza niske kristaliničnosti kubnog titan-monoksida, sa kristalitima nanometarskih dimenzija. Nakon zagrevanja na različitim temperaturama kristaliničnost uzoraka je porasla, a struktura je ostala neuređena. Jedini izuzetak je uzorak sa odnosom reaktanata 1,25:1 kod kojeg su se nakon zagrevanja na 900 °C pojavili pikovi uređene monoklinične faze TiO_y. Optičkom mikroskopijom zapažene su vrlo različite boje (intenzivnoplava, ljubičasta, zlatnožuta, mrka i srebrnosiva). To se verovatno može pripisati nestehiometriji i zaprljanju gvožđem, sa obzirom da je EDS analizom nađen prosečan sadržaj gvožđa od oko 2,5 mas.%.

Fazni prelaz TiO_y iz kubnog u monoklinični i obrnuto ispitivan je DSC-analizom u atmosferi argona do 1300 °C. Ni u jednom slučaju nije potvrđeno postojanje očekivane fazne transformacije.

CRYSTAL STRUCTURE OF SODIUM CITRATE DIHYDRATE, $Na_3C_6H_5O_7 \cdot 2H_2O$, DOPED WITH Mn^{3+} IONS

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Complexes of citric acid are important intermediates in production of high conductivity materials, such as $LaNiO_3$ and $LaMnO_3$ [1,2] using modified Pechini method [3]. However, not much is known about transition metals-citrate complexes and their crystal structures. The title compound is obtained during attempts to grow single crystals of a Mn(III) citrate from a strong alkali aqueous solution (pH ≈ 13) in the presence of NaOH. The title compound crystallise during the slow evaporation of the mother liquor as small light brown prismatic crystals together with many large (up to 25 mm) colourless needle-like crystals, which were not further characterized. The colour of the investigated crystals indicated the possible presence of Mn^{3+} ions, which were latter proved using the qualitative EDX analysis. However, their space group was identical and their unit-cell parameters were practically equal to the data published for $Na_3C_6H_5O_7 \cdot 2H_2O$ [4].

The crystal structure refinement showed that light brown crystals are actually $Na_3C_6H_5O_7 \cdot 2H_2O$, with the crystal structure essentially the same as published previously [4]. However, the compound contains about 0.01 mol of Mn^{3+} ions per formula unit. They were identified in the ΔF map as a maximum of only 1.25 e $Å^{-3}$. The coordination number of Mn^{3+} ions is six with the following Mn–O bond lengths: 1.1914(15) (×2), 2.149(6) (×2) and 2.584(10) (×2) Å. The MnO_6 polyhedron can be described as a strongly deformed octahedron, or optionally as an apex split square pyramid with tetrahedraly deformed basal plane. Mn^{3+} ions are moved out from the basal plane toward the apex of the pyramid.

Crystal data: $C_6H_9Mn_{0.01}Na_3O_9$, $Mr = 1004.26$, monoclinic system, space group $C2/c$, $a = 15.7070(3)$, $b = 12.4990(2)$, $c = 11.2710(2)$ Å, $\beta = 103.5990(10)°$, $V = 2150.71(7)$ $Å^3$, $Z = 8$, $F(000) = 1202$, $\rho_x = 1.820$ g cm^{-1}, $\mu = 0.279$ mm^{-1}, $S = 1.037$, $R_1 = 0.0289$ for 2508 reflections with $I > 2\sigma(I)$, $wR_2 = 0.0782$ for 2661 independent reflections and 202 refined parameters, $(\Delta/\sigma)_{max} < 0.001$, $\Delta\rho_{max} = 0.70$ e $Å^{-3}$, $\Delta\rho_{min} = -0.44$ e $Å^{-3}$.

[1] M. Počuča, G. Branković, Z. Branković, D. Vasiljević-Radović, D. Poleti, *J. Eur. Ceram. Soc.* **27** (2007) 1083.
[2] K. Đuriš, G. Branković, Z. Branković, M. Počuča, D. Poleti, *Mater. Sci. Forum* **555** (2007) 237.
[3] M. Pechini, US Patent 3,330,697, 1967.
[4] A. Fischera, G. Palladino, *Acta Cryst.* **E59** (2003) m1080.

STRUKTURA NATRIJUM-CITRATA-DIHIDRATA, $Na_3C_6H_5O_7\cdot 2H_2O$, DOPIRANOG Mn^{3+}-JONIMA

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Kompleksi limunske kiseline su važni međuproizvodi pri korišćenju modifikovane Pechini metode [1] za dobijanje materijala sa visokom električnom provodnošću, kao što su $LaNiO_3$ i $LaMnO_3$ [2,3]. Međutim, saznanja o citratnim kompleksima prelaznih elemenata i njihovoj strukturi vrlo su ograničena. Opisano jedinjenje nastalo je tokom pokušaja da se dobiju monokristali nekog Mn(III)-citrata iz jako alkalnog vodenog rastvora ($pH \approx 13$) u prisustvu NaOH. Tokom sporog uparavanja matičnog luga dobijeno je puno velikih (do 25 mm), igličastih i bezbojnih kristala koji nisu dalje okarakterisani i samo nekoliko manjih prizmatičnih kristala svetlo-mrke boje. Njihova boja ukazivala je na moguće prisustvo Mn^{3+}-jona, što je potvrđeno i kvalitativnom EDX-analizom. Međutim, prostorna grupa tih kristala bile je jednaka, a parametri jednične ćelije praktično identični ranije publikovanim podacima za $Na_3C_6H_5O_7\cdot 2H_2O$ [4].

Rešavanje kristalne strukture pokazalo je da se zaista radi o natrijumovoj soli limunske kiseline, $Na_3C_6H_5O_7\cdot 2H_2O$, čija se struktura suštinski ne razlikuje od ranije opisane [4]. Međutim, jedinjenje sadrži i oko 0,01 mol Mn^{3+}-jona po formulskoj jedinici, koji su identifikovani na osnovu maksimuma od samo 1,25 e Å^{-3} na ΔF-mapi. Joni Mn^{3+} imaju koordinacioni broj 6 sa dužinama Mn–O veza: 1,9514(15) (×2), 2,149(6) (×2) i 2,584(10) (×2) Å. Koordinacioni poliedar može se opisati kao jako deformisani oktaedar, ili kao kvadratna piramida sa rascepljenim vrhom i tetraedarski deformisanom osnovom, pri čemu su joni Mn^{3+} pomereni iz bazne ravni ka vrhu piramide.

Kristalografski podaci: $C_6H_9Mn_{0,01}Na_3O_9$, $M_r = 294{,}72$, monokliničan sistem, prostorna grupa $C2/c$, $a = 15{,}7070(3)$, $b = 12{,}4990(2)$, $c = 11{,}2710(2)$ Å, $\beta = 103{,}5990(10)^\circ$, $V = 2150{,}71(7)$ Å^3, $Z = 8$, $F(000) = 1202$, $\rho_x = 1{,}820$ g cm^{-3}, $\mu = 0{,}279$ mm^{-1}, $S = 1{,}037$, $R_1 = 0{,}0289$ za 2508 refleksija sa $I > 2\sigma(I)$, $wR_2 = 0{,}0782$ za 2661 nezavisne refleksije i 202 utačnjavana parametra, $(\Delta/\sigma)_{max} < 0{,}001$, $\Delta\rho_{max} = 0{,}70$ e Å^{-3}, $\Delta\rho_{min} = -0{,}44$ e Å^{-3}.

[1] M. Pechini, US Patent 3,330,697, 1967.

[2] M. Počuča, G. Branković, Z. Branković, D. Vasiljević-Radović, D. Poleti, *J. Eur. Ceram. Soc.* **27** (2007) 1083.

[3] K. Đuriš, G. Branković, Z. Branković, M. Počuča, D. Poleti, *Mater. Sci. Forum* **555** (2007) 237.

[4] A. Fischera, G. Palladino, *Acta Cryst.* **E59** (2003) m1080.

Grain size influence on dielectric permittivity of nanocrystalline zinc ferrite

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In this paper the grain size influence on dielectric permittivity of nanoparticle zinc-ferrite was examined. $ZnFe_2O_4$ was synthesized by sedimentation from liquid phase, and for the purpose of further examination heated to 773 K.

The obtained powders were scanned by Siemens D5000 difractometer in Bragg-Breantano geometry (Θ-2Θ), using ″step-scan″ technique in 10-80^0 2Θ angle range, at every 0.02^0. Counting time on each step was 15s, and intensity of monochromatic radiation had $CuK_{\alpha1}$:$CuK_{\alpha2}$=0.514 ratio.

Determined by FullProf computer programme, the average crystallite size was 21(4) and 81(6) Å for as prepared (S_1) and heated (S_2) sample, respectively.

Dielectric permittivety was measured in 300-630K temperature range, on 1 Hz, 10 Hz, 100 Hz, 1 kHz i 10 kHz frequencies, using Dielectric Analyzer 2970 (DEA 2970). Samples (tablets d=10 mm) were prepared by pressing to 500MPa.

Temperature dependence of permittivety of S_1 and S_2 samples on different frequencies are shown in Figures 1. i 2., respectively.

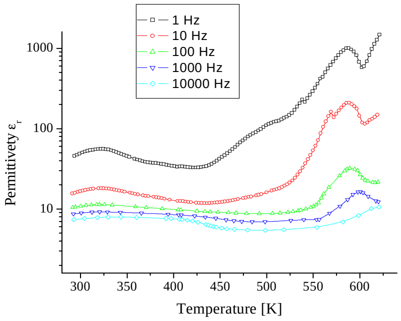

Figure 1.

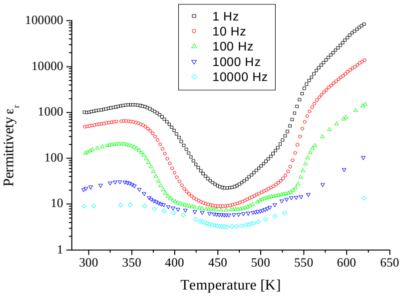

Figure 2.

The obtained values of permittivety in examined temerature and frequency region are significantly higher for S_1 samle than for S_2 sample. The first peaks of permittivety (caused by interfaced polarization) of S_1 sample are noticed in lower temperature interval (300-325K) than those of S_2 sample (350-375K). Registrated shift is consenquence of growth of grain size and decreased contact area. The second peak of S_1 sample (550-575K) refers to dipol polarization. Since grain size increasing of S_2 sample and the stabilization of the system ocuured, there is no peak refered to this type of polarization in observed temperature region.

Uticaj veličine zrna na vrednost dielektrične konstante nanokristalnog cink ferita

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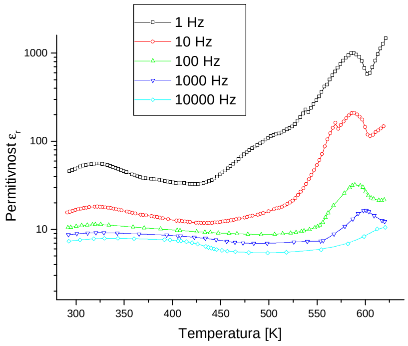
U ovom radu ispitivan je uticaj veličine zrna na vrednost dielektrične konstante nanočestičnog zink ferita. $ZnFe_2O_4$ dobijen je taloženjem iz tečne faze, i za potrebe daljeg istraživanja odgrejan na 773K .

Dobijeni prahovi su snimani pomoću difraktometra Siemens D5000 u Bragg-Breantano geometriji (Θ-2Θ), ″step-scan″ tehnikom u rasponu uglova 2Θ 10-80^0 i korakom $0{,}02^0$. Vreme zadržavanja na svakom koraku iznosilo je 15s, a intenzitet monohromatizovano zračenje je imao odnos $CuK_{\alpha1}$:$CuK_{\alpha2}$=0.514

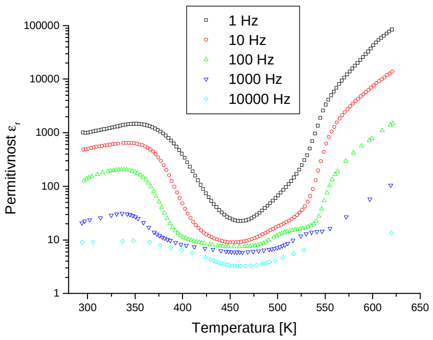
Primenom FullProf programa određena je srednja veličina kristalita koja je za neodgrejan (S_1) i odgrejan (S_2) uzorak iznosila 21(4) i 81(6) Å, respektivno.

Merenje dielektrične konstante uzraka je vršeno u opsegu 300-630K, na frekvencijama 1 Hz, 10 Hz, 100 Hz, 1 kHz i 10 kHz, pomoću uređaja Dielectric Analyzer 2970 (DEA 2970). Uzorci (tablete d=10 mm) su pripremljeni presovanjem na 500MPa.

Zavisnosti izmerenih vrednosti dielektrične konstante kod S_1 i S_2 uzorka na različitim frekvencijama prikazana je na slikama 1. i 2., respektivno.



Slika 1.



Slika 2.

Izmerene vrednosti dielektrične konstante u ispitivanom temperaturskom i frekventnom regionu kod S_1 uzorka značajno su veće nego kod S_2 uzorka. Kod S_1 uzorka prvi lokalni maksimumi merene veličine (uzrokovani međuslojnom polarizacijom) se uočavaju u nižem intervalu temperatura (300-325K) nego kod S_2 uzorka (350-375K). Uočeno pomeranje posledica je ukrupnjavanja zrna i smanjenja dodirnih površina između njih. Drugi maksimum kod S_1 uzorka (550-575K) odgovara dipolnoj polarizaciji. Kako je kod S_2 došlo do ukrupnjavanja zrna ali i do stabilisanja sistema u merenom opsegu nema maksimuma koji bi se pripisao ovoj vrsti polarizacije.

Unexpected appearance of doped and undoped γ-Bi_2O_3 phases in the same sample

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Metastable γ-Bi_2O_3 phase is one of five Bi_2O_3 polymorphs. Interest for this phase is motivated by its outstanding properties, which are a consequence of noncentrosymmetric space group (*I*23). Our previous research was focused on cations that could be used to stabilize γ-Bi_2O_3 phase at room temperature, and many practically single-phase samples with γ-Bi_2O_3 structure containing Co, Fe, Mn, Si, Pb, Ti, V or Zn as dopants have been successfully prepared [1]. However, three of them (Mn, Ti, V) showed some particularities.

In the simplest case, when dopants are M^{4+} ions, the formula of γ-phases is $Bi_{12}MO_{20}$, whereas for M^{5+} the formula is $Bi_{12}(M^{5+}_{0.8})O_{20}$. Hence, the "ideal" Bi:M molar ratio should be 12:1 for Mn- and Ti-, and 15:1 for V-doped samples. Our previous study [1] also showed that even smaller quantity of dopants could stabilize γ-Bi_2O_3 phase. The exceptional behaviour of the systems containing Mn^{4+}, Ti^{4+} or V^{5+} ions is their ability to give two different γ-Bi_2O_3 phases in the same sample with a smaller quantity of dopants.

In order to test this phenomenon two sets of syntheses were performed: one using the ideal Bi:M (M = Mn, Ti, V) molar ratios and other with half of an ideal dopant quantity. Six different mixtures of α-Bi_2O_3 and dopant oxides were homogenized in an agate mortar, heated at 750 ºC for 3 hours in an open Pt crucible and then annealed to room temperature. The products were characterized by XRPD, SEM/EDXS, SAED and HRTEM analysis.

The results listed in next table showed that the syntheses with ideal molar ratios produced only one γ-Bi_2O_3 phase, while the syntheses with half a quantity of dopants yielded the mixtures of two, γ_1 and γ_2 phases with different mass ratios (*w*).

Sample	$a(\gamma_1$-$Bi_2O_3)$/Å, *w*/wt.%	$a(\gamma_2$-$Bi_2O_3)$/Å, *w*/wt.%	Impurity, *w*/wt.%
$6Bi_2O_3 \cdot MnO_2$	10.221(1), 100	–	–
$12Bi_2O_3 \cdot MnO_2$	10.2181(6), 65	10.2627(7), 32	α-Bi_2O_3, 3
$6Bi_2O_3 \cdot TiO_2$	10.1839(6), 100	–	–
$12Bi_2O_3 \cdot TiO_2$	10.1874(6), 60	10.2630(7), 38	α-Bi_2O_3, 2
$15Bi_2O_3 \cdot V_2O_5$	10.2251(3), 100	–	–
$30Bi_2O_3 \cdot V_2O_5$	10.2310(7), 44	10.260(1), 56	–

It is obvious that γ_1-phases have similar unit cell parameters, *a*, as corresponding γ-phases obtained for ideal molar ratios, while the parameter of γ_2-phases is close to the parameter of undoped γ-Bi_2O_3 (10.268 Å). Hence, we can conclude that the produced mixtures consist of doped and undoped γ-Bi_2O_3. This is also confirmed by the results of SEM/EDXS, SAED and HRTEM analyses, which will be discussed in detail.

[1] D. Poleti, Lj. Karanović, A. Hadži-Tonić, *Z. Kristallogr,* **222** (2007) 59-72.

Neočekivana pojava dopirane i nedopirane γ-$\mathrm{Bi_2O_3}$ faze u istom uzorku

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Metastabilna γ-$\mathrm{Bi_2O_3}$ faza predstavlja jednu od pet polimorfnih modifikacija $\mathrm{Bi_2O_3}$. Izuzetne osobine ove faze, koje su posledica njene necentrosimetrične prostorne grupe (*I*23), motivisale su nas da je detaljnije proučimo. Naša ranija istraživanja svodila su se na određivanje koji to katjoni mogu stabilizovati γ-$\mathrm{Bi_2O_3}$ fazu na sobnoj temperaturi, pa su tako dobijeni mnogi jednofazni uzorci sa strukturom γ-$\mathrm{Bi_2O_3}$ dopirane sa Co, Fe, Mn, Si, Pb, Ti, V i Zn [1]. Međutim, tri dopanta (Mn, Ti, V) pokazala su specifično ponašanje.

U najprostijem slučaju, kada je dopant $\mathrm{M^{4+}}$-jon, formula γ-faze je $\mathrm{Bi_{12}MO_{20}}$, dok je za $\mathrm{M^{5+}}$-jon formula $\mathrm{Bi_{12}(M^{5+}{}_{0,8})O_{20}}$. Iz tog razloga idealni molski odnos Bi:M jednak je 12:1 za uzorke dopirane sa Mn ili Ti i 15:1 za uzorke dopirane sa V. Naša prethodna istraživanja [1] pokazala su da i manje količine dopanta mogu stabilizovati γ-$\mathrm{Bi_2O_3}$ fazu pa su upravo pri manjem sadržaju dopanta, sistemi sa $\mathrm{Mn^{4+}}$, $\mathrm{Ti^{4+}}$ ili $\mathrm{V^{5+}}$-jonima pokazali neočekivano ponašanje, dajući dve različite γ-$\mathrm{Bi_2O_3}$ faze u istom uzorku.

U nameri da se ispita ovaj fenomen izvršene su dve serije sinteza: jedna, sa idealnim molskim odnosom Bi:M (M = Mn, Ti, V) i druga, sa duplo manjom količinom dopanta od idealne. Šest različitih smeša α-$\mathrm{Bi_2O_3}$ i oksida dopanata homogenizovane su u ahatnom avanu, grejane tokom 3 h na 750 ºC u otvorenim Pt lončićima i potom sporo hlađene do sobne temperature. Proizvodi su okarakterisani XRPD, SEM/EDXS, SAED i HRTEM analizom.

Rezultati prikazani u sledećoj tabeli pokazuju da sinteze sa idealnim molskim odnosom daju samo jednu γ-$\mathrm{Bi_2O_3}$ fazu, dok sinteze sa upola manjom količinom dopanta daju smešu dve γ-faze, γ_1 i γ_2, sa različitim masenim odnosom (*w*).

Uzorak	*a*(γ_1-$\mathrm{Bi_2O_3}$)/Å, *w*/mas.%	*a*(γ_2-$\mathrm{Bi_2O_3}$)/Å, *w*/mas.%	Nečistoće, *w*/mas.%
$\mathrm{6Bi_2O_3{\cdot}MnO_2}$	10,221(1), 100	–	–
$\mathrm{12Bi_2O_3{\cdot}MnO_2}$	10,2181(6), 65	10,2627(7), 32	α-$\mathrm{Bi_2O_3}$, 3
$\mathrm{6Bi_2O_3{\cdot}TiO_2}$	10,1839(6), 100	–	–
$\mathrm{12Bi_2O_3{\cdot}TiO_2}$	10,1874(6), 60	10,2630(7), 38	α-$\mathrm{Bi_2O_3}$, 2
$\mathrm{15Bi_2O_3{\cdot}V_2O_5}$	10,2251(3), 100	–	–
$\mathrm{30Bi_2O_3{\cdot}V_2O_5}$	10,2310(7), 44	10,260(1), 56	–

Očigledno je da γ_1-faze imaju parameter ćelije, *a*, sličan parametru odgovarajućih γ-faza dobijenih za idealni molski odnos, dok je parametar γ_2-faze blizak parametru nedopiranog γ-$\mathrm{Bi_2O_3}$ (10,268 Å). Stoga se može zaključiti da dobijena smeša sadrži i dopiran i nedopiran γ-$\mathrm{Bi_2O_3}$. Ovo je potvrđeno rezultatima SEM/EDXS, SAED i HRTEM analiza, koji će biti detaljno prikazani i diskutovani.

[1] D. Poleti, Lj. Karanović, A. Hadži-Tonić, *Z. Kristallogr,* **222** (2007) 59-72.

NONCOVALENT π TYPE INTERACTIONS IN CRYSTAL STRUCTURES OF bis(ARENE)-METAL COMPLEXES

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Metal ions, atoms, surfaces and compounds interact with aromatic hydrocarbons and often form stable complexes through overlap of the ring π and π^* orbitals with appropriate orbitals of the metal atom. Hein and his co-workers isolated the first molecular arene-metal complexes in 1919, but definitive compositional and structural characterization of these complexes was not achieved until the mid-fifties. *Bis*(arene)-metal complexes are compounds in which a metal atom is coordinated by two planar and parallel (or nearly parallel) molecules of aromatic hydrocarbons. These complexes are also known as "sandwich" complexes.

There is intensive research of noncovalent interactions involving π-systems. It was shown that these interactions are very important for many biological molecules. Analyzing CH/π interactions in proteins shows that these interactions play an important role in the stability of proteins.

Bis(arene)-metal complexes can be involved in three different types of noncovalent interactions. Due to coordination electron density is transferred from aromatic molecules to metal atom leaving hydrogen atoms from aromatic molecules more positive. These hydrogen atoms can be involved in strong CH/π interactions. Calculations of magnetic properties of arene-metal complexes have shown that complexation to metal atom does not reduce the aromaticity of arene ligand so it can be involved in XH/π (X=O, N, C) interactions as hydrogen atom acceptor. Also, because of high symmetry and delocalized electrons we can expect existence of strong stacking interactions in crystal structures of sandwich complexes.

Cambridge Structural Database (CSD) search has been performed for all structures where *bis*(arene)-metal complexes are involved in CH/π interactions either as hydrogen atom donors or as π systems. The search was done for two types of *bis*(arene)-metal complexes: complexes with benzene molecules as aromatic ligands and complexes with cyclopentadienyl anions as aromatic ligands.

By searching CSD we found a number of compounds with CH/π interactions in crystal structures of *bis*(arene)-metal complexes. The results have shown that there is a larger number of CH/π interactions in complexes with cyclopenadyenil anion as a ligand. Also, the search has shown that complexes with coordinated cyclopentadienyl anions are better hydrogen atom acceptors, while complexes with coordinated benzene molecules are better hydrogen atom donors in CH/π interactions.

[1] M.K. Milčić, V.B. Medaković, D.K. Sredojević, N. Juranić, S.D.Zarić, Inorg. Chem. 45 (2006) 4755.

NEKOVALENTNE INTERAKCIJE π TIPA U KRISTALNIM STRUKTURAMA *bis*(AREN) KOMPLEKSIMA METALA

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Joni, atomi, površina i jedinjenja metala interaguju sa aromatičnim ugljovodonicima i grade stabilne komplekse preklapanjem π i π^* orbitala prstena sa odgovarajućim orbitalama atoma metala. Ovi aren-kompleksi metala prvi put su sintetisani još 1919. godine, ali su tek pedesetih godina prošlog veka i strukturno okarakterisani. *Bis*(aren)-kompleksi metala su kompleksi u kojima su dva planarna i paralelna (ili skoro paralelna) aromatična ugljovodonika vezana za atom metala. Ovakvi kompleksi se nazivaju još i „sendvič“ kompleksi.

Nekovalntne interakcije u π sistemima mnogo su proučavane u poslednjih dvadesetak godina[1]. Pokazano je da su ove interakcije veoma važne u biološkim molekulima, kao na primer CH/π interakcije, koje imaju veoma značajnu ulogu u stabilizaciji nativne konformacije proteina.

Bis(aren)-kompleksi mogu graditi tri različite vrste nekovalentnih interakcija π tipa. Zbog prelaska elektronske gustine sa aromatičnog liganda na atom metala vodonici aromatičnog molekula postaju pozitivniji i mogu graditi jače CH/π inteakcije nego nekoordinovani aromatični molekul. Najnoviji proračuni magnetnih osobina pokazali su da aromatični ligand koordinacijom zadržava (i u nekim slučajevima pojačava) svoje aromatične osobine tako da može učestvovati u XH/π (X=O, N, C) interakcijama kao akceptor vodonikovog atoma. Takođe, zbog toga što poseduju visoku simetriju i delokalizovane elektrone očekuje se da u kristalnim strukturama ovih sendvič kompleksa mogu postojati jake steking interakcije između susednih molekula kompleksa ili između molekula kompleksa i aromatičnih molekula rastvarača.

Kembrička banka kristalografskih podataka (CSD) pretražena je na sve strukture u kojima *bis*(aren)-kompleksi metala učestvuju u CH/π interakcijama, bilo kao donori vodonikovog atoma, bilo kao π sistemi. Pretraga je urađena za dve vrste bis(aren)-kompleksa: komplekse u kojima je arenski ligand molekul benzena i komplekse u kojima je arenski ligand ciklopentadienilni anjon.

Pretragom kristalografske banke podataka nađen je veliki broj struktura u kojima postoje CH/π interakcije u *bis*(aren)-kompleksima. Rezultati pretrage su pokazali da postoji veći broj CH/π interakcija u kompleksima u kojima je ligand ciklopentadienilni anjon. Takođe, na osnovu broja pronađenih struktura može se videti da su kompleksi sa koordinovanim ciklopentadienilnim anjonom bolji akceptori vodonikovog atoma, dok su kompleski sa koordinovanim molekulom benzena bolji donori vodonikovog atoma u CH/π interakcijama.

[1] M.K. Milčić, V.B. Medaković, D.K. Sredojević, N. Juranić, S.D.Zarić Inorg. Chem. 45 (2006) 4755.

POSTER PRESENTATIONS
ПОСТЕРСКА СЕКЦИЈА

COMPARISON OF OH/π INTERACTIONS OF COORDINATED AND NONCOORDINATED WATER MOLECULE

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Large number of studies of noncovalent interactions involving π-systems in many areas of chemistry, biochemistry and molecular biology as well as importance of water molecule in these systems motivated us to study noncovalent interactions between π-systems of aryl group and water molecule. Water involved in OH/π interactions can be noncoordinated or coordinated to a metal atom. Coordination of water molecule to a metal atom has important influence on OH/π interactions [1], hence, these interactions are named metal ligand OH/π interactions or MLOH/π interactions.

The crystal structures containing water molecule and C_6-aromatic group were obtained from Cambridge Structural Database (CSD). The structures of these complexes were screened for intermolecular OH/π interactions using geometrical criteria. We searched for structures in which the distance between a hydrogen atom of aqua ligand and the center (Ω) of any phenyl ring was shorter than 3.5 Å, the angle O-H-Ω was less than 110º, and the angle between H-Ω line and the normal on the ring plane was less than 30º.

By searching crystal structures from CSD we found 84 structures with 102 intermolecular interactions where aqua ligand is hydrogen atom donor while π-system of C6-aromatic ring is acceptor (MLOH/π interactions), and 248 structures with 278 intermolecular interactions where water molecule is hydrogen atom donor (OH/π interactions). The geometries of MLOH/π and OH/π interactions were analyzed. The analysis showed that charge of the aqua complex has important influence on MLOH/π interactions, and that interactions of coordinated water molecule are stronger than interactions of noncoordinated.

[1] M. K. Milčić, Z. D. Tomić, S. D. Zarić, Inorg. Chim. Acta, 357, (2004), 4327-4329.

POREĐENJE OH/π INTERAKCIJE KOORDINOVANOG I NEKOORDINOVANOG MOLEKULA VODE

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Veliki broj istraživanja nekovalentnih interakcija, u kojima učestvuju π-sistemi, u oblasti hemije, biohemije i molekularne biologije, kao i izuzetan značaj i prisustvo vode u svim ovim sistemima, motivisali su nas da ispitamo nekovalentne interakcije između π-sistema aril grupe i vode. Voda koja gradi OH/π interakcije može biti nekoordinovana i koordinovana. Koordinovanje vode za metal ima velikog uticaja na OH/π interakcije [1], pa se zbog toga interakcije zovu metal ligand OH/π interakcije ili MLOHπ interakcije.

Kristalne strukture koje sadrže molekul vode, bilo koordinovan za metalni jon, bilo nekoordinovan, i C_6-aromatičnu grupu, pronađene su pretraživanjem Kembridžke kristalografske banke podataka (CSD). Korišćenjem geometrijskih kriterijuma u ovim strukturama su pronađene OH/π interakcije. Analizirali smo samo one strukture kod kojih je rastojanje između vodonikovog atoma, iz molekula vode, i centra aril grupe (Ω) manje od 3.5Å, ugao O-H-Ω manji od 110º, a ugao koji zaklapa duž H-Ω sa normalom na ravan prstena manji od 30º.

Pretraživanjem CSD dobijeno je 84 strukture, sa 102 intermolekulske interakcije, u kojima je akva ligand donor vodonikovog atoma, dok π-sistem C6-aromatičnog prstena je akceptor (MLOH/π interakcije), i 248 struktura, sa 278 intermolekulskih interakcija, u kojima je nekoordinovan molekul vode donor vodonikovog atoma (OH/π interakcije). Analizirane su geometrije MLOH/π i OH/π interakcija. Ova analiza je pokazala da naelektrisanje akva kompleksa ima značajnog uticaja na MLOH/π interakcije i da su interakcije koordinovanog molekula vode jače od interakcija nekoordinovanog molekula vode.

[1] M. K. Milčić, Z. D. Tomić, S. D. Zarić, Inorg. Chim. Acta, 357, (2004), 4327-4329.

STACKING INTERACTIONS IN CRYSTAL STRUCTURES OF BIPYRIDYL METAL COMPLEXES

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It was shown that in structures of metal complexes there are specific types of noncovalent interactions involving π-systems. Hence, in the structures of metal complexes there are stacking interactions involving organic aromatic fragments, however, in stacking interactions can be also involved planar chelate rings with delocalized π-systems [1,2]. Since in bipyridyl complexes there are organic aromatic as well as planar chelate rings that can be involved in stacking interactions, we studied stacking interactions in crystal structures of bipyridyl metal complexes.

By searching Cambridge Structural Database (CSD), crystal structures that contain bipyridyl fragment coordinated to a metal were found; there are 322 of such structures in CSD. Analysis of geometrical parameters in the crystal structures indicate stacking interactions between bipyridyl ligands coordinated to a metal atom. However, bipyridyl ligand can be involved in stacking interactions with some other fragments.

The results indicate that in most of the structures two interacting complexes are oriented in the way that are two bipyridyl ligands are one above another (value of torsion angle is 0°) (Figure 1.a), or two bipyridyl groups can be oriented in the way that value of torsion angle is 180° (Figure 1.b).

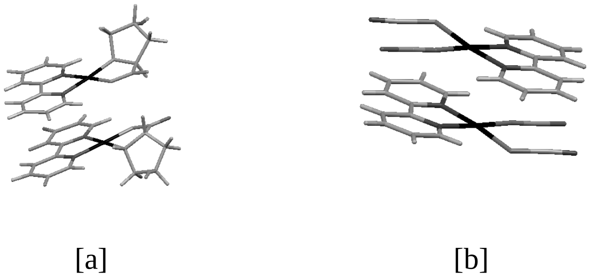

Figure 1. Strucutres with torsion angle 0° [a] and torsion angle 180° [b]

[1] Zoran D. Tomić, Dušan N. Sredojević, Snežana D. Zarić, Crystal Growth & Design, 2006, 6, 29-31.
[2] Dušan N. Sredojević, Zoran D. Tomić, Snežana D. Zarić, Central European Journal of Chemistry, 2007, 5, 20-31.

STEKING INTERAKCIJE U KRISTALNIM STRUKTURAMA BIPIRIDINSKIH KOMPLEKSA METALA

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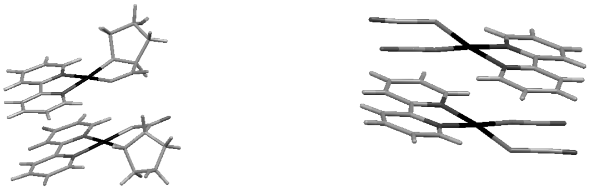
Pokazano je da u strukturama kompleksa metala postoje specifični tipovi nekovalentnih interakcija u koje su uključeni π-sistemi. Tako u strukturama kompleksa metala postoje steking interakcije u koje su uključeni oraganski aromatični fragmenti, ali u steking interakcije mogu da budu uključeni i planarni helatni prstenovi sa delokalizovanim π-sistemom [1,2]. S obzirom da u bipiridinskim kompleksima postoje i organski aromatični fragmenti i helatni prstenovi koju mogu biti uključeni u interakcije, mi smo proučavali staking interakcije u kristalnim strukturama bipiridinskih kompleksa.

Kristalne strukture koje sadrže bipiridinski fragment koordinovan za bilo koji metal pronađene su pretraživanjem Kembridžke kristalografske banke podataka (CSD); pronadjeno je 322 takvih kristalnih struktura. Analiza geometrijskih parametara u kristalnim strukturama ukazuje na postojanje steking interakcija između bipiridinskih fragmenata kordinovanih za metal. Međutim, bipiridinski fragment može biti uključen u staking interakcije i sa drugim fragmentima

Dobijeni podaci ukazuju da su kod najvećeg broja struktura dva susedna kompleksa orjentisana tako da su bipiridinski fragmenti jedan iznad drugog, gde je torzioni ugao 0° (slika 1.a), ili tako da su jedan nasuprot drugog, gde je torzioni ugao 180° (slika 1.b).



[a] [b]

Slika 1. Prikaz dve strukture sa torzionim uglom 0° [a] i torzionim uglom 180° [b]

[1] Zoran D. Tomić, Dušan N. Sredojević, Snežana D. Zarić, Crystal Growth & Design, 2006, 6, 29-31.
[2] Dušan N. Sredojević, Zoran D. Tomić, Snežana D. Zarić, Central European Journal of Chemistry, 2007, 5, 20-31.

STRUCTURAL PROPERTIES OF STACKING INTERACTION BETWEEN PYRAZOLE RINGS

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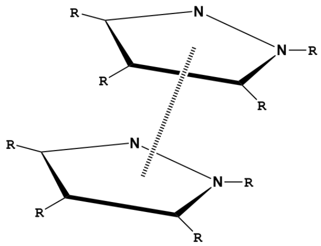
One of the fundamental problems in chemistry of solid state is determination of factors relevant for the association of molecules into the crystal structure. This process is largely determined by the energetic and structural properties of the intermolecular interactions between the molecules in question. The role of interactions between cyclic aromatic systems (*stacking* interactions), in the association of molecules has been documented in a number of examples. However, in spite of the large amount of data, there is no clear description of structural parameters relevant for the stacking arrangement of molecules. In the case of pyrazolyl molecules, it is especially evident in inability to differentiate π-π interaction between pyrazole rings and interaction between supstituents on pyrazoles. It is important to note that both type of contacts lead to the similar arrangement of molecules, i.e. the *stacking* contacts.

In this work we are presenting database study (by using the Cambridge Structural Data Bank) of the intermolecular contacts between the pyrazole rings (figure below illustrate the intermolecular contacts between the pyrazole rings). In most of the investigated structures, ring-ring distance and dihedral angle between the ring planes, is in accordance with the presence of interaction between the pyrazole rings. It was found that absence of stacking contacts is associated with the presence of voluminous groups attached on the pyrazole rings. Larger overlap between the closest pyrazole rings lead to shorter ring-ring distance. Stacking contacts are observed in the '*normal height*' range of 3-4 Å. The value of torsion angle associated with the mutual orientation of the closest pyrazolyl N-N bonds tends to have values of 0 and 180°. It was found that this property is not related to the position and properties of the pyrazole substituents.

We found geometrical criteria for differentiation of stacking arrangements caused by the ring-ring interactions, and those associated with the interactions between substituents on pyrazole rings.



STRUKTURNA SVOJSTVA *STACKING* INTERAKCIJA IZMEĐU PIRAZOLOVIH PRSTENOVA

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Jedan od osnovnh problema u hemiji čvrstog stanja je utvrđivanje činioca koji određuju način udruživanja molekula i formiranje uređene kristalne strukture. Ovaj proces je u velikoj meri određen energetskim i strukturnim svojstvima međumolekulskih interakcija koje ispitivani molekuli mogu da ostvare.

Jedna vrsta slabih interakcija čija se uloga u udruživanju molekula dosta ispituje u poslednje vreme su interakcije između cikličnih aromatičnih sistema, *stacking* interakcije. I pored velikog broja primera koji ukazuju na njihov značaj za obrazovanje uređene kristalne strukture, u literaturi nedostaje potpuniji opis strukturnih svojstava koji se odnose na takve međumolekulske kontakte. Kod pirazolnih molekula, ovo se posebno odnosi na definisanje strukturnih kriterijuma koji bi omogućili razlikovanje π-π interakcija između pirazolovoh prstenova od interakcija koje se ostvaruju između njihovih substitenata. Pri čemu treba naglasiti da obe vrste kontakata dovode do formiranja *stacking* rasporeda molekula.

U ovom radu su izloženi rezultati analize strukturnih svjstava međumolekuslih pirazol-pirazol kontakata. Kembridžka Banka Kristalografkslh podataka je sistematski pretražena i izdvojene su informacije koje se odnose na strukturna svojstva pirazol-piarzol kontakta, kod kristalnih struktura koje ne sadrže druge aromatske sisteme.

Analiza raspodele rastojanja između centara pirazolovih prstenova i uglova između ravni prstenova je pokazala da u najvećem broju slučajeva postoji *stacking* interakcija između pirazolovih molekula. Za strukture kod kojih ne postoji *stacking* kontakt utvrđeno je da sadrže voluminozne grupe. Varijacija rastojanja između prstenova i stepena njihovog preklapanja kod struktura kod kojih postoji *stacking*, pokazala je da postoji korelacija između ova dva parametra tj. da veće preklapanje dovodi i do jače interakcije. Utvrđeno je da do *stacking* rasporeda u najvećem broju slučajeva dolazi kada je normalna visina u opsegu 3-4 Å. Torzioni ugao koji opisuje međusobnu orjentaciju N-N veza ima vrednosti bliske 0 i 180° . Na osnovu analize položaja i vrste supstituenata utvrdili smo da se položaj i svojstva supstituenata ne razlikuju bitno kod struktura sa različitom međusobnom orjentacijom N-N veza.

Ova analiza je ukazala i na geometrijske kriterijume koji omogućavaju razlikovanje *stacking* uređenja kod koga postoje interakcije pirazolnih prstenova od *stacking* uređenja koje je posledica interakcija između substituenata na pirzolovim prstenovima.

CRYSTAL STRUCTURE OF BIS(2-QUINOLINECARBOXALDEHYDE SELENOSEMICARBAZONATO)NICKEL(II)

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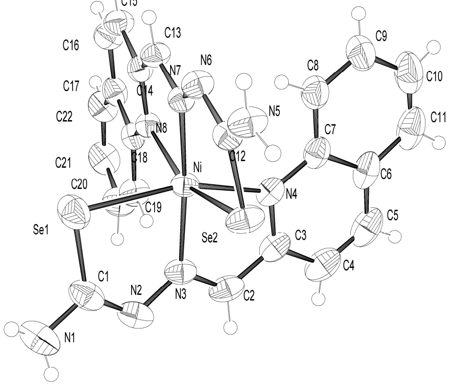
The title complex was synthesized by reaction of nickel acetate tetrahydrate with 2-quinolinecarboxaldehyde selenosemicarbazone (Hqasesc) in equimolar ratio in ethanol, and purified by vapour diffusion using the DMSO solution as an inner solution and ethanol as an outer solvent. Single crystal X-ray analysis showed that two deprotonated qasesc^{-} ligands coordinate the metal in a tridentate fashion, *via* NNSe donor atom set, giving the angularly distorted octahedral complex [Ni(qasesc)$_2$]·2DMSO with four chelate rings. The ligand skeletons are essentially planar within 0.08 and 0.12 Å for C1−C11−N1−N4 and C12−C22−N5−N8, respectively. The selenium atoms, Se1 and Se2, deviate slightly from the mean planes by 0.14 and 0.32 Å, respectively.



Crystallographic data: $C_{26}H_{30}N_8NiO_2S_2Se_2$, M_r = 767.33, triclinic system, space group $P\bar{1}$, a = 10.4907(8), b = 10.8951(8), c = 15.036(1) Å, α = 92.330(1), β = 94.134(1), γ = = 116.412(1)°, V = 1530.1(2) Å^3, Z = 2, $F(000)$ = 772, D_c = 1.665 Mg m^{-3}, μ(Mo $K\alpha$) = = 3.188 mm^{-1}, R_1 = 0.0286 (wR_2 = 0,0689) for 7359 reflections with $I > 2\sigma(I)$.

KRISTALNA STRUKTURA BIS(2-HINOLINKARBOKSALDEHID SELENOSEMIKARBAZONATO)NIKLA(II)

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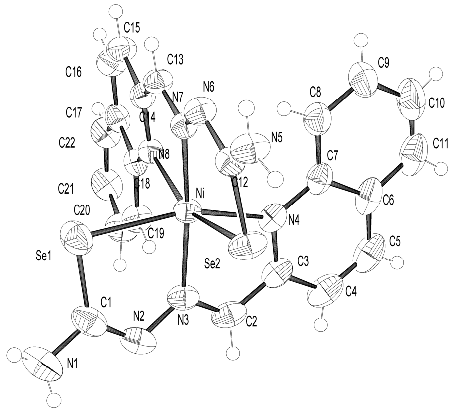
Kompleks bis(2-hinolinkarboksaldehid selenosemikarbazonato)nikl(II) sintetisan je reakcijom ekvimolarnih količina nikl(II)-acetat-tetrahidrata i 2-hinolinkarboksaldehid-selenosemikarbazona (Hqasesc) u etanolu, a prečišćen je difuzijom para etanola kao spoljašnjeg rastvarača u DMSO rastvor kompleksa. Rendgenska strukturna analiza je pokazala da su dva deprotonovana qasesc$^-$ liganda koordinovana tridentatno, preko NNSe seta donorskih atoma, gradeći kompleks [Ni(qasesc)$_2$]·2DMSO ugaono deformisane oktaedarske geometrije sa četiri helatna prstena. Liganadi su u osnovi planarni, pri čemu odstupanje od srednjih ravni iznosi 0,08 i 0,12 Å za C1−C11−N1−N4 i C12−C22−N5−N8, respektivno. Atomi Se1 i Se2 takođe pokazuju neznatno odstupanje od srednjih ravni (0,14 i 0,32 Å, respektivno).



Kristalografski podaci: $C_{26}H_{30}N_8NiO_2S_2Se_2$, $M_r = 767{,}33$, triklinični sistem, prostorna grupa $P\bar{1}$, $a = 10{,}4907(8)$, $b = 10{,}8951(8)$, $c = 15{,}036(1)$ Å, $\alpha = 92{,}330(1)$, $\beta = 94{,}134(1)$, $\gamma = 116{,}412(1)^\circ$, $V = 1530{,}1(2)$ Å^3, $Z = 2$, $F(000) = 772$, $D_c = 1{,}665$ Mg m^{-3}, μ(Mo $K\alpha$) = $3{,}188$ mm^{-1}, $R_1 = 0{,}0286$ ($wR_2 = 0{,}0689$) za 7359 refleksija koje zadovoljavaju uslov $I > 2\sigma(I)$.

CRYSTAL STRUCTURE OF DICHLORO-{ETHYL (*E*)-2-[*N*'-(1-PYRIDIN-2-YL-ETHYLIDENE)HYDRAZINO]ACETATE} COPPER(II)

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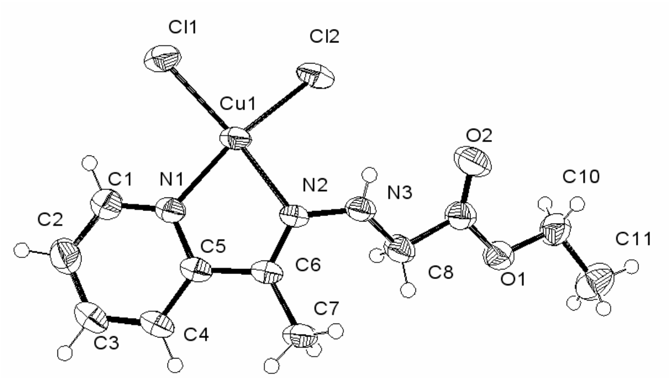
The title complex, [$CuCl_2$(aphaoet)] (aphaoet = ethyl (*E*)-2-[*N*'-(1-pyridin-2-yl-ethylidene)hydrazino]acetate), was synthesized by template reaction of equimolar quantities of ethyl hydrazinoacetate hydrochloride, 2-acetylpyridine and copper(II) perchlorate hexahydrate in 95 % ethanol. The structure of the complex was determined by X-ray structural analysis. The ligand aphaoet coordinates the Cu(II) in a bidentate fashion, *via* the pyridine and the *N'* hydrazone nitrogen atoms, while two remaining coordination sites are occupied by the chloride ions. The obtained complex has a tetrahedrally distorted square-planar geometry.



Crystallographic data: $C_{11}H_{15}Cl_2CuN_3O_2$, M_r = 355.7, triclinic system, space group $P\bar{1}$, a = = 7.2437(9), b = 9.0418(9), c = 11.7914(11) Å, α = 96.947(2), β = 102.856(3), γ = 106.879(4)°, V = 706.10(13) Å^3, Z = 2, μ(Mo $K\alpha$) = 1.925 mm^{-1}. The structure was solved using the SHELXS-97, and refined using the SHELXL-97. The final R-value, for 4286 reflexions with $I > 2\sigma(I)$, was 4.48 %.

KRISTALNA STRUKTURA DIHLORO-{ETIL (*E*)-2-[*N*'-(1-PIRIDIN-2-IL-ETILIDEN)HIDRAZINO]ACETAT} BAKRA(II)

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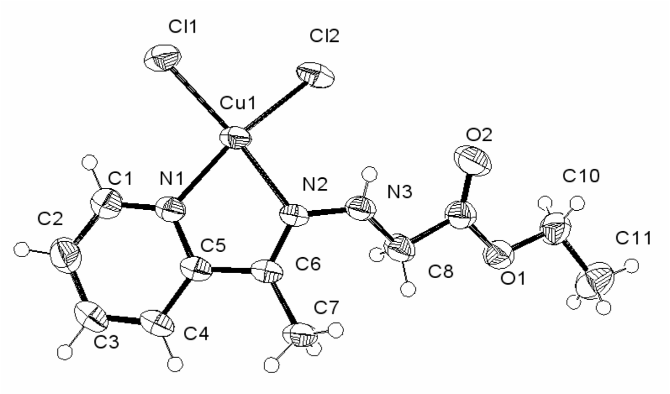
Templatnom reakcijom ekvimolarnih količina etil-hidrazinoacetat-hidrohlorida, 2-acetilpiridina i bakar(II)-perhlorat-heksahidrata, u 95% etanolu, dobiven je kompleks [CuCl$_2$(aphaoet)] (aphaoet = etil (*E*)-2-[*N*'-(1-piridin-2-il-etiliden)hidrazino]acetat). Struktura kompleksa određena je rendgenskom strukturnom analizom. Ligand aphaoet koordinovan je bidetnatno za Cu(II), preko piridinskog i hidrazonskog atoma azota, dok preostala dva koordinaciona mesta zauzimaju hloridni joni. Dobiveni kompleks je tetraedarski deformisane kvadratno-palanarne geometrije.



Kristalografski podaci: $C_{11}H_{15}Cl_2CuN_3O_2$, M_r = 355,7, triklinični sistem, prostorna grupa $P\bar{1}$, a = 7,2437(9) Å, b = 9,0418(9), c = 11,7914(11), α = 96,947(2), β = 102,856(3), γ = = 106,879(4)°, V = 706,10(13) Å^3, Z = 2, μ(Mo $K\alpha$) = 1,925 mm^{-1}. Struktura je rešena pomoću programa SHELXS-97, a utačnjena programom SHELXL-97. Konačna vrednost R-faktora, za 4286 refleksija sa $I > 2\sigma(I)$, iznosi 4,48 %.

CRYSTAL STRUCTURE OF A DINUCLEAR Cd(II) COMPLEX WITH *N',N'*^{2}-BIS[(1*E*)-1-(2-PYRIDYL)ETHYLIDENE]PROPANEDIHYDRAZIDE

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By reaction of equimolar quantities of $Cd(ClO_4)_2 \cdot 6H_2O$ with the ligand *N',N'*^{2}-bis[(1*E*)-1-(2-pyridyl)ethylidene]propanedihydrazide (H_2L) in ethanol, the binuclear Cd(II) complex, $[Cd_2(H_2O)_2(H_2L)_2](ClO_4)_4 \cdot 4H_2O$, was obtained. The structure of the complex was determined by X-ray structural analysis. Both Cd(II) ions are located in a pentagonal bipyramidal environment, where each ligand arm is tridentately coordinated *via* the pyridine and imine nitrogens and the hydrazide carbonyl. Each cadmium is surrounded by two ligand arms making three chelate rings, and the heptacoordination is completed by a water molecule. The pentagonal plane of the bipyramidal coordination is constituted by three NNO donors from one ligand, the imine nitrogen of the other ligand, and the water molecule. The intramolecular Cd…Cd separation is 7.1Å.

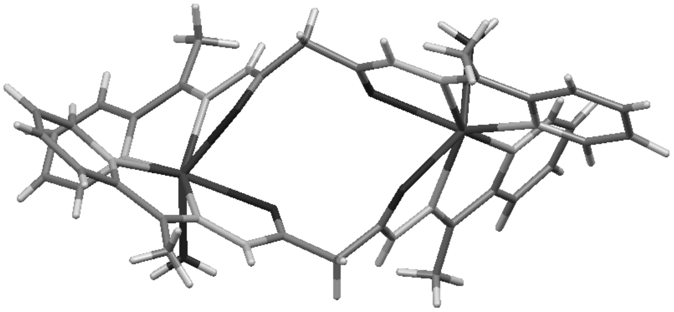

Figure 1. Crystal structure of $[Cd_2(H_2O)_2(H_2L)_2](ClO_4)_4 \cdot 4H_2O$

Crystallographic data: $C_{17}H_{24}CdCl_2N_6O_{13}$, $M_r = 703.72$, monoclinic system, space group $P2_1/n$, $a = 16.658(5)$, $b = 19.043(5)$, $c = 16.918(5)$ Å, $\beta = 94.51(2)°$, $V = 5350(3)$ Å^3, $Z = 8$, $F(000) = 2832$, $D_c = 1.747$ Mg m^{-3}, μ(Mo Kα) = 1.090 mm^{-1}, $R_1 = 0.0558$ ($wR_2 = 0.1210$) for 15595 reflections with $I > 2\sigma(I)$.

KRISTALNA STRUKTURA DINUKLEARNOG KOMPLEKSA Cd(II) SA *N'*,*N'*^{2}-BIS[*(*1*E)*-1-*(*2-PIRIDIL*)*ETILIDEN]PROPANDIHIDRAZIDOM

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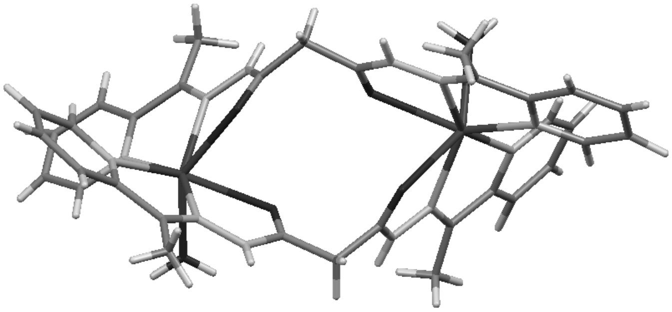
Reakcijom ekvimolarnih količina $Cd(ClO_4)_2 \cdot 6H_2O$ i *N',N'*^{2}-bis[(1*E*)-1-(2-piridil)etiliden]propandihidrazida (H_2L) u etanolu dobiven je binuklearni kompleks Cd(II), $[Cd_2(H_2O)_2(H_2L)_2](ClO_4)_4 \cdot 4H_2O$. Struktura kompleksa određena je rendgenskom strukturnom analizom. Oba Cd(II)-jona nalaze se u pentagonalno-bipiramidalnom okruženju, pri čemu je svaki bočni lanac liganda koordinovan tridentatno preko piridinskog i iminskog atoma azota i hidrazidnog karbonilnog kiseonika. Svaki kadmijum je okružen sa dva bočna lanca liganda koji grade tri helatna prstena, a heptakoordinacija je kompletirana molekulima vode. Pentagonalna ravan sastoji se od tri NNO donora jednog liganda, iminskog azota drugog liganda i molekula vode. Intramolekulsko rastojanje Cd…Cd iznosi 7,1Å.



Slika 1. Kristalna struktura $[Cd_2(H_2O)_2(H_2L)_2](ClO_4)_4 \cdot 4H_2O$

Kristalografski podaci: $C_{17}H_{24}CdCl_2N_6O_{13}$, M_r = 703,72, monoklinični sistem, prostorna grupa $P2_1/n$, a = 16,658(5), b = 19,043(5), c = 16,918(5) Å, β = 94,51(2)°, V = = 5350(3) Å^3, Z = 8, F(000) = 2832, D_c = 1,747 Mg m^{-3}, μ(Mo $K\alpha$) = 1,090 mm^{-1}, R_1 = = 0,0558 (wR_2 = 0,1210) za 15595 refleksija koje zadovoljavaju uslov $I > 2\sigma(I)$.

NONCOVALENT INTERACTIONS WITH PORPHYRIN RING IN PORPHYRIN CONTAINING PROTEINS

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Hydrogen bonds, salt bridges and hydrophobic interactions are considered to play major role in protein stability; however, recent studies showed that weaker XH/π interactions also play a role in protein stability [1-3].

In order to find out all noncovalent interactions of porphyrins in proteins we searched structures of porphyrin containing proteins from the Protein Data Bank (PDB) Select January 2007, the list of non-redundant protein chains (25% threshold). The results revealed that the significant number of conventional hydrogen bonds with acethyl and propionate groups of porphyrins was founded. The most frequently observed donors are charged amino acid residues from porphyrin surrounding. Side-chains hydrogen bonds are more frequent than those with peptide donors; they involve water molecules sometimes that are classified as bridged hydrogen bonds. Besides, π-system of every porphyrin ring is involved in XH/π interactions, most of the porphyrins are making several interactions. We found interactions with C-H and N-H groups as hydrogen atom donors, however, the number of CH/π interactions is much larger than number of NH/π interactions. Both five-membered pyrol rings and six-membered chelate rings are involved in noncovalent interactions; the number of interactions with five-membered is larger than the number of the interactions with six-membered rings. Hydrophobic interactions between amino acid residues and porphyrin rings were also found.

The conservation scores were calculated for all amino acids in the binding pocket The average conservation score for the amino acids making noncovalent interactions with the porphyrin is statistically significantly higher than for the amino acids that do not make interactions.

The results show that every porphyrin is involved in a number of noncovalent interactions. High conservation score of amino acids that are involved in these interactions is a strong argument for their importance.

[1] M. Brandl et al., J.Mol.Biol. (2001), 307:357-377
[2] T. Steiner and G. Koellner, J.Mol.Biol. (2001), 305:535-557
[3] S. Stojanović et al., J.Biol.Inorg.Chem. (2007), *in press*

NEKOVALENTNE INTERAKCIJE PORFIRINSKOG PRSTENA U PROTEINIMA KOJI SADRŽE PORFIRIN

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Smatra se da vodonične veze, soni mostovi i hidrofobne interakcije imaju glavnu ulogu u stabilnosti proteina, međutim, nedavna proučavanja pokazuju da slabe XH/π interakcije takođe doprinose stabilnosti proteina [1-3].

Za ova istraživanja je korišćena proteinska baza podataka (PDB Select) iz janura 2007. ne-redundantna lista (verzija 25%). Rezultati pokazuju prisustvo značajnog broja konvencionalnih vodoničnih veza acetatnih i propionatnih grupa porfirinskih prstenova. Najučestaliji donori su naelektrisani ostaci aminokiselina iz okoline porfirinskog prstena. Vodonične veze bočnih ostataka aminokiselina su učestalije od istih sa donorima iz peptidnih veza; one ponekad uključuju molekule vode i klasifikuju se kao umrežene vodonične veze. Osim toga, π-sistem svakog porfirinskog prstena je uključen u XH/π interakcije, mnogi od njih grade i nekoliko interakcija. Pronađene su interakcije sa C-H i N-H grupama kao donorima, pri čemu je broj CH/π interakcija znatno veći od broja NH/π interakcija. U nekovalentne interakcije su uključeni petočlani i šestočlani helatni prstenovi; dok je broj interakcija sa petočlanim prstenovima znatno veći. Takođe su pronađene hidrodobne interakcije između aminokiselinskih ostataka i porfirinskih prstenova.

Određen je indeks konzervativnosti aminokiselina koje se nalaze u vezivnom mestu porfirina. Indeks konzervativnosti aminokiselina koje grade nekovalentne interakcije sa porfirinima su statistički značajno povećani u odnosu na aminokiseline koje ne grade interakcije.

Rezultati pokazuju da je svaki porfirin uključen u nekovalentnim interakcijama. Visok indeks konzervativnosti aminokiselina uključenih u ovim interakcijama je jak argument njihove važnosti.

[1] M. Brandl et al., J.Mol.Biol. (2001), 307:357-377
[2] T. Steiner and G. Koellner, J.Mol.Biol. (2001), 305:535-557
[3] S. Stojanović et al., J.Biol.Inorg.Chem. (2007), *in press*

INVESTIGATION OF SLAG FINDINGS FROM ARCHAEOMETALLURGICAL SITES IN EASTERN SERBIA

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Eastern Serbia is well known for its longlasting tradition in mining, and continuing activities on production and processing of non-ferrous and noble metals, as well as ferrous metals. There are numerous archaeometallurgical sites testifying these facts, where traces of early metallurgical production could be found – furnaces remains, large ammounts of slag, metal objects, ceramics, etc. Slag findings are of greatest importance for the archaeometallurgical investigation, having in mind that based on their composition adequate metallurgical technology could be predicted in early stages of metallurgy development.

The results of slag findings from chosen archaeometallurgical sites in Eastern Serbia - Čoka Kazak, Tilva Njagra, Rgotski Kamen i Felix Romuliana, from different historical periods are presented in this paper. Characterization of slag findings has been performed using following methods - XRD, DTA, SEM-EDX, LOM, and chemical analysis.

[1] Metalurgija - Journal of Metallurgy, Special Issue: Archaeometallurgy, Guest-Editor: Dragana Živković, 12 (2-3) (2006) 83-227.
[2] D.Živković et al., Geoarchaeological and Bioarchaeological Studies, 3 (2005) 407-409.
[3] D.Živković, N.Štrbac, et al., Journal of Thermal Analysis and Calorimetry, 76 (2004) 227-235.

ISPITIVANJE NALAZA ŠLJAKE SA ARHEOMETALURŠKIH LOKALITETA U ISTOČNOJ SRBIJI

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[1]Univerzitet u Beogradu, Tehnički fakultet, Bor; [2]Univerzitet u Ljubljani, Naravnoslovnotehniška fakulteta,Ljubljana, Slovenija; [3]Institut za bakar, Bor
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Istočna Srbija je poznata po viševekovnoj rudarsko-metalurškoj tradiciji i kontinuiranim aktivnostima na dobijanju i preradi, pre svega, obojenih i plemenitih metala, ali i gvoždja i čelika. O tome svedoči veliki broj arheometalurških nalazišta na ovom području, na kojima su prisutni tragovi nekadašnje proizvodnje metala - ostaci peći, veće količine šljake, metalnih predmeta, keramike, itd. Nalazi šljake se za arheometalurška ispitivanja od najvećeg značaja, imajući u vidu da se na osnovu njihovog sastava može predočiti tehnologija dobijanja metala u ranim periodima razvoja metalurgije.

U ovom radu su predstavljeni rezultati ispitivanja nalaza šljake iz različitih istorijskih perioda sa odabranih arheometalurških lokaliteta u Istočnoj Srbiji, i to Čoka Kazak, Tilva Njagra, Rgotski Kamen i Felix Romuliana. Karakterizacija nalaza šljake je izvršena metodama XRD, DTA, SEM-EDX, LOM, kao i korišćenjem hemijske analize.

[1] Metalurgija - Journal of Metallurgy, Special Issue: Archaeometallurgy, Guest-Editor: Dragana Živković, 12 (2-3) (2006) 83-227.
[2] D.Živković et al., Geoarchaeological and Bioarchaeological Studies, 3 (2005) 407-409.
[3] D.Živković, N.Štrbac, et al., Journal of Thermal Analysis and Calorimetry, 76 (2004) 227-235.

INVESTIGATION OF DIFFERENT MINERALIZERS INFLUENCE ON ALLUMINUM-HYDROXIDE CALCINATION PROCESS

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Calcination process involves annealing of alluminum-hydroxide at 1100-1300 °C, and is accompanied by dehydration process and structural transformations of dehydrated aluminum oxide. The rate of γ-aluminum oxide into α-phase increases in the presence of different mineraliyers - AlF_3, CaF_2, MgF_2, Na_3AlF_6, NaF and LiF.

Simulation of aluminum hydroxide calcination process with added fluorides has been done using Derivatograph 1500 (MOM, Budapest), and the temperature of α-Al_2O_3 formation is accompanied by exothermic peak displacement characteristic for this process. Characterization of such obtained calcined alumina has been done by XRD analysis and IR spectrophotometry, which results are presented in this paper..

[1] N.Štrbac, Doctoral Thesis, Technical Faculty Bor, 1996.
[2] L.A.Paškevič et al., Cvet.Metal., 2 (1971) 37.
[3] K.Nakamoto, Infrared spectra of Inorganic Coordination Compounds, Willey-Interscience, New York, 1963.

ISPITIVANJE UTICAJA RAZLIČITIH MINERALIZATORA NA PROCES KALCINACIJE ALUMINIJUM-HIDROKSIDA

N. Štrbac, Ž. Živković, D. Živković

Univerzitet u Beogradu, Tehnički fakultet, VJ 12, 19210 Bor
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Proces kalcinacije se sastoji u žarenju aluminijum-hidorksida na 1100-1300^{o}C, i praćen je procesom dehidratacije i strukturnim transformacijama dehidratisanog aluminijum- oksida. Brzina kristalizacije gama-aluminijum-oksida u alfa-fazu raste u prisustvu različitih mineralizatora - AlF_3, CaF_2, MgF_2, Na_3AlF_6, NaF i LiF.

Simulacija procesa kalcinacije aluminijum hidroksida sa dodatim fluoridima izvršena je na Derivatographu 1500 (MOM, Budapest), a temperatura nastajanja alfa-Al_2O_3 je praćena pomeranjem egzotermnog pika karakterističnog za ovaj proces. Karakterizacija ovako dobijene kalcinirane glinice vršena je XRD analizom i IR spektrofotometrijom, čiji se rezultati prezentuju u ovom radu.

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