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SERBIAN CRYSTALLOGRAPHIC SOCIETY

**XVIII КОНФЕРЕНЦИЈА
СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА**

Изводи радова

**XVIII CONFERENCE OF THE
SERBIAN CRYSTALLOGRAPHIC SOCIETY**

Abstracts

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PLENARY LECTURES

ПЛЕНАРНА ПРЕДАВАЊА

THE PROTEIN AS VARIABLE IN CRYSTALLIZATION AND STRUCTURE DETERMINATION: THE STORY OF HUMAN CYCLIN B

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Growth of well-ordered protein crystals which diffract X-rays to high resolution is the single biggest obstacle to protein crystal structure determination. Many important proteins of biological interest have resisted crystallization attempts, and manipulation of traditional crystallization variables such as the precipitant, pH and temperature, have failed to overcome these problems. Cyclin B was first discovered in July 1982, by Nobel Laureate Prof. Sir Tim Hunt, who later demonstrated its central role in cell division. Cyclin B binds and activates cyclin-dependent kinase 1, CDK1, forming a heterodimeric complex that drives mitosis in all eukaryotic cells. Despite its essential function in possibly the most fundamental biological process of life, the crystal structure of Cyclin B remained unsolved for decades. Numerous labs attempted to solve the structure of the protein, but problems with protein expression, solubility, and aggregation, prevented crystallization. Limited proteolysis and biophysical analysis identified an N-terminal 165 residue unstructured domain, which we demonstrated is natively unfolded [1]. Recombinant expression of $\Delta 165$ cyclin B in bacteria resulted in small amounts of soluble protein; reducing the incubator temperature during cyclin B expression from 37 °C to 10 °C significantly increased the fraction of soluble, folded protein (monitored by circular dichroism), and enabled growth of the first crystals of Cyclin B. Because cysteine oxidation was detected, we mutated 3 cysteine residues to serine; resulting in increased solubility, reduced aggregation and improved crystals. Reaching a dead end, we decided to consider the protein itself as a crystallization variable. Using rational mutagenesis, we optimized the Cyclin B protein for crystallization trials; treating the protein as a modifiable parameter. Growth of well-ordered, X-ray diffracting crystals required point mutations of contiguous charged surface glutamate residues to alanine, resulting in improved crystal lattice contacts. This increased the range of crystallization conditions and improved crystal morphology, reproducibility and crystal growth kinetics. Extension of the observable diffraction limit from 4-5 Å to 2.9 Å was achieved through crystal dehydration, by post-crystallization soaking in saturating concentrations of sodium bromide; enabling us to solve the crystal structure of Cyclin B to 2.9 Å resolution [2]. The availability of large quantities of active, soluble Cyclin B1 has enabled detailed biochemical and biophysical analysis of its cell cycle function, development of

peptide-based Cyclin B specific inhibitors and the crystal structure of a Cyclin B/CDK complex [3].

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SUPERSPACE DESCRIPTION OF BROWNMILLERITES AND LAYERED BROWNMILLERITES

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Brownmillerite-type materials exhibit a wide range of structures, which vary in the arrangement of tetrahedral chains. In brownmillerites perovskite-like layers of octahedra alternate with layers of tetrahedral chains. The tetrahedral chains can adopt two mirror-related configurations, which allow different inter- and intra-layer ordering patterns to form. The simplest of them result in space groups *Pnma* and *I2mb*.

High-temperature modifications of the brownmillerite solid solution series $\text{Ca}_2(\text{Al}_x\text{Fe}_{1-x})_2\text{O}_5$ show modulated intra-layer order, which exhibits commensurate or incommensurate sequences depending on composition and temperature [1-3]. All structures of this series can be described using the superspace group *Imma(00 γ)s00*.

D'Hondt *et al.* [4] found an alternating intra-layer sequence in $\text{Sr}_2\text{Fe}_2\text{O}_5$, which allows stacking faults and various stacking sequences, that are all covered by superspace group *I2/m(0 β γ)0s*.

We observed diffuse scattering related to stacking faults in layered brownmillerites $\text{Ca}_4(\text{Fe,Al})_2(\text{Mn,Ti})\text{O}_9$, which exhibit separated blocks (OTO) of the brownmillerite structure. Similar to $\text{Sr}_2\text{Fe}_2\text{O}_5$ [4], the layered brownmillerites show a certain degree of order according to superstructures with different stacking sequences, as evident by electron diffraction experiments. All possible superstructures can be described using superspace group *A2₁/m(0 β γ)0s* with different modulation wave vectors.

As shown by these examples, the superspace approach is a powerful tool to unify the description of brownmillerites, layered brownmillerites and their superstructures.

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SUPERPROSTORNO PREDSTAVLJANJE BRAUNMILERITA I SLOJEVITIH BRAUNMILERITA

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Materijali braunmileritskog tipa pokazuju širok spektar struktura, koje se razlikuju po uređenju tetraedarskih lanaca. U braunmileritima se perovskitski tip oktaedarskih slojeva naizmenično smenjuje sa tetraedarskim lancima. Tetraedarski lanci mogu da zauzimaju jednu od dve moguće konfiguracije (povezane preko ogledalske ravni), što uslovljava nastajanje različitog stepena uređenja kako unutar samih slojeva tako i između njih. Strukture sa najjednostavnijim načinom slaganja slojeva kristališu u dve prostorne grupe, $Pnma$ i $I2mb$.

Visokotemperaturne modifikacije čvrstog rastvora braunmilerita $Ca_2(Al_xFe_{1-x})_2O_5$ pokazuju modulirano uređenje slojeva, koje se manifestuje periodičnim ili aperiodičnim redosledom slojeva u strukturi, zavisno od hemijskog sastava i temperature [1-3]. Sve strukture ovog niza mogu se opisati koristeći superprostornu grupu $Imma(00\gamma)s00$.

D'Hondt *et al.* [4] su otkrili da u $Sr_2Fe_2O_5$ unutar slojeva dolazi do naizmeničnog redosleda slaganja, usled čega mogu u strukturi da nastanu greške u slaganju slojeva kao i različiti redosledi slaganja slojeva, što može da se opiše u superprostornoj grupi $I2/m(0\beta\gamma)0s$.

Mi smo uočili difuzno rasejanje koje pokazuju izdvojeni (OTO) blokovi, a koje je povezano sa greškama u slaganju slojeva u slojevitim braunmileritima $Ca_4(Fe,Al)_2(Mn,Ti)O_9$. U eksperimentima sa elektronskom difrakcijom dokazano je da slojeviti braunmileriti, slično $Sr_2Fe_2O_5$ [4], pokazuju određeni stepen uređenosti u poređenju sa superstrukturama različitog redosleda slaganja slojeva. Sve moguće superstrukture mogu se opisati koristeći superprostornu grupu $A2_1/m(0\beta\gamma)0s$ sa različitim talasnim vektorom modulacije.

Kao što je pokazano iz ovih primera, superprostorni prilaz omogućava da se objedini opis braunmilerita, slojevitih braunmilerita i njihovih superstruktura.

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ROLE OF STRUCTURAL BIOLOGY AND BIOPHYSICS IN UNCOVERING THE MOLECULAR BASIS OF POLYCYSTIC KIDNEY DISEASE

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Autosomal dominant polycystic kidney disease (ADPKD) is the most common, monogenic cause of kidney failure in humans; and is linked with mutations in polycystin-1 (PC1) and polycystin-2 (PC2) [1]. PC2 is a calcium (Ca^{2+}) permeable channel in the TRP channel family. Deletion of the C-terminus of PC2 (PC2C) alters Ca^{2+} -signaling and most pathogenic mutations in PC2 are premature truncations. Efforts to crystallize full-length PC2C failed due to protein flexibility and susceptibility to degradation. Through limited proteolysis and molecular modeling, we identified two stable domains within the C-terminus of PC2: a Ca^{2+} binding EF-hand domain (PC2EF) and a previously unreported coiled-coil domain [2-4]. We show that the coiled-coil is responsible for PC2 oligomerization using Small-Angle X-ray Scattering (SAXS), Analytical Ultracentrifugation and Size Exclusion Chromatography [3,4]. Using our initial model as a guide, we constructed molecular models of the coiled-coil and EF-hand domains, which we validated by circular dichroism [1]. Based on these models, we created a library of PC2C constructs for crystallization trials, and crystallized the coiled-coil domain. We found that we could alter crystallization conditions, crystal morphology and diffraction properties by altering the length of the coiled-coil domain and by rational mutagenesis of contiguous charged residues. Using Isothermal Titration Calorimetry, we demonstrate that the EF-hand domain binds Ca^{2+} and that mutations in the predicted Ca^{2+} binding loop abolish the affinity for Ca^{2+} . We hypothesize that the EF-hand serves as a Ca^{2+} -sensor/switch, and show that PC2 undergoes Ca^{2+} -induced conformational changes by NMR, circular dichroism, and SAXS. Because PC2EF resisted attempts at crystallization due to conformational exchange, we solved the NMR structure of Ca^{2+} -bound PC2-EF and have identified residues with chemical shift changes upon Ca^{2+} -titration [4]. PC2-EF contains a novel unpaired EF-hand fold, with a divergent helix-loop-helix in place of a second EF-hand, which may have evolved from a canonically paired EF-hand found in invertebrate PC2 homologs. Temperature-dependent steady state NOE experiments and NMR linewidth measurements indicate increased molecular motion in the EF-hand consistent with a role for PC2-EF as a Ca^{2+} -sensitive regulator. Structure-based sequence conservation analysis revealed a conserved hydrophobic pocket, which may mediate Ca^{2+} -dependent protein interactions. Using results of our structural studies, we examined the role of the EF-hand and coiled-coil on PC2 channel function in single-channel lipid bilayers. Our results suggest that the coiled coil regulates PC2 by serving as a homo-oligomerization motif, whereas the EF-hand modulates the

Ca²⁺-dependence of PC2 channel activity. We propose a mechanism of regulation of the Ca²⁺-dependence of PC2 channel activity by PC2-EF.

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RECOGNIZING NEW TYPES OF NONCOVALENT INTERACTIONS ANALYZING DATA IN CRYSTALLOGRAPHIC DATABASES

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Noncovalent interactions with π -systems have been studied intensively in recent years and the importance of these interactions has been shown for different molecular systems, from crystal structures to biomolecules. Analyzing geometrical parameters in the crystal structures from Cambridge Structural Database and Protein Data Bank and using quantum chemical calculations we found several new types of noncovalent interactions with π -systems.

Cation- π interactions between ligands coordinated to a metal and π -system of various aromatic groups have been found in crystal structures of metalloproteins and transition-metal complexes. These interactions, named metal-ligand-aromatic cation- π interactions (MLAC π), can be also considered as a type of XH/ π hydrogen bonds [1]. Study of the water molecule OH/ π interactions show that coordinated water forms stronger interactions than noncoordinated water molecule.

It has been observed that planar chelate rings with delocalized π -bonds can be involved in noncovalent interactions in a manner similar to that of organic aromatic rings. Both CH/ π and stacking interactions with chelate rings were observed. Analysis of the crystal structures of the metal complexes and quantum chemical calculations showed that a chelate ring can be a hydrogen atom acceptor in CH/ π interactions [2]. Analysis of geometrical parameters in the crystal structure of square-planar complexes from Cambridge Structural Database showed phenyl-chelate [3] and chelate-chelate [4] stacking interactions.

Study of the interactions between water and C₆-aromatic rings revealed the existence of conformations where the water molecule or one of its O-H bonds is parallel to the aromatic ring plane. Study showed that the water/aromatic parallel alignment interactions can be significantly strong at large horizontal displacements. We calculated the strongest energies for the water position with the large horizontal displacements, out of the aromatic ring and out of the C-H bond region. The calculated energies of the interactions are significant, up to $\Delta E_{\text{CCSD(T)}(\text{limit})} = -2.45$ kcal/mol (at horizontal displacement of 2.6 Å), and comparable with the energy of slipped-parallel benzene/benzene dimer [5].

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OTKRIVANJE NOVIH TIPOVA NEKOVALENTNIH INTERAKCIJA NA OSNOVU ANALIZE PODATAKA U KRISTALOGRAFSKIM BANKAMA

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Nekovalentne interakcije π -sistema intenzivno su proučavane poslednjih godina i dokazan je značaj ovih interakcija u različitim molekulskim sistemima, od kristalnih struktura do biomolekula. Analiziranjem geometrijskih parametara u kristalnim strukturama iz Kembričke banke kristalografskih podataka i Proteinske banke podataka, kao i korišćenjem kvantno hemijskih proračuna, pronašli smo nekoliko novih tipova nekovalentnih interakcija π -sistema.

U kristalnim strukturama metaloproteina i kompleksa prelaznih metala pronađene su katjon- π interakcije između liganada koordinovanih za metal i π -sistema različitih aromatičnih grupa [1]. Ove interakcije, koje su nazvane metal-ligand-aromatične kation- π interakcije (MLAC π), mogu se takođe smatrati XH/ π vodoničnim vezama. Proučavanje OH/ π interakcija molekula vode pokazalo je da su interakcije koordinovane vode značajno jače od interakcija nekoordinovane vode.

Opaženo je da planarni helatni prstenovi sa delokalizovanim π -vezama mogu da grade nekovalentne interakcije slično organskim aromatičnim prstenovima. Oba tipa, i CH/ π i steking interakcije helatnih prstenova su opažene. Analiza kristalnih struktura kompleksa metala i kvantno hemijski proračuni su pokazali da helatni prsten može biti akceptor vodonika u CH/ π interakcijama [2]. Analiza geometrijskih parametara u kristalnim strukturama kvadratno planarnih kompleksa iz Kembričke banke podataka pokazala je da postoje fenil-helat [3] i helat-helat [4] steking interakcije.

Proučavanje interakcija između molekula vode i C₆-aromatičnih prstenova otkrilo je postojanje konformacija u kojima je molekul vode ili jedna od njegovih O-H veza paralelna ravni aromatičnog prstena. Proučavanje je pokazalo da paralelne voda/aromatične interakcije mogu biti prilično jake na velikim horizontalnim rastojanjima. Najjače interakcije su izračunate za položaj vode na velikim horizontalnim rastojanjima, izvan prstena i izvan regiona C-H veza. Izračunate energije interakcija su značajne, mogu imati vrednosti do $\Delta E_{\text{CCSD(T)}(\text{limit})} = -2,45$ kcal/mol (na horizontalnom rastojanju od 2,6 Å), i one su uporedive sa energijom stekinga u najstabilnijem benzen/benzen dimeru [5].

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NEW LIQUID CRYSTALLINE MESOPHASES OF BENT CORE MATERIALS

Packing, polar orders, ferro- and anti-ferroelectricity, biaxiality

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Bent-core (BC) materials exhibit quite different mesophases than the linear shaped liquid crystals. BC molecules usually have a dipole moment transversal to their molecular long axis, which makes packing of the BC molecules with polar order possible. That leads to a macroscopic polarization of the formed smectic layers and thus to the appearance of antiferro- and/or ferroelectricity in non-chiral systems. Here it should be mentioned that ferroelectricity has earlier been observed only in *chiral* linear shaped molecules.

Even the nematic phase of BC compounds exhibit different properties than that of the linear shaped compounds. Theoretically the biaxial nematic phase is predicted. The early investigation on bent-core liquid crystals has concentrated on symmetrical BC molecules [1, 2]. Recently symmetry breaking has become the most important target for researchers; that is why the interest has been turned to the asymmetrical structures. In the lecture an overview will be given of recent results on the structure-property relationship of the BC materials showing how do changes of the chemical structures influence the mesophase property [3-5]. Polarizing optical microscopy, differential scanning calorimetry, electro-optical, 2H NMR [6] investigations will be summarized. Not only single molecules, but mixtures will also be presented [7].

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ORAL PRESENTATIONS

САОПШТЕЊА

MONOCLINIC SUPERSTRUCTURE OF MULLITE-TYPE $\text{KAl}_9\text{O}_{14}$

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The chemical composition of the Al, Si–mullites is given by the general formula $\text{Al}_2(\text{Al}_{2+2x}\text{Si}_{2-2x})\text{O}_{10-x}$. The amount of Si^{4+} substituted by Al^{3+} is correlated with the sum of oxygen vacancies necessary to retain charge balance. In mullite-type aluminates $X^{2-2x}\text{Al}_2(\text{Al}_4)\text{O}_{10-x}$ negative charge is compensated by incorporation of equivalent number $(2 - 2x)$ positively charged X cations [1].

Single crystals of $\text{KAl}_9\text{O}_{14}$ (or $\text{K}_{0.67}\text{Al}_6\text{O}_{9.33}$) were grown using a flux method. Purity of the sample was confirmed by SEM-EDX analyses. Colourless needle-like prisms of $\text{KAl}_9\text{O}_{14}$, some as long as 1 cm, show with cross-polarised light twin planes perpendicular to the needle axis. The structure was determined from single-crystal data and refined to a residual $R|F| = 0.031$. The compound crystallizes in the monoclinic space group $P2_1/n$ ($a = 8.1937(6)$, $b = 7.6734(6)$, $c = 8.7930(6)$ Å, $\beta = 110.747(6)^\circ$, $V = 516.99(7)\text{Å}^3$, $Z = 2$). A detailed analysis based on oriented sections of reciprocal space revealed that the crystal is also subject to twinning by partial merohedry which was accounted for during the refinement. Furthermore, distinct one-dimensional diffuse scattering parallel to $c^* - (a^*/3)$ could be observed.

Crystals of $\text{KAl}_9\text{O}_{14}$ have a typical mullite-type structure with linear edge sharing AlO_6 octahedral chains connected with inner-chain groups comprising two AlO_4 tetrahedra and one AlO_5 trigonal bipyramid. The 4+1 coordinated aluminium has four shorter (1.75 – 1.86 Å) and one longer bond (2.16 Å) to oxygen atoms. K-atoms are located in the centre of cavities originating from oxygen vacancies. Differences between the calculated powder diffraction pattern of this structure and known powder diagrams of $\text{K}_{0.67}\text{Al}_6\text{O}_{9.33}$ [2] clearly confirmed that this structure is a new polymorph.

The monoclinic superstructure of $\text{KAl}_9\text{O}_{14}$ can be transformed to a $3 \times c$ orthorhombic supercell ($a = 7.69$, $b = 7.68$, $c = 8.82$ Å). A similar ($3 \times a$) superstructure was postulated for the 4:1 mullite earlier [3].

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MONOKLINIČNA MULITSKA SUPERSTRUKTURA KAl_9O_{14}

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Hemijski sastav Al, Si -mulita predstavlja se opštom formulom $Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$. Količina Al^{3+} koja zamenjuje Si^{4+} direktno je povezana sa sumom nepopunjenih položaja kiseonika neophodnih da se održi ravnoteža naelektrisanja. U aluminatima sa mulitskim tipom strukture $X^{2-2x}Al_2(Al_4)O_{10-x}$ negativno naelektrisanje je neutralisano uvođenjem odgovarajućeg broja $(2-2x)$ pozitivno naelektrisanih X katjona [1].

Kristali KAl_9O_{14} (ili $K_{0,67}Al_6O_{9,33}$) su sintetisani pomoću fluks metode. Hemijski sastav uzorka potvrđen je SEM-EDX analizom. Providni igličasto-prizmatični kristali KAl_9O_{14} , neki i do 1 cm dužine, pokazuju pod polarizovanim svetlom ravni bližnjenja normalne na osu izduženja. Struktura kristala je rešena i utučnjena do R -faktora $R|F| = 0,031$ iz podataka rendgenske difrakcije na monokristalu. Jedinjenje kristališe u monokliničnoj prostornoj grupi $P2_1/n$ ($a = 8,1937(6)$, $b = 7,6734(6)$, $c = 8,7930(6)$ Å, $\beta = 110,747(6)^\circ$, $V = 516,99(7)$ Å³, $Z = 2$). Detaljna analiza orjentisanih preseka recipročnog prostora pokazala je da su kristali delimično-mercedarski bližnjeni što je uvršćeno u utučnjavanje. Uočeno je i jednodimenzionalno difuzno rasejanje refleksija paralelno $c^* - (a^*/3)$ pravcu.

Kristali KAl_9O_{14} imaju karakterističnu mulitsku strukturu sa linearnim nizovima AlO_6 oktaedara međusobno povezanih ivicama. Ovi nizovi oktaedara su povezani unutrašnjom grupom lanaca sačinjenih od dva AlO_4 tetraedra i jedne AlO_5 trigonalne bipiramide. Aluminijum sa 4+1 koordinacijom ima četiri kraće (1,75 – 1,86 Å) i jednu dužu vezu (2,16 Å) do atoma kiseonika. K-atomi su smešteni u centrima praznina, koje potiču od nepopunjenih položaja kiseonika. Razlika između izračunatog dijagrama praha ove strukture i već poznatog dijagrama $K_{0,67}Al_6O_{9,33}$ [2] jasno pokazuje da je ova struktura novi polimorf.

Monoklinična superstruktura KAl_9O_{14} može biti transformisana u $3 \times c$ rombičnu superćeliju ($a = 7,69$; $b = 7,68$; $c = 8,82$ Å). Slična ($3 \times a$) superstruktura je mnogo ranije predviđena za 4:1 mulite [3].

[1] H. Schneider, S. Komarneni, *Mullite*, WILEY-VCH, Weinheim, 2005

[2] R. X. Fischer, M. Schmücker, P. Angerer, H. Schneider, *American Mineralogist*, 86 (2001), str. 1513-1518

[3] R. X. Fischer, *American Mineralogist*, 79 (1994), str. 983-990

CRYSTAL STRUCTURES OF THREE 3-(ARYLAMINO)-1-FERROCENYLPROPAN-1-ONES

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The crystal structures of the three novel ferrocene containing Mannich bases: 1-Ferrocenyl-3-(o-tolylamino)propan-1-one (**1**), 1-Ferrocenyl-3-(m-tolylamino)propan-1-one (**2**) and 1-Ferrocenyl-3-(p-tolylamino)propan-1-one (**3**), were determined at room temperature. In all three derivatives the cyclopentadienyl rings adopt a nearly eclipsed geometry. The values of the torsion angles C1–Cg1–Cg2–C6 (which relate the substituted C1 and corresponding, eclipsed C6 atoms through centroids of the Cp rings, Cg1 and Cg2) are all below 13°.

The orientation of the phenyl ring with regard to the ferrocene (Fc) unit represents the most pronounced difference between the three derivatives. In the case of **2** and **3** the mean plane of the phenyl ring and the C1/Cg1/Cg2/C6 plane passing through the Fc unit form the similar dihedral angles of 82.2 and 83.2°, respectively. The corresponding dihedral angle for the compound **1** is 14.0°. Accordingly, **2** and **3** derivatives exhibit very similar crystal packing where the dimers formed *via* the cyclic N–H...O hydrogen bonds represent the main structural motif. The molecules of compound **1** show markedly different arrangement where the strong C–H...O hydrogen bond represents the dominant interaction. All crystal structures are additionally stabilized by numerous C–H... π interactions.

Crystallographic data: (**1**) C₂₀H₂₁FeNO, monoclinic, *P*2₁/*c*, *Z* = 4, *V* = 1627.8(13) Å³, *R*₁ = 3.93% for 2843 independent reflections and 212 parameters; (**2**) C₂₀H₂₁FeNO, monoclinic, *C*2/*c*, *Z* = 8, *V* = 3398.2(9) Å³, *R*₁ = 4.03% for 2787 independent reflections and 212 parameters; (**3**) C₂₀H₂₁FeNO, triclinic, *P*-1, *Z* = 2, *V* = 897.5(5) Å³, *R*₁ = 4.29% for 2829 independent reflections and 212 parameters.

KRISTALNE STRUKTURE TRI 3-(ARILAMINO)-1-FEROCENILPROPAN-1-ONA

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Kristalne strukture tri Manihove baze koje sadrže ferocen: 1-Ferocetil-3-(o-tolilamino)propan-1-ona (**1**), 1-Ferocetil-3-(m-tolilamino)propan-1-ona (**2**) i 1-Ferocetil-3-(p-tolilamino)propan-1-ona (**3**), određene su na sobnoj temperaturi. Ciklopentadienilni prstenovi (Cp) u sva tri derivata zauzimaju približno eklipsnu geometriju. Torzioni uglovi C1–Cg1–Cg2–C6 (koji povezuju supstituisani atom C1 i odgovarajući, eklipsni atom C6 preko cetroida Cp prstenova, Cg1 and Cg2) imaju vrednosti ispod 13°.

Orijentacija fenilnog prsten u odnosu na ferocensku jedinicu (Fc) predstavlja najizraženiju razliku između tri derivata. U slučaju **2** i **3** srednja ravan fenilnog prstena i ravan C1/Cg1/Cg2/C6 koja prolazi kroz Fc jedinicu formira sličan diedarski ugao od 82,2, odnosno 83,2°. Odgovarajući diedarski ugao u jedinjenju **1** je 14,0°. U skladu sa tim, derivati **2** i **3** pokazuju vrlo slično kristalno pakovanje u kome dimeri nastali preko cikličnih N–H...O vodoničnih veza predstavljaju glavni strukturni motiv. Molekuli jedinjenja **1** imaju značajno drugačije uređenje u kome jake C–H...O vodonične veze predstavljaju dominantnu interakciju. Sve kristalne strukture su dodatno stabilizovane brojnim C–H... π interakcijama.

Kristalografski podaci: (**1**) C₂₀H₂₁FeNO, monokličan, P2₁/c, Z = 4, V = 1627,8(13) Å³, R₁ = 3,93% za 2843 nezavisnih refleksija i 212 parametara; (**2**) C₂₀H₂₁FeNO, monokličan, C2/c, Z = 8, V = 3398,2(9) Å³, R₁ = 4,03% za 2787 nezavisnih refleksija i 212 parametara; (**3**) C₂₀H₂₁FeNO, trikličan, P-1, Z = 2, V = 897,5(5) Å³, R₁ = 4,29% za 2829 nezavisnih refleksija i 212 parametara.

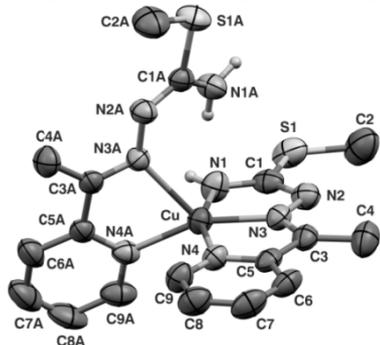
STRUCTURE OF [Cu(L)(HL)]ClO₄ COMPLEX (HL = 2-ACETYL-PYRIDINE S-METHYLISOTHIOSEMICARBAZONE)

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In this work the structure of the Cu(II) complex with 2-acetylpyridine S-methylisothiosemicarbazone of the coordination formula [Cu(L)(HL)]ClO₄ is reported (figure shows the complex cation; H-atoms attached to C-atoms are omitted for clarity). In previously reported structurally characterized complexes of HL [1] NNN tridentate coordination mode of neutral ligand form was found. The title complex is the first one in which NN bidentate coordination mode of one ligand molecule in neutral form (HL), as well as NNN tridentate coordination mode of other ligand molecule in monoanionic (L⁻) form is unequivocally proven. The Cu(II) is situated in a square-pyramidal (4+1) environment ($\tau = 0,02$) of five nitrogen atoms. The lengths of equatorial Cu–N bonds are in accordance with the reported Cu(II) complexes [1]. Exception is axial Cu–N(3A) bond which is longer ($d = 2.358(3) \text{ \AA}$), and as such characteristic for square-pyramidal Cu(II) complexes. Monoanionic L⁻ form, which is formed by deprotonation of hydrazine nitrogen atom, takes practically planar conformation, along with two five-membered



metallocycles. Bidentate coordination of the neutral HL form *via* pyridine and azomethine nitrogen atoms resulted in formation of the five-membered metalocycle twisted on Cu–N(3A) bond. HL significantly deviates from planarity and torsions along C(5A)–C(3A) and N(3A)–N(2A) bonds are present. The torsion of uncoordinated isothioamide moiety is consequence of steric repulsion due to absence of coordination of the third nitrogen atom. It should be noted that perchlorate ion is disordered and thus, hydrogen bonding and crystal packing cannot be discussed in detail.

Data were collected with Oxford Diffraction Gemini S diffractometer using MoK α radiation ($\lambda = 0.71069 \text{ \AA}$). Structure is solved by direct methods (*SIR92*) and refined by least square methods on F^2 (*SHELXL-97*) to $R_1 = 0.0377$. *Crystallographic data*: C₁₈H₂₃ClCuN₈O₄S₂, $M_r = 289.28$, triclinic, space group $P-1$, $a = 10.7538(6)$, $b = 11.1614(5)$, $c = 12.0512(8) \text{ \AA}$, $\alpha = 78.423(5)^\circ$, $\beta = 66.885(6)^\circ$, $\gamma = 66.713(5)^\circ$, $V = 1220.20(12) \text{ \AA}^3$, $Z = 2$, $\mu(\text{MoK}\alpha) = 1.218 \text{ mm}^{-1}$, $S = 0.866$.

- [1] V.M. Leovac, V.I. Češljević, Lj.S. Vojinović-Ješić, V. Divjaković, K. Mészáros Szécsényi, M.V. Rodić, *Polyhedron* **28** (2009) 3570–3576

STUDY OF MLOH/ π INTERACTIONS BETWEEN COORDINATED WATER MOLECULE AND C₆-AROMATIC RING

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The conformations and functions of molecules depend on the interactions with the surrounding solvent, in particular with water molecules. Statistical study of OH/ π interactions between water molecule and the aromatic groups of amino acids in crystal structures of proteins confirmed relatively frequent occurrence of OH/ π interactions in proteins [1]. The interactions of coordinated water molecules and π -system of C₆-aromatic group, were recognized and studied in crystal structures of metalloproteins and metal complexes [2,3].

In this study, results on intermolecular MLOH/ π interactions of aqua ligand with C₆-aromatic rings in the crystal structures from the Cambridge Structural Database (CSD) and DFT calculations are presented. To determine if the charge of aqua complex has influence on the H \cdots Ω distances (Ω is centre of C₆-aromatic ring), the complexes were separated into groups. The crystallographic data shows that positively charged aqua complexes have a tendency to make shorter H \cdots Ω distances. To support these observations, quantum chemical calculations of the interacting energies were performed. DFT calculations were done on different aqua complex/benzene model systems and carried out using the Gaussian 03 program. DFT calculations are in good agreement with results of geometrical analysis of crystal structures. Based on the results of the DFT calculations, the energy of the most stable MLOH/ π orientation between aqua ligand and aromatic ring was estimated to -4.9 kcal/mol, for neutral complex, and -12.5 kcal/mol for positively charged aqua complex. This calculated interaction energy of the MLOH/ π interaction is larger than the interaction energy of the OH/ π interaction calculated for a water molecule and the aromatic ring. The calculated energy of the most stable intermolecular OH/ π interaction between noncoordinated water and benzene molecule is -3.19 kcal/mol.

[1] T. Steiner, *Biophys.Chem.*, (2002), 95, 195.

[2] S. D. Zarić, D. Popović, E. W. Knapp, *Chem. Eur. J.*, (2000), 6, 213.

[3] M. K. Milčić, S. D. Zarić, *Eur. J. Inorg. Chem.*, (2001), 2143.

PROUČAVANJE MLOH/ π INTERAKCIJA IZMEĐU KOORDINOVANOG MOLEKULA VODE I C₆ –AROMATIČNOG PRSTENA

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Konformacija i funkcija molekula zavisi od interakcija sa rastvaračem koji ih okružuje, naročito sa molekulima vode. Statistička proučavanja OH/ π interakcija između molekula vode i aromatičnih grupa aminokiselina u kristalnim strukturama proteina potvrdila su retativno čestu pojavu OH/ π interakcija u proteinima [1]. Interakcije koordinovanih molekula vode i π –sistema C₆-aromatičnih grupa primećene su i proučavane u kristalnim strukturama metaloproteina i kompleksa metala [2,3].

U ovom radu predstavljeni su rezultati proučavanja međumolekulskih interakcija između koordinovanog molekula vode i C₆-aromatičnog prstena (MLOH/ π interakcije) u kristalnim strukturama dobijenih pretragom Kembričke kristalografske banke podataka (CSD), kao i rezultati DFT proračuna. Radi utvrđivanja uticaja naelektrisanja akva kompleksa na dužinu H \cdots Ω rastojanja (Ω centar C₆-aromatičnog prstena) kompleksi su podeljeni u grupe. Kristalografski podaci ukazuju na tendenciju pozitivno naelektrisanih akva-kompleksa da grade kraća H \cdots Ω rastojanja. Radi potvrde ovih zapažanja urađeni su kvantno-hemijski proračuni energija interakcija. DFT proračuni su urađeni na različitim akva-kompleks/benzen model sistemima koristeći program Gaussian 03. Proračuni su dali dobro slaganje sa geometrijskom analizom kristalnih struktura. Prema rezultatima DFT proračuna, energija najstabilnije MLOH/ π orijentacije između koordinovanog molekula vode i aromatičnog prstena ima vrednosti od -4,9 kcal/mol za neutralne komplekse, dok je za pozitivno naelektrisane akva komplekse -12,5 kcal/mol. Izračunate vrednosti energija MLOH/ π interakcija veće su od energija OH/ π interakcija, između molekula nekoordinovane vode i aromatičnog prstena. Energija najstabilnije OH/ π interakcije između nekoordinovanog molekula vode i aromatičnog prstena procenjena je na oko -3,19 kcal/mol.

[1] T. Steiner, *Biophys.Chem.*, (2002), 95, 195.

[2] S. D. Zarić, D. Popović, E. W. Knapp, *Chem. Eur. J.*, (2000), 6, 213.

[3] M. K. Milčić, S. D. Zarić, *Eur. J. Inorg. Chem.*, (2001), 2143.

INFLUENCE OF C₆-ARYL GROUP SUBSTITUENTS ON GEOMETRY OF C-H...O INTERACTIONS

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The C-H...O interactions are very important in many systems, especially in biomolecules. One of the very important properties of the hydrogen bonds is directionality. It was shown based on directionality that the C-H...O interactions (although they can be weak) are hydrogen bonds and not the van der Waals interaction [1]. The analysis of the angular distributions of C-H...O interactions, using the data from the Cambridge Structural Database (CSD), indicated that the interactions for different types of the C-H groups show decreasing directionality with decreasing C-H polarization.

In this work, geometry of C-H...O interactions of aromatic C-H donors was studied using crystal structures from the CSD. Crystal structures involving C₆-H aromatic groups and oxygen atoms were screened for intermolecular contacts. Following systems with oxygen atom were taken: HOH (non-coordinated), HOZ, Z₁OZ₂, O=CZ and O=YZ (Z, Z₁, and Z₂ are not hydrogen atoms, Y is not carbon atom). In order to study the preference for linear contact geometries in the C-H...O interactions of the aromatic C-H groups, the interactions of every type of acceptors were analyzed separately. The preference for linear contact geometries in C-H...O interactions of aromatic C-H groups can be observed by the distributions of angle α . To obtain more reliable data cone correction was used.

The results reveal that the preference for the linear contact depends on the type of the atom in the o-position to the interacting C-H group. The C-H...O interactions of the aromatic molecules with two hydrogen atoms in the o-position do not show preference for the linear contacts. This is caused by the presence of the bifurcated interactions; the acceptor oxygen atom has the possibility for the simultaneous hydrogen bond with the hydrogen atom in the o-position to the interacting C-H group. The bifurcated interactions are observed in substantial number of the crystal structures. In the structures with substituent in o-position there is also possibility for the simultaneous hydrogen bond, depending on the nature of the substituent.

[1] T. Steiner and G. R. Desiraju, *Chem. Commun.*, (1998), 891-892.

УТИЦАЈ СУПСТИТУЕНАТА ВЕЗАНИХ ЗА С₆-АРИЛ ГРУПУ НА ГЕОМЕТРИЈУ С-Н...О ИНТЕРАКЦИЈА

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С-Н...О интеракције су од великог значаја у многим системима, нарочито у биомолекулима. Једна од важнијих особина водоничне везе је усмереност. На основу ње је доказано да С-Н...О интеракције (иако могу бити слабе) спадају у водоничне везе, а не у Ван дер Валсове интеракције [1]. Расподеле угла С-Н...О интеракција, добијена коришћењем података из Кембричке банке података (CSD), указује да ове интеракције за различите типове С-Н група показују смањену усмереност са смањењем поларизације С-Н групе.

У овом раду проучавана је геометрија С-Н...О интеракција ароматичних С-Н донора коришћењем кристалних структура из Кембричке банке података. У циљу налажења ових интеракција, анализирани су кристалне структуре које садрже С₆-Н ароматичну групу и атом кисеоника. У обзир су узети следећи системи са атомом кисеоника: НОН (некоординована), НОZ, Z₁OZ₂, O=CZ и O=YZ (Z, Z₁, и Z₂ нису атоми водоника, Y није атом угљеника). Да би се проучила тежња С-Н...О интеракција ка линеарном распореду, посебно су проучаване интеракције за различите типове акцептора. Тежња ка линеарном распореду атома у С-Н...О интеракцијама ароматичних С-Н група може се уочити на основу расподеле угла α . Да би се добили што поузданији резултати коришћена је конусна корекција.

Резултати показују да тежња ка линеарном распореду зависи и од типа атома у о-положају у односу на интерагујућу С-Н групу. С-Н...О интеракције ароматичних молекула са два атома водоника у орто положају не показују тежњу ка линеарном распореду. Разлог за ово је присуство бифуркованих интеракција; акцепторски атом кисеоника има могућност да награди и симултану водоничну везу са водоником у орто положају у односу на интерагујућу С-Н групу. Бифурковане интеракције су примећене у значајном броју кристалних структура. У структурама у којима је у орто положају неки супституент такође постоји могућност за грађење симултаних водоничних веза, у зависности од природе супституента.

[1] T. Steiner and G. R. Desiraju, *Chem. Commun.*, (1998), 891-892.

STRUCTURAL AND MAGNETIC PROPERTIES OF THE ORDERED PEROVSKITE $\text{Pb}_2\text{CoTeO}_6$

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Magnetoelectric materials, in which both ferromagnetic and ferroelectric orders coexist, have attracted significant attention because of their technological applications as well as fundamental physical characteristics. However, magnetoelectrics are rare in nature and magnetic order may coexist with long-range polar order only in a few structure types. Lead-based perovskites have attracted attention because of their excellent dielectric, piezoelectric, and electrostrictive properties, which are useful in many modern applications. In the same time Pb perovskites have recently been investigated in great detail because of interesting magnetic properties. These perovskites are good candidates to show both spin and dipole orderings. Spontaneous polarized states are expected from the distorted lead coordination. Paramagnetic ions at the B position (Co^{2+} in our case) can lead to the magnetic ordering. $\text{Pb}_2\text{CoTeO}_6$ has been investigated from 5 K to 450 K and undergoes a number of temperature induced phase transitions from monoclinic to cubic structure. The different crystal structures and the magnetic structure which appear below 20 K will be discussed.

STRUKTURNE I MAGNETNE OSOBINE UREĐENOG PEROVSKITA $\text{Pb}_2\text{CoTeO}_6$

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Magnetoelektrični materijali, u kojima istovremeno postoji feromagnetno i feroelektrično uređenje, postali su veoma interesantni za istraživanje zbog primene u tehnologiji, kao i zbog svojih fundamentalnih fizičkih karakteristika. Međutim, magnetoelektrici se retko sreću u prirodi, a magnetno uređenje može koegzistirati sa dugodometnim polarnim uređenjem samo u nekoliko struktura. Perovskiti na bazi olova su posebno interesantni kao izuzetni dielektrični, piezoelektrični i elektrostriktivni materijali koji se koriste u mnogim modernim aplikacijama. Istovremeno, perovskiti na bazi olova su veoma detaljno ispitivani u poslednje vreme zbog interesantnih magnetnih osobina koje ispoljavaju. Ovi perovskiti su perspektivni materijali u smislu koegzistencije spinskog i dipolnog uređenja. Očekuje se da stanje spontane polarizacije potiče usled lokalne distorzije okruženja jona olova. Paramagnetni joni u B položajima (u ovom slučaju Co^{2+} joni) mogu da prouzrokuju magnetno uređenje. U ovom radu je istražen $\text{Pb}_2\text{CoTeO}_6$ perovskit u opsegu temperatura od 5 K do 450 K, u kome su uočeni brojni toplotno prouzrokovani fazni prelazi, od monoklinske do kubne strukture. Ovde će biti razmotrene različite kristalne strukture, kao i magnetna struktura koja se javlja na temperaturama nižim od 20 K.

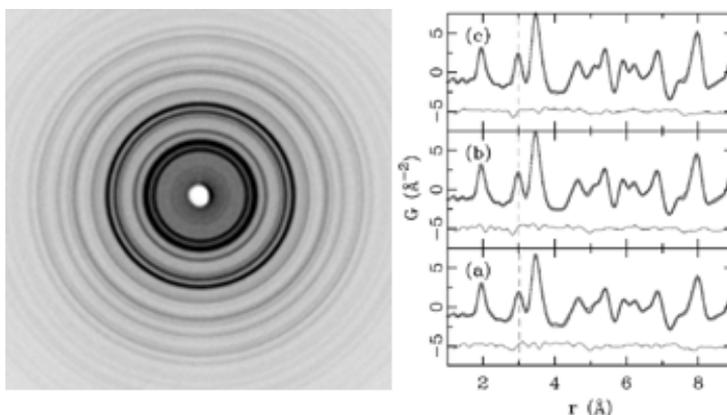
RIETVELD vs. PDF METHOD IN ANALYSIS OF NANOCRYSTALLINE LITHIUM FERRITE

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The crystal structure and microstructure analysis of nanocrystalline lithium ferrite have been done using transmission electron microscopy (TEM) and X-ray diffraction (XRD) data collected on a synchrotron source. The high-energy XRD experiments were performed on the 6-ID-D beamline at the Advanced Photon Source at Argonne National Laboratory, Illinois. Diffraction data were collected at room temperature with an X-ray energy of 86.8406 keV, using the rapid acquisition pair distribution (RAPDF) technique [1], and an image plate camera (Mar345). 2D diffraction patterns (shown on figure left) were integrated and converted to intensity vs. 2θ using the FIT2D software, and then corrected and normalized by the PDFgetX2 program. The Sine Fourier transform of obtained signals, i.e. the atomic PDF functions are shown in figure (right), for lithium ferrite nanopowders annealed at different temperatures. XRD data were analyzed using the Rietveld and the pair distribution function (PDF) methods. The obtained results were compared [2].



- [1] P. J. Chupas, X. Qui, J. C. Hanson, P. L. Lee, C. P. Grey, S. J. L. Billinge, *J. Appl. Crystallogr.*, 36 (2006), pp. 1342-47
- [2] N. G. Jović, A. S. Masadeh, A. S. Kremenović, B. V. Antić, J. L. Blanuša, N. D. Cvjetičanin, G. F. Goya, M. Vittori Antisari, E. Božin, *J. Phys. Chem. C*, 113 (2009), pp. 20559-567

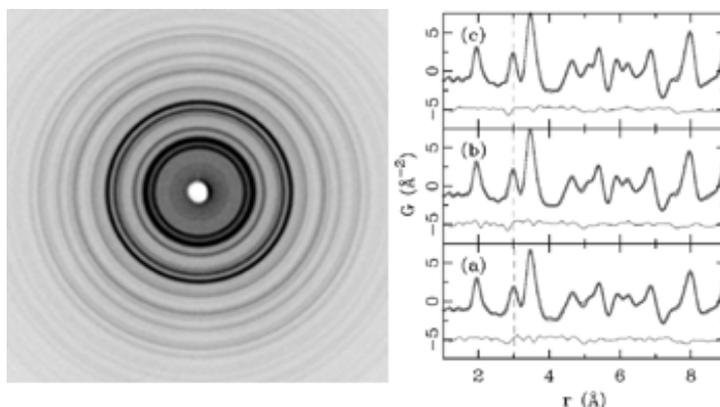
POREĐENJE RITVELDOVE I PDF METODE U ANALIZI NANOKRISTALNOG LITIJUM FERITA

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Kristalna i mikrostrukturalna analiza nanokristalnog praha litijum ferita urađena je koristeći transmisionu elektronsku mikroskopiju (TEM) i difrakciju X-zraka (XRD) sa sinhrotronskog izvora zračenja. Difrakcija X-zraka visoke energije izvedena je na 6-ID-D liniji izvora fotona u nacionalnoj laboratoriji Argone, Illinois. Difrakcioni podaci su prikupljeni na sobnoj temperaturi koristeći X-zrake energije 86,8406 keV, tehniku brzog prikupljanja podataka (RAPDF) [1], i *image plate* kameru (Mar345). Dobijeni 2-dimenzionalni difrakcioni podaci (prikazani na slici levo) su integrisani i prevedeni u oblik zavisnosti intenziteta od ugla 2θ , koristeći FIT2D program, a potom korigovani i normalizovani pomoću PDFgetX2 programa. Sinusnim furijeovim transformacijama ovih signala, dobijene su tzv. atomske PDF funkcije prikazane na slici desno za nanoprahove litijum ferita žarene na različitim temperaturama. Rezultati rendgenske analize su analizirani koristeći Ritveldovu metodu i metodu distribucije funkcije parova (PDF metodu). Dobijeni rezultati su upoređeni [2].



- [1] P. J. Chupas, X. Qui, J. C. Hanson, P. L. Lee, C. P. Grey, S. J. L. Billinge, *J. Appl. Crystallogr.*, 36 (2006), str. 1342-47
- [2] N. G. Jović, A. S. Masadeh, A. S. Kremenović, B. V. Antić, J. L. Blanuša, N. D. Cvjetičanin, G. F. Goya, M. Vittori Antisari, E. Božin, *J. Phys. Chem. C*, 113 (2009), str. 20559-567

LITHIUM SELF-DIFFUSION IN LiAlSi₂O₆ GLASS AND SINGLE CRYSTALS

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Understanding the mechanisms of lithium diffusion is of great interest for geo- and material sciences. Optimizing the performance of Li-bearing solid media has a significant impact in developing new technologies. Knowledge of kinetic Li-isotopic fractionation leads to better understanding of geological processes in which lithium geochemistry plays a major role.

Our ongoing research is aimed to investigate Li diffusion in aluminosilicate media. In the scope of this study, spodumene (LiAlSi₂O₆) like materials were selected as representative model system since lithium, as the only mobile species, migrates through a static aluminosilicate network. Crystalline and glassy materials are compared in order to determine the effect of structural order on Li-diffusion. Glasses were produced by melting of oxide and carbonate mixtures as well as by melting natural spodumene. Natural crystals are from different pegmatites worldwide. Synthetic single crystals were obtained in a slow crystallization process using a flux method. The samples were tested by impedance spectroscopy for ionic conductivity in the range between 1 Hz to 10 MHz at temperatures up to 940 K. Additionally, lithium self-diffusion coefficients were determined by diffusion couple experiments using two halves with same base composition but different Li isotopic abundancies. Li isotope profiles were measured using UV fs laser ablation coupled with ICP-MS. Raman spectroscopy aided in better understanding the local structural features which coordinate lithium migration.

Ionic conductivity was found to be 6 - 7 orders of magnitude slower in natural spodumene crystals than in the glasses while the activation energy for Li conduction is about the same for both materials (0.66 kJ/mol for the glass, 0.76. kJ/mol for the crystal). This implies that the barrier for Li-migration is not sensitive to structural order in aluminosilicate materials. Comparison of Li isotope diffusion data and dc ionic conductivity yields a correlation factor of 0.5 for Li-diffusion in LiAlSi₂O₆-glasses.

САМОДИФУЗИЈА ЛИТИЈУМА У $\text{LiAlSi}_2\text{O}_6$ СТАКЛУ И МОНОКРИСТАЛИМА

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Разумевање механизма дифузије литијума је од велике важности за геологију као и за науку о материјалима. Оптимизација својстава литијумских материјала има директан утицај на развитак разноврсних нових технологија. Познавање кинетике фракционације изотопа литијума води бољем дефинисању процеса у којима је пресудна геохемија литијума.

Главни фокус нашег истраживања је дифузија литијума у алумосиликатима. У оквиру овог истраживања су коришћени узорци који по хемијском саставу одговарају сподумени ($\text{LiAlSi}_2\text{O}_6$) и у којима је литијум једини мобилни јон у оквиру статичне алуминосиликатне мреже. Поликристални и узорци стакла су упоређени у циљу одређивања утицаја степена структурне уређености на дифузију литијума. Стакла су добијена стапањем мешавине оксида и карбоната у стехиометријском односу као и стапањем природног минерала. Природни сподумени испитивани у оквиру ове студије су пореклом из различитих пегматитских лежишта широм света. Синтетички монокристали су добијени спором кристализацијом методом флукса. Проводљивост узорака је тестирана спектроскопијом импеданце у опсегу 1 Hz to 10 MHz на температурама до 940 K. Такође, коефицијенти самодифузије литијума су одређивани уз помоћ изотопске измене међу два половина дифузног пара са истом хемијом али различитим односом изотопа литијума. Изотопски профили су мерени методом UV fs ласерске аблације у комбинацији са ICP-MS методом. Раманском спектроскопијом су испитана локална структурна својства која утичу на миграцију литијума.

Јонска проводљивост се показала као 10^6 - 10^7 пута мања у природним сподуменима у односу на стакло, док је активациона енергија за проводљивост литијума била скоро иста за обе врсте узорака. На основу овога се може закључити да енергетска баријера за дифузију литијума није осетљива на степен структурно уређења у алуминосиликатним материјалима. Комбинацијом изотопске самодифузије литијума са јонском проводљивошћу једносмерне струје добијен је корелациони фактор у вредности 0,5 за дифузију литијума у $\text{LiAlSi}_2\text{O}_6$ стаклима.

DISSOLUTION OF SODIUM CHLORATE CRYSTALS IN SUPERSATURATED SOLUTIONS

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Results of investigations of the growth and dissolution behavior of small sodium chlorate crystals at temperatures near saturation temperature $T_s = (31.00 \pm 0.02)^\circ\text{C}$ are presented. Above T_s all observed crystals dissolved, as was expected. At the temperatures below T_s , crystals grew mainly, with significant growth rate dispersion, as was noticed earlier [1], i.e. the growth rates of the crystals were different, even when the growth was performed under the same macroscopic external conditions (temperature, supersaturation). Crystal growth was performed at $(29.00 \pm 0.02)^\circ\text{C}$, corresponding to supersaturation of $\sigma = 0.89\%$. Then the temperature was gradually increased in steps of 0.02°C . Some of the observed crystals (less than 1%), dissolved at the temperatures below T_s , although they were placed in supersaturated solution, i.e. simultaneous growth and dissolution of crystals existed. Decreasing of solution temperature below $(30.60 \pm 0.02)^\circ\text{C}$, corresponding to supersaturation of $\sigma = 0.18\%$, induced refaceting and regrowth of all of these crystals. Simultaneous growth and dissolution of crystals is explained, so far, by so-called Ostwald ripening [2]. This process occurs by the growth of large particles at the expense of smaller ones which dissolve. For example, dissolution of smaller crystals $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4$ close to bigger crystal, with keeping of crystal form, was observed earlier in supersaturated solution [3].

Dissolving of sodium chlorate crystals in supersaturated solution was occurred in different parts of crystallization cell. They had different orientation with respect to solution flow. This phenomenon occurred on crystals far from the other crystals, and also on crystals with close neighbours. Process of dissolution proceeded through dissolution of higher indices faces, as it was expected. Crystals became rounded, i.e. they did not keep the form, as in Ref. [2]. Reason for dissolving sodium chlorate crystals in supersaturated solution is unknown. This phenomenon can not be explained by Ostwald ripening, since the sizes of the growing and dissolving crystals were similar and the crystals which did not have neighbours in their ambience also dissolved. Possible reasons might be the different impurities concentrations or the lattice strain in various crystals.

[1] M. M. Mitrović, A. A. Žekić, Z. Z. Ilić, Chem. Phys. Lett. 361, (2002) 312.

[2] W. Ostwald, Z. Phys. Chem. 37, (1901) 385.

[3] F. H. Mischgofsky, J. Cryst. Growth, 65, (1983) 500.

RASTVARANJE KRISTALA NATRIJUM HLORATA U PRESIĆENIM RASTVORIMA

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U radu su predstavljeni rezultati istraživanja rasta i rastvaranja malih kristala natrijum hlorata na temperaturama bliskim temperaturi zasićenja $T_s = (31,00 \pm 0,02)^\circ\text{C}$. Na temperaturama iznad T_s svi posmatrani kristali su se rastvarali, što je i bilo očekivano. Na temperaturama ispod T_s posmatrani kristali su uglavnom rasli, sa značajnom disperzijom brzina, što je i ranije primećeno [1], odnosno, kristali su rasli različitim brzinama iako su svi bili pod istim makroskopskim spoljašnjim uslovima (temperatura, presićenje). Rast kristala se odvijao na $(29,00 \pm 0,02)^\circ\text{C}$, što je odgovaralo presićenju od $\sigma = 0,89\%$. Zatim je temperatura povećavana u koracima od $0,02^\circ\text{C}$. Primećeno je da se neki od posmatranih kristala (manje od 1%) rastvaraju na temperaturama ispod T_s iako su se nalazili u presićenom rastvoru. Dakle, primećeni su istovremeno i rast i rastvaranje kristala. Snižavanje temperature rastvora ispod $(30,60 \pm 0,02)^\circ\text{C}$, što je odgovaralo presićenju od $\sigma = 0,18\%$, indukovalo je refacetiranje i ponovni rast ovih kristala. Do sada su istovremeni rast i rastvaranje kristala objašnjavani tzv. Ostwald ripeningom [2]. Ovaj proces se manifestuje kroz rast velikih kristala na račun manjih koji se rastvaraju. Na primer, rastvaranje malih kristala $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{CuCl}_4$ u blizini velikih, uz zadržavanje forme, uočen je u ranijim istraživanjima [3].

Rastvaranje kristala natrijum hlorata u našim eksperimentima primećeno je u različitim delovima ćelije za kristalizaciju. Kristali su imali različitu orijentaciju u odnosu na tok rastvora. Ova pojava je primećena na kristalima udaljenim od susednih kao i na kristalima koji se nalaze u neposrednoj blizini susednih kristala. Kristali su se rastvarali preko pljosni viših indeksa, što je i očekivano. Postajali su zaobljeni, odnosno nisu zadržavali formu kao što je to bio slučaj u referenci [2]. Razlog rastvaranja kristala natrijum hlorata nije poznat. Ova pojava ne može biti objašnjena Ostwald ripeningom s obzirom da su veličine kristala koji rastu i onih koji se rastvaraju veoma slične i da su se rastvarali i kristali koji u svojoj neposrednoj blizini nisu imali susede. Mogući razlozi mogu biti različite koncentracije primesa ili naprezanja rešetke različitih kristala.

[1] M. M. Mitrović, A. A. Žekić, Z. Z. Ilić, Chem. Phys. Lett. 361, (2002) 312.

[2] W. Ostwald, Z. Phys. Chem. 37, (1901) 385.

[3] F. H. Mischgofsky, J. Cryst. Growth, 65, (1983) 500.

SYNTHESIS AND CHARACTERIZATION OF $\text{CeO}_2\text{-Bi}_2\text{O}_3$ SOLID SOLUTION

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Nanocrystalline powders of solid solution $\text{CeO}_2\text{-Bi}_2\text{O}_3$ were synthesized by self-propagating room temperature reaction (SPRT) procedure with composition $(\text{Ce}_{1-x}\text{Bi}_x\text{O}_{2-\delta})$ where the $x = 0.1 - 1$. X-ray diffraction analyses show that for $x < 0.50$ a solid solution with fluorite structure is formed. Rietveld's structure refinement method was applied to characterize prepared powder and its microstructure (size-strain). The lattice parameters increase according to Vegard's law with increasing of Bi concentration. The average crystal size is about 2 - 3 nm. Spectroscopic ellipsometry and Raman scattering measurements were used to characterize the samples at room temperature. The Raman measurements demonstrated electron molecular vibrational coupling and increase of oxygen vacancy concentration whereas doping provokes a small decrease of optical absorption edge in comparison with pure ceria. Specific surface area of obtained powder was measured by Brunauer-Emmet-Teller (BET) method.

SINTEZA I KARAKTERIZACIJA ČVRSTOG RASTVORA $CeO_2-Bi_2O_3$

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Čvrsti rastvori $CeO_2 - Bi_2O_3$ su dobijeni primenom samostalno propagirajuće sinteze na sobnoj temperaturi (SPRT metoda), pri čemu su sintetisani nanočestični prahovi sledećeg sastava: $Ce_{1-x}Bi_xO_{2-\delta}$ gde je $x = 0.1 - 1$. Rendgenskom difrakcijom praha otkriveno je da za $x \leq 0.50$ dolazi do formiranja serije čvrstih rastvora sa fluoritskim tipom strukture. Ritveldova metoda utalnjanja primenjena je za karakterizaciju strukturnih i mikrostrukturnih osobina sintetizovanih prahova. Utvrđeno je da dolazi do porasta parametara jedinične ćelije sa porastom koncentracije bizmuta, shodno Vegardovom zakonu. Prosečna veličina kristalita svih uzoraka iznosi oko 2 – 3 nm. Ramanskom spektroskopijom potvrđeno je da dolazi do formiranja čvrstih rastvora, kao i da dolazi do povećanja koncentracije kiseoničnih vakancija sa povećanjem koncentracije Bi. Elipsometrijska istraživanja su pokazala da dopiranje bizmutom dovodi do smanjenja energetskog procepa karakterističnog za poluprovodničke materijale, u poređenju sa čistim CeO_2 . Primenom BET metode izmerena je i specifična površina dobijenih nanočestičnih prahova.

REINVESTIGATION OF PURE Na-NEPHELINE LIKE COMPOUNDS OBTAINED BY THERMAL CONVERSION OF LTA-ZEOLITE

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As a natural rock-forming tectosilicate, nepheline has the idealized composition $\text{Na}_6\text{K}_2[\text{Al}_8\text{Si}_8]_{16}\text{O}_{32}$. Nepheline is not only among the important constituents of Earth's crust, but also has widespread applications in glass and ceramics industries. Its TO_4 ($T = \text{Si}, \text{Al}$) framework consists of single six-membered rings (S6R) as tetrahedral building units connected in a tridymite-type topology. The nepheline structure is a stuffed derivative modification of high-tridymite, where half of Si^{4+} cations are replaced by Al^{3+} . For charge balance 75 % of cavities are adapted to the smaller size of sodium ions, while the remaining 25 % are mainly occupied by potassium ions. Synthetic samples of nepheline can contain only sodium.

In this contribution a nepheline-like sample synthesized by thermal transformation of Na-LTA zeolite was investigated. In a previous work [1] the product of such thermal treatment has been described as a standard pure sodium nepheline [2]. Further TEM investigations conducted on synthesized polycrystalline material proved the presence of a structure with a tripled c -unit cell parameter compared with that observed in classical nepheline [3]. Consequently, we compared the theoretical X-ray powder diagrams of all known trinepheline compounds with the experimental powder pattern and concluded that the material is actually a mixture of two phases. Rietveld refinement against XRPD data using structural models of (a) classical Na-nepheline [3] (S. G. $P6_3$, $a = 9.971(3)$, $c = 8.349(2)$ Å) and (b) monoclinic trinepheline [4] (S. G. $P112_1$, $a = 9.995(4)$, $b = 9.963(4)$, $c = 24.988(7)$ Å, $\gamma = 119.75(3)^\circ$) resulted in a satisfying agreement between calculated and observed step intensities ($\chi^2 = 1.96$, $R_{\text{wp}} = 11.3$, $R_p = 8.77\%$). The additional quantitative analyses of samples obtained in a temperature range of nepheline stability (900 – 1100 °C) showed the presence of both structures, and also a gradual increase of the monoclinic trinepheline phase weight fraction with increasing temperature.

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НОВА КАРАКТЕРИЗАЦИЈА Na-НЕФЕЛИНСКИХ ФАЗА ДОБИЈЕНИХ ТЕРМАЛНОМ ТРАНСФОРМАЦИЈОМ ЗЕОЛИТА ТИПА LTA

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Идеална хемијска формула минерала нефелина који структурно припада групи тектосиликата јесте $\text{Na}_6\text{K}_2[\text{Al}_8\text{Si}_8]_{16}\text{O}_{32}$. Нефелин није само један од најважнијих градитеља Земљине коре, већ има и широку примену у керамичкој и стакларској индустрији. Просторна TO_4 ($T = \text{Si}, \text{Al}$) мрежа овог минерала састоји се од једноструких шесточланих прстенова (S6R) као основних тетраедарских градивних јединица које су повезане тако да одговарају топологији тридимита. Структура нефелина је попуњени дериват високо-температурне модификације тридимита, где је половина Si^{4+} катјона замењена Al^{3+} катјонима. Баланс наелектрисања се постиже попуњавањем 75 % шупљина мањим јонима натријума, док у преосталих 25 % улази јон калијума. Синтетички добијени узорци нефелина могу садржати само натријум.

Предмет истраживања у овом раду су узорци фаза нефелина добијени термалном трансформацијом Na-LTA зеолиита. У ранијем истраживању [1] производ ове термалне трансформације описан је као чисти Na-нефелин [2]. Испитивања синтетисаног поликристалног материјала ТЕМ методом показала су присуство структуре са три пута већим c -параметром јединичне ћелије у односу на класичну структуру нефелина [3]. Поређењем теоријских рендгенских дијаграма праха са дијаграмима праха свих познатих структура тринефелина закључено је да је добијени материјал мешавина две фазе. Подаци добијени рендгенском дифракцијом на праху утањавани су Ритвелдовом методом као мешавина (а) класичног Na-нефелина [3] [П. Г. $P6_3$, $a = 9,971(3)$; $c = 8,349(2)$ Å] и (б) моноклиничног тринефелина [4] [П. Г. $P112_1$, $a = 9,995(4)$; $b = 9,963(4)$; $c = 24,988(7)$ Å; $\gamma = 119,75(3)^\circ$] и добијено је добро слагање израчунатих и измерених интензитета ($\chi^2 = 1,96$; $R_{\text{wp}} = 11,3$; $R_p = 8,77$ %). Додатна квантитативна анализа узорака добијених у температурном опсегу стабилности нефелина (900 – 1100 °C) показала је присуство обе фазе и постепени пораст масеног удела моноклиничног тринефелина са повећањем температуре.

Ово истраживање финансијски су помогли Аустријски научни фонд (FWF), уговор I62-N10 и Швајцарски национални научни фонд (SNSF), уговор IZ73Z0-127961.

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STRUCTURAL TRANSFORMATIONS OF HYDROTHERMALLY SYNTHESIZED α - $\text{Li}_{2-x}\text{TiO}_{3-0,5x} \cdot (\text{H}_2\text{O})_y$

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Lithium titanium oxides are attracted much attention, especially since their usage in Li-ion batteries ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ is commercially used as anode and $\text{Li}_2\text{Ti}_3\text{O}_7$ is a good candidate as new anode material). Li_2TiO_3 is one more compound and in recent years it is considered as a solid breeder material in the blanket of DT fusion reactors. Li_2TiO_3 exists in three crystal modifications: monoclinic β - Li_2TiO_3 has a narrow homogeneity range with atomic Li:Ti ratio from 1.84 to 2.24, while α - and γ - Li_2TiO_3 have the NaCl structure type and much broader stoichiometry range Li:Ti = 1.02 – 2.76. The high-temperature γ - Li_2TiO_3 cannot be quenched to room temperature without its transition to β - Li_2TiO_3 . Metastable α - Li_2TiO_3 is identical to γ -phase and can be synthesized hydrothermally at low temperatures.

In this work, α - $\text{Li}_{2-x}\text{TiO}_{3-0,5x} \cdot (\text{H}_2\text{O})_y$ phases with atomic Li:Ti ratios: 1.76, 1.66 and 1.06 are synthesized by hydrothermal lithiation of anatase powders in aqueous LiOH solutions of different concentrations (for 24 h at 200 °C under autogenous pressure). Further structural transformations were followed by a combination of TG/DSC and XRPD analysis. As prepared samples were gradually annealed at temperatures between 300 and 1000 °C with 100 °C interval and characterized by XRPD at each step. Cyclic TG/DSC analysis was performed by heating samples in an air atmosphere up to 1200, 1250 or 1300 °C, cooling to 600 °C and repeating the cycle.

In short, cubic α -phase is stable up to about 250 °C when its transformation to spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ begins. This process is followed by transformation of remaining α -phase to disordered β - Li_2TiO_3 , starting at about 390 °C. These two transitions are overlapped and the relative ratio of produced $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and β - Li_2TiO_3 depends on the sample stoichiometry. Generally, the lower Li content the more spinel is found in the mixture. Disordered β - Li_2TiO_3 progressively orders up to 1000 °C and it is stable up to about 1150 °C, when its transition to γ -phase is observed. Depending on final temperature of DSC analysis and the stoichiometry of the sample, the phase transitions were severely different on cooling. For example, when α -phase with Li:Ti = 1.76 was heated to 1200 °C, the freshly formed γ -phase was almost immediately back to β -phase, while after heating to 1250 °C, the same transition was a little delayed. After heating to 1300 °C, $\gamma \rightarrow$ spinel transition was preferred over $\gamma \rightarrow \beta$ transition. This can be explained by the sample stoichiometry that is very close to the ideal β - Li_2TiO_3 composition line in the Li–Ti–O phase diagram. At lower temperatures the sample behaves like a stoichiometric β - Li_2TiO_3 compound, while when heated to higher temperature it shifts to other regions of the phase diagram. These observations and behavior of other samples will be discussed in detail.

STUKTURNE TRANSFORMACIJE HIDROTHERMALNO SINTETISANIH α -Li_{2-x}TiO_{3-0,5x}·(H₂O)_y

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Litijum-titanati privlače veliku pažnju, posebno zbog primene u savremenim Li-jonskim baterijama (Li₄Ti₅O₁₂ je već komercijalna anoda, dok je Li₂Ti₃O₇ potencijalni materijal za istu namenu). U poslednje vreme ispituje se mogućnost primene Li₂TiO₃ u oplodnim DT reaktorima. Jedinjenje se javlja u tri strukturne modifikacije. Monoklinični β-Li₂TiO₃ ima uzak opseg stehiometrije sa atomskim odnosom Li:Ti = 1,84 – 2,24, dok se α- i γ-Li₂TiO₃ sa strukturom NaCl javljaju u veoma širokom opsegu stehiometrije sa odnosom Li:Ti = 1,02 – 2,76. Visokotemperaturnu fazu, γ-Li₂TiO₃, nije moguće ohladiti bez transformacije u monoklinični β-Li₂TiO₃. Metastabilna α-Li₂TiO₃ faza identična je γ-fazi i lako se dobija hidrotermalnim tretmanom na niskim temperaturama, jer je stabilizuju protoni iz vode.

U ovom radu hidrotermalnom litijacijom anatasa u vodenim rastvorima LiOH različite koncentracije sintetisane su tri nestehiometrijske α-Li_{2-x}TiO_{3-0,5x}·(H₂O)_y faze sa odnosom Li:Ti = 1,76; 1,66 i 1,06. Hidrotermalni tretmani u trajanju od 24 h izvedeni su u autoklavu na 200 °C pri autogenom pritisku. Strukturne transformacije pripremljenih faza ispitivane su kombinacijom XRPD i TG/DSC analize. Uzorci su postepeno žareni na 300 – 1000 °C sa intervalom od 100 °C, dok je XRPD analiza rađena na svakom koraku. Ciklična DSC analiza rađena je u atmosferi vazduha zagrevanjem do 1200, 1250 ili 1300 °C, hlađenjem do 600 °C i ponavljanjem ciklusa.

Ukratko, α-faza je stabilna do oko 250 °C, kada počinje njena transformacija u spinel Li₄Ti₅O₁₂; na to se nadovezuje transformacija ostatka α-faze u neuređenu β-fazu sa početkom na oko 390 °C. Ove dve transformacije su u znatnoj meri preklapljene, a međusobni odnos nastalih Li₄Ti₅O₁₂ i β-Li₂TiO₃ zavisi od stehiometrije uzorka, pri čemu važi pravilo: manje Li daje više spinela u smeši. Neuređeni β-Li₂TiO₃ postepeno se uređuje do oko 1000 °C i stabilan je do oko 1150 °C, kada se transformiše u γ-fazu. U zavisnosti od krajnje temperature DSC analize i stehiometrije uzorka fazne transformacije prilikom hlađenja bitno su različite. Na primer, kada je α-faza sa odnosom Li:Ti = 1,76 grejana do 1200 °C, nastala γ-faza skoro momentalno se relaksirala u β-fazu, dok se posle zagrevanja do 1250 °C ista transformacija odigravala na nešto nižoj temperaturi. Posle zagrevanja do 1300 °C prelaz γ → spinel dominira u odnosu na prelaz γ → β. Ovakvo ponašanje može se objasniti sastavom uzorka koji je veoma blizak liniji za β-Li₂TiO₃ na faznom dijagramu sistema Li–Ti–O. Na nižim temperaturama uzorak se ponaša kao β-Li₂TiO₃ faza idealnog sastava, dok je pri zagrevanjima na više temperature dolazilo do promene, odnosno do pomeranja u druge oblasti na faznom dijagramu. Pomenuti i ostali ekperimentalni rezultati biće detaljno diskutovani u radu.

Pb-DOPED γ -Bi₂O₃ PHASE IN THE Bi₂O₃-PbO PHASE DIAGRAM

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The possibility to obtain single, Pb-doped γ -Bi₂O₃ phase starting from x Bi₂O₃· y PbO mixtures of various compositions was investigated. Namely, according to the existing Bi₂O₃-PbO phase diagram [1], the single, Pb-doped γ -phase can be isolated only from 6Bi₂O₃·PbO (14.3 mole% PbO) starting mixture. This is not in agreement with our previous experience. So the aim of this work was to check reliability of the current Bi₂O₃-PbO phase diagram and to determine the area of stability of Pb-doped γ -Bi₂O₃ phase.

The products were prepared by high temperature solid state reactions between bismite (α -Bi₂O₃) and massicot (PbO) with different oxide proportions: 1.5Bi₂O₃·PbO, 1.67Bi₂O₃·PbO, 2.75Bi₂O₃·PbO, 4Bi₂O₃·PbO, 5.5Bi₂O₃·PbO, 6Bi₂O₃·PbO, 12Bi₂O₃·PbO, 18Bi₂O₃·PbO, 19Bi₂O₃·PbO, 38Bi₂O₃·PbO. All products were characterized by X-ray powder diffraction (XRPD) and differential thermal analysis (DTA). Selected starting mixtures (5.5Bi₂O₃·PbO, 6Bi₂O₃·PbO, 19Bi₂O₃·PbO) were also examined by DTA.

In all cases, the addition of PbO into α -Bi₂O₃ causes the stabilization of metastable γ -Bi₂O₃ phase down to room temperature with unit cell parameters in a narrow 10.24 – 10.27 Å range, no matter whether a single or multiphase sample was obtained. However, single-phase products were obtained from the following starting mixtures: 5.5Bi₂O₃·PbO, 6Bi₂O₃·PbO, 12Bi₂O₃·PbO, 18Bi₂O₃·PbO and 19Bi₂O₃·PbO, or in 5.0 – 15.4 mole% PbO range.

As shown by cyclic DTA curves, when starting mixtures are heated, the α -Bi₂O₃ → γ -Bi₂O₃ transition occurs in one step at about 635 °C, while γ -Bi₂O₃ → δ -Bi₂O₃ transition occurs in two steps at 710 and 730 °C independently of the Bi₂O₃:PbO molar ratio. On cooling, δ -Bi₂O₃ → γ -Bi₂O₃ transition occurs at 680–650 °C, and this temperature depends on the Bi₂O₃:PbO molar ratio (higher Bi₂O₃:PbO molar ratio, lower temperature). No γ -Bi₂O₃ → α -Bi₂O₃ transitions were observed on cooling indicating that the opposite process appearing on heating is irreversible.

The cyclic DT analysis of the single γ -phase products confirms the above temperatures for γ -Bi₂O₃ → δ -Bi₂O₃ and δ -Bi₂O₃ → γ -Bi₂O₃ transitions. These temperatures are not well defined in the current phase diagram. The melting points are at 770–820 °C dependently of the Bi₂O₃:PbO molar ratio (higher Bi₂O₃:PbO molar ratio, higher temperature) what is in agreement with the actual phase diagram.

OBLAST γ - Bi_2O_3 FAZE DOPIRANE OLOVOM U FAZNOM DIJAGRAMU Bi_2O_3 - PbO

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U ovom radu ispitivana je mogućnost sinteze mikrokristalnih jednofaznih uzoraka γ - Bi_2O_3 dopiranih olovom polazeći od smeša $x\text{Bi}_2\text{O}_3 \cdot y\text{PbO}$ različitog sastava. Naime, prema postojećem faznom dijagramu sistema Bi_2O_3 - PbO [1], takav uzorak je moguće dobiti jedino iz polazne smeše sastava $6\text{Bi}_2\text{O}_3 \cdot \text{PbO}$ (14,3 mol. % PbO). Kako to nije u saglasnosti sa našim prethodnim saznanjima, cilj istraživanja bio je da se proveriti pouzdanost faznog dijagrama Bi_2O_3 - PbO i da se odredi oblast stabilnosti γ - Bi_2O_3 faze dopirane olovom.

Proizvodi su sintetisani reakcijama u čvrstom stanju iz homogenizovanih smeša bizmita (α - Bi_2O_3) i masikota (PbO) sa sledećim polaznim odnosima: $1,5\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $1,67\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $2,75\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $4\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $5,5\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $6\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $12\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $18\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $19\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $38\text{Bi}_2\text{O}_3 \cdot \text{PbO}$. Dobijeni uzorci su okarakterisani rendgenskom difrakcionom i diferencijalnom termijskom analizom. Odabrane polazne smeše ($5,5\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $6\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $19\text{Bi}_2\text{O}_3 \cdot \text{PbO}$) takođe su ispitivane diferencijalnom termijskom analizom.

Rezultati su pokazali da u svim ispitivanim uzorcima nastaje γ - Bi_2O_3 faza koja je (meta)stabilna na sobnoj temperaturi. Ipak, jednofazni uzorci koji sadrže isključivo γ - Bi_2O_3 dobijeni su polazeći od pet smeša: $5,5\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $6\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $12\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, $18\text{Bi}_2\text{O}_3 \cdot \text{PbO}$ i $19\text{Bi}_2\text{O}_3 \cdot \text{PbO}$, to jest u opsegu od 5,0 do 15,4 mol. % PbO . Parametri jediničnih ćelija sintetisanih γ - Bi_2O_3 faza leže u uskom intervalu (10,24 – 10,27 Å) i ne zavise od toga da li je dobijen jednofazan ili višefazan uzorak.

DT analizom u cikličnom režimu rada, utvrđeno je da se pri zagrevanju polaznih smeša prelaz α - $\text{Bi}_2\text{O}_3 \rightarrow \gamma$ - Bi_2O_3 odigrava u jednom koraku na oko 635 °C, dok se prelaz γ - $\text{Bi}_2\text{O}_3 \rightarrow \delta$ - Bi_2O_3 odvija u dva koraka na oko 710 i 730 °C. Ove temperature ne zavise od molskog odnosa $\text{Bi}_2\text{O}_3 \cdot \text{PbO}$. Temperatura povratnog δ - $\text{Bi}_2\text{O}_3 \rightarrow \gamma$ - Bi_2O_3 prelaza, koji se odigrava pri hlađenju, zavisi od molskog odnosa $\text{Bi}_2\text{O}_3 \cdot \text{PbO}$ (veći molski odnos daje nižu temperatura) i nalazi se između 680 i 650 °C. Pri daljem hlađenju ne dolazi do prelaza γ - $\text{Bi}_2\text{O}_3 \rightarrow \alpha$ - Bi_2O_3 , što znači da je suprotan proces, do koga dolazi pri zagrevanju, nepovratan.

Temperature faznih transformacija γ - $\text{Bi}_2\text{O}_3 \rightarrow \delta$ - Bi_2O_3 i δ - $\text{Bi}_2\text{O}_3 \rightarrow \gamma$ - Bi_2O_3 potvrđene su i cikličnom DT analizom sintetisanih jednofaznih uzoraka γ - Bi_2O_3 . Upravo te temperature nisu jasno definisane u postojećem faznom dijagramu Bi_2O_3 - PbO . Temperatura topljenja zavisi od molskog odnosa $\text{Bi}_2\text{O}_3 \cdot \text{PbO}$ (veći molski odnos daje višu temperatura) i nalazi se u intervalu od 770 do 820 °C, što je u saglasnosti sa aktuelnim faznim dijagramom.

POSTER PRESENTATIONS

POSTERSKA SEKCIJA

CRYSTAL STRUCTURE OF DICHLORIDO-BIS(TRIHYDROXYCHLORO)PALLADIUM(II) COMPLEX

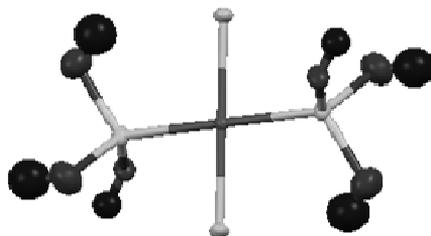
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In attempt to prepare a palladium(II) complex with *O,O'*-dipentyl-ethylenediamine-*N,N'*-di-(*S,S*)-2(4-methyl)-pentanoate, this ligand was combined with an aqueous solutions of $K_2[PdCl_4]$ and lithium hydroxide in a molar ratio 1:1:2, at room temperature. Single crystals suitable for X-ray crystal structure determination were obtained by slow evaporation from a chloroform-water solution of complex compound. However, the structure determination showed unexpected molecular formula of the complex, $[PdCl_2(Cl(OH)_3)_2]$.

Crystallographic data: $Cl_4H_6O_6Pd$, monoclinic system, space group $P2_1/c$, $a = 6.3410(4)$, $b = 9.3486(4)$, $c = 12.8706(7)$ Å, $\alpha = 90$, $\beta = 136.402(4)$, $\gamma = 90^\circ$, $V = 526.13(5)$ Å³, $Z = 2$, $\mu = 2.211$ mm⁻¹, $F(000) = 336$, crystal size 0.0716×0.0482×0.0295 mm, $R(int) = 0.0448$, $R_1[I > 2\sigma(I)] = 0.0495$, $wR_2(all\ data) = 0.1472$. The crystal packing shows zigzag layers along *b*-axis linked with intermolecular hydrogen bonds, involving two oxygen atoms: O2–H2...O3 (H...A = 2.536; D...A = 3.324 Å) and connecting the molecules within and between the layers.



KRISTALNA STRUKTURA DIHLORIDO-BIS(TRIHIDROKSIHLORO)PALADIUM(II) KOMPLEKSA

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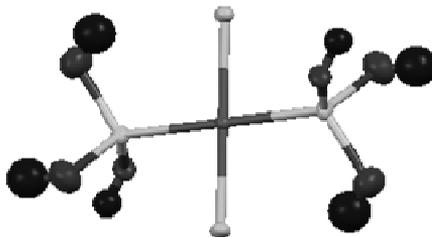
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U pokušaju da se dobije paladium(II)-kompleks sa *O,O'*-dipentil-etilendiamin-*N,N'*-di-(*S,S*)-2(4-metil)-pentanoatom pomešani su vodeni rastvori navedenog liganda, $K_2[PdCl_4]$ i litijum-hidroksida u molarnom odnosu 1:1:2, na sobnoj temperaturi. Kristali pogodni za rendgensku strukturnu analizu dobijeni su sporim uparavanjem hloroformsko-vodenog rastvora kompleksa. Međutim, rendgenska strukturna analiza pokazala je kompleks neočekivane molekulske formule, $[PdCl_2(Cl(OH)_3)_2]$.

Kristalografski podaci: $Cl_4H_6O_6Pd$, monokliničan sistem, prostorna grupa $P2_1/c$, $a = 6,3410(4)$, $b = 9,3486(4)$ Å, $c = 12,8706(7)$ Å, $\alpha = 90$, $\beta = 136,402(4)$, $\gamma = 90$ °, $V = 526,13(5)$ Å³, $Z = 2$, $\mu = 2.211$ mm⁻¹, $F(000) = 336$, veličina kristala $0,0716 \times 0,0482 \times 0,0295$ mm, $R(int) = 0,0448$, $R_1[I > 2\sigma(I)] = 0,0495$, $wR_2 = 0,1472$. Kristalno pakovanje pokazuje cik-cak slojeve duž *b*-ose i povezano je intermolekulskim vodoničnim vezama između dva atoma kiseonika: O(2)–H(2)...O(3) (H...A = 2,536; D...A = 3.324 Å). Vodonične veze povezuju molekule kompleksa unutar i između slojeva.



SYNTHESIS AND CRYSTAL STRUCTURE OF TETRACHLORIDE-(*O,O'*-DIETHYL-(*S,S*)-ETHYLENEDIAMINE- -*N,N'*-DI-2-PROPANOATO)-PLATINUM(IV)

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The titled compound was obtained by direct reaction from a water solution of $K_2[PtCl_6]$ and bidentate ligand *O,O'*-diethyl-(*S,S*)-ethylenediamine-*N,N'*-di-2-propanoate dihydrochloride (det-(*S,S*)-eddp·2HCl) in molar ratio 1:1. The reaction mixture was heated on a steam bath for 3 h, during this period water solution of $LiOH \cdot H_2O$ was added. The compound, $[PtCl_4(\text{det-(}i>S,S)-eddp)]$, as a yellow precipitate was separated by filtration, washed with water and air-dried. Yield: 0.032 g (26.3%). The complex was recrystallized from the system DMSO-water. *Anal. Calc.* for $C_{12}H_{24}Cl_4N_2O_4Pt$ ($M_r = 597.23$) (%): C, 24.13; H, 4.69; N, 4.05. Found: C, 24.01; H, 4.54; N, 4.31.

Crystal data: orthorhombic, space group $P2_12_12_1$, crystal size $0.32 \times 0.27 \times 0.17$ mm, $a = 8.038(5)$, $b = 11.444(5)$, $c = 21.646(5)$ Å, $V = 1991.1(16)$ Å³, $Z = 4$, $\rho_x = 1.992$ g cm⁻³, $\mu = 7.60$ mm⁻¹. The refinement on F^2 (248 parameters and 4341 independent reflections), $R[F^2 > 2\sigma(F^2)] = 0.033$, $wR(F^2) = 0.059$, $S = 0.94$.

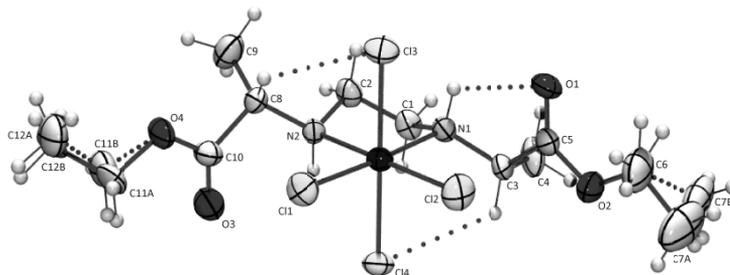


Figure 1. ORTEP plot for $[PtCl_4(\text{det-(}i>S,S)-eddp)]$ complex with the intramolecular hydrogen bonds ($N1-H1 \cdots O1$, $C3-H3 \cdots Cl4$ and $C8-H8 \cdots Cl3$)

SINTEZA I KRISTALNA STRUKTURA TETRAHLORIDO-(*O,O'*-DIETIL-(*S,S*)-ETILENDIAMIN-*N,N'*-DI-2-PROPANOATO)-PLATINA(IV) KOMPLEKSA

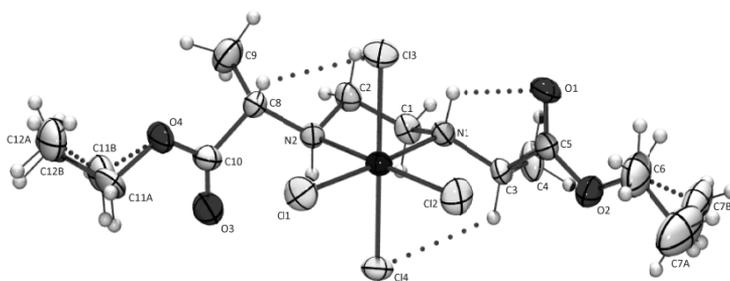
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Navedeno jedinjenje dobijeno je direktnom reakcijom između vodenog rastvora $K_2[PtCl_6]$ i bidentatnog liganda *O,O'*-dietil-(*S,S*)-etilendiamin-*N,N'*-di-2-propanoato dihidrohlorida (det-(*S,S*)-eddp·2HCl) u molskom odnosu 1:1. Reakciona smeša je zagrevana na vodenom kupatilu 3 sata uz dodavanje vodenog rastvora LiOH·H₂O. Jedinjenje $[PtCl_4(\text{det-(}i>S,S)-eddp)]$ je kao žut talog odvojeno ceđenjem, isprano vodom i sušeno na vazduhu. Prinos: 0,032 g (26,3%). Monokristali su dobijeni prekrizacijom iz sistema DMSO-voda. Rezultati mikroanalize za $C_{12}H_{24}Cl_4N_2O_4Pt$ ($M_r = 597,23$) (%): C, 24,13; H, 4,69; N, 4,05. Nađeno: C, 24,01; H, 4,54; N, 4,31.

Kristalografski podaci: rombičan sistem, prostorna grupa $P2_12_12_1$, veličina kristala $0,32 \times 0,27 \times 0,17$ mm, $a = 8,038(5)$, $b = 11,444(5)$, $c = 21,646(5)$ Å, $V = 1991,1(16)$ Å³, $Z = 4$, $\rho_x = 1,992$ g cm⁻³, $\mu = 7,60$ mm⁻¹. Utačnjavanje za F^2 (248 parametara i 4341 nezavisne refleksije), dalo je $R[F^2 > 2\sigma(F^2)] = 0,033$, $wR(F^2) = 0,059$, $S = 0,94$.



Slika 1. ORTEP slika $[PtCl_4(\text{det-(}i>S,S)-eddp)]$ kompleksa sa intramolekulskim vodoničnim vezama (N1–H1···O1, C3–H3···Cl4 i C8–H8···Cl3)

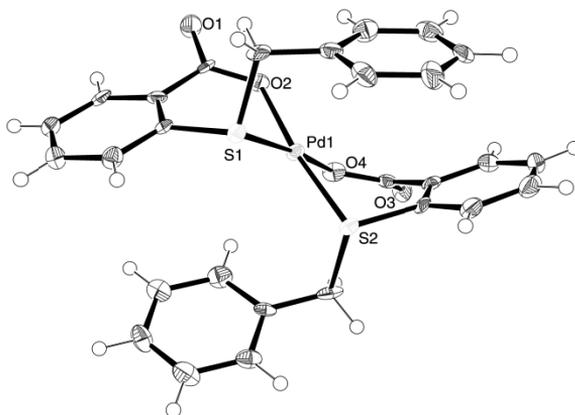
CRYSTAL STRUCTURE OF *bis*-(S-BENZYL- -THIOSALICYLATE)-PALLADIUM(II) COMPLEX, [Pd(S-bz-thiosal)₂]

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Complex, *bis*-(S-benzyl-thiosalicylate)-palladium(II) was obtained by direct reaction of K₂[PdCl₄], (S-benzyl)-2-thiosalicylic acid and LiOH in molar ratio 1:2:2. The mixture was heated on 50°C and stirred for 2 h and during this period water solution of LiOH was introduced. The complex, [Pd(S-bz-thiosal)₂] as a yellow precipitate, was filtered, washed with water and air-dried. Suitable crystal for X-ray was obtained by recrystallization from system DMSO-water.

Crystallographic data: C₂₈H₂₂O₄PdS₂, formula weight 592.98, temperature 123(2) K, monoclinic system, space group P21/c, a = 12.0280(5), b = 21.0330(8), c = 9.5049(4), α = 90, β = 92.578(2), γ = 90, V = 2402.16(17) Å³, Z = 4, ρ_x = 1.640 g·cm⁻³, μ = 0.981 mm⁻¹, F(000) = 1200, crystal size 0.16 x 0.04 x 0.02 mm. The refinement on F² (316 parameters and 4212 independent reflections), R1 = 0.0624, wR2 = 0.1179.



Molecular structure of [Pd(S-bz-thiosal)₂] complex

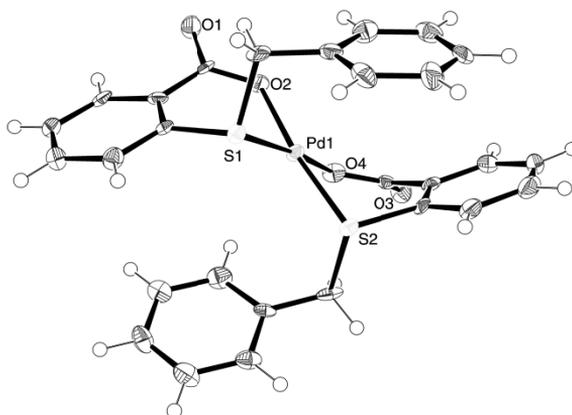
KRISTALNA STUKTURA *bis*-(S-BENZIL- -TIOSALICILATO)PALADIUM(II) KOMPLEKSA, [Pd(S-bz-thiosal)₂]

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Kompleks, *bis*-(S-benzil-thiosalicilato) palladium(II) je dobijen direktnom reakcijom između K₂[PdCl₄], (S-benzil)-2-tiosalicilne kiseline i LiOH u molskom odnosu 1:2:2. Reakciona smeša je zagrevana na 50°C i mešana 2 sata i za to vreme dodavan je vodeni rastvor LiOH. Žuti talog kompleksa, [Pd(S-bz-thiosal)₂] je proceden, ispran vodom i sušen na vazduhu. Odgovarajući kristali za rendgensku stukturu analizu su dobijeni prekrystalisavanjem iz sistema DMSO-voda.

Kristalografski podaci: C₂₈H₂₂O₄PdS₂, molekulska masa 592,98, temperatura 123(2) K, monoklinični sistem, prostorna grupa P21/c, a = 12,0280(5), b = 21,0330(8), c = 9,5049 (4), α = 90°, β = 92,578(2)°, γ = 90°, V = 2402,16(17) Å³, Z = 4, ρ_x = 1.640 g·cm⁻³, μ = 0,981 mm⁻¹, F(000) = 1200, veličina kristala 0.16 x 0.04 x 0.02 mm. Utačnjavanje za F² (316 parametara i 4212 nezavisnih refleksija), R₁ = 0,0624, wR₂ = 0,1179.



Struktura molekula kompleksa [Pd(S-bz-thiosal)₂]

CRYSTAL STRUCTURE OF THREE FERROCENE CONTAINING QUINOLINONE DERIVATIVES

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Crystal structure of all three heterocycles containing a ferrocene unit was determined using single-crystal X-ray diffraction data collected at room temperature. The compounds crystallize in the monoclinic system with very similar unit cell dimensions and the same space group, $P2_1/c$. Consequently molecular geometry, geometrical parameters and intermolecular interactions are very similar for all three crystal structures. The results of a comparative analysis for these ferrocene derivatives will be given in detail.

Crystallographic data.

Compound 1: 2-ferrocenyl-2,3-dihydroquinolin-4(1*H*)-one, $C_{19}H_{17}FeNO$, monoclinic, space group $P2_1/c$, $a = 12.991(4)$, $b = 8.482(2)$, $c = 13.972(3)$ Å, $\beta = 98.80(2)^\circ$, $V = 1521.4(7)$ Å³, $Z = 4$, $\rho_x = 1.446$ g cm⁻³, $\mu = 0.991$ mm⁻¹. The refinement on F^2 (203 parameters and 2977 independent reflections), $R_1 = 0.0733$, $wR_2 = 0.2337$, $S = 1.096$.

Compound 2: 6-chloro-2-ferrocenyl-2,3-dihydroquinolin-4(1*H*)-one, $C_{19}H_{16}FeNOCl$, monoclinic, space group $P2_1/c$, $a = 13.785(5)$, $b = 8.061(5)$, $c = 13.970(5)$ Å, $\beta = 94.997(5)^\circ$, $V = 1546.5(12)$ Å³, $Z = 4$, $\rho_x = 1.570$ g cm⁻³, $\mu = 1.151$ mm⁻¹. The refinement on F^2 (212 parameters and 3573 independent reflections), $R_1 = 0.0475$, $wR_2 = 0.0976$, $S = 1.098$.

Compound 3: 6-bromo-2-ferrocenyl-2,3-dihydroquinolin-4(1*H*)-one, $C_{19}H_{16}FeNOBr$, monoclinic, space group $P2_1/c$, $a = 14.101(5)$, $b = 7.999(5)$, $c = 14.015(5)$ Å, $\beta = 96.104(5)^\circ$, $V = 1571.8(13)$ Å³, $Z = 4$, $\rho_x = 1.733$ g cm⁻³, $\mu = 3.504$ mm⁻¹. The refinement on F^2 (212 parameters and 3622 independent reflections), $R_1 = 0.0562$, $wR_2 = 0.1054$, $S = 1.132$.

KRISTALNA STRUKTURA TRI DERIVATA HINOLINONA KOJI SADRŽE FEROCEN

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Kristalna struktura sva tri heterociklična jedinjenja koja sadrže ferocen određena je rendgenskom strukturnom analizom korišćenjem eksperimentalnih podataka difrakcije rendgenskog zračenja sa monokristala na sobnoj temperaturi. Jedinjenja kristališu u monokliničnom kristalnom sistemu sličnih dimenzija jedinične ćelije i iste prostorne grupe, $P2_1/c$. Ovo za posledicu ima da su molekulska geometrija, geometrijski parametri i intermolekulske interakcije veoma slični za sva tri jedinjenja. Rezultati uporedne analize za tri derivata ferocena biće detaljno opisani.

Kristalografski podaci.

Jedinjenje 1: 2-ferocenil-2,3-dihidrohinolin-4(1*H*)-on, $C_{19}H_{17}FeNO$, monoklinični sistem, prostorna grupa $P2_1/c$, $a = 12,991(4)$, $b = 8,482(2)$, $c = 13,972(3)$ Å, $\beta = 98,80(2)^\circ$, $V = 1521,4(7)$ Å³, $Z = 4$, $\rho_x = 1,446$ g cm⁻³, $\mu = 0,991$ mm⁻¹. Utačnjavanje za F^2 (203 parametara i 2977 nezavisnih refleksija), $R_1 = 0,0733$, $wR_2 = 0,2337$, $S = 1,096$.

Jedinjenje 2: 2-ferocenil-6-hlor-2,3-dihidrohinolin-4(1*H*)-on, $C_{19}H_{16}FeNOCl$, monoklinični sistem, prostorna grupa $P2_1/c$, $a = 13,785(5)$, $b = 8,061(5)$, $c = 13,970(5)$ Å, $\beta = 94,997(5)^\circ$, $V = 1546,5(12)$ Å³, $Z = 4$, $\rho_x = 1,570$ g cm⁻³, $\mu = 1,151$ mm⁻¹. Utačnjavanje za F^2 (212 parametara i 3573 nezavisnih refleksija), $R_1 = 0,0475$, $wR_2 = 0,0976$, $S = 1,098$.

Jedinjenje 3: 6-brom-2-ferocenil-2,3-dihidrohinolin-4(1*H*)-on, $C_{19}H_{16}FeNOBr$, monoklinični sistem, prostorna grupa $P2_1/c$, $a = 14,101(5)$, $b = 7,999(5)$, $c = 14,015(5)$ Å, $\beta = 96,104(5)^\circ$, $V = 1571,8(13)$ Å³, $Z = 4$, $\rho_x = 1,733$ g cm⁻³, $\mu = 3,504$ mm⁻¹. Utačnjavanje za F^2 (212 parametara i 3622 nezavisnih refleksija), $R_1 = 0,0562$, $wR_2 = 0,1054$, $S = 1,132$.

STRUCTURE OF SPHENE MONOCRYSTALS FROM LEŠNICA RIVER DEPOSITS ON CER MOUNTAIN

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River drift Lešnica, from which sphene crystals are separated for analysis, consists of a large number of minerals of different grain size. Sphene was found in a fraction of the grain size of 0.25 mm to 0.5 mm in association with garnet, apatite, cassiterite, zircon and other minerals.

Sphene was analyzed by different methods. Density was measured by pycnometer, the color was determined by tristimulus colorimetry, vibrations were analyzed by infrared spectroscopy while chemical composition was analyzed by electron microprobe. The crystal structure of sphene was determined by X-ray single crystal diffraction. The structure was refined in space groups $C2/c$ and the $P2_1/c$, and then transformed into the new space groups $A2/a$ and $P2_1/a$, respectively. For the graphical representation of the complete structure computer program *ATOMS* was used [1].

The experimental results are comparable to those of sphene from Grisoms, Switzerland [2], because of chemical similarities. The distances Ti-O, Si-O Ca-O in space group $A2/a$ show good agreement with literature data, which is not the case with structure model described in the space group $P2_1/a$ due to lack of displacement of the Ti atom from the geometric center of the Ti octahedra. On the basis of the statistical indicators of the quality of the refinement (R-value, Goof, residual electron density on differential Fo-Fc map), the structure for this sphene was established in the space group $P2_1/a$.

Structural formula obtained from electron microprobe is taken to be:
(Ca²⁺_{1,008}Mn²⁺_{0,002})_{1,010} (Ti⁴⁺_{0,901}Fe³⁺_{0,033}Al³⁺_{0,060}P⁵⁺_{0,001})_{0,995}Si⁴⁺_{1,024}O²⁻₅.

- [1] Dowty, E. (1994) *ATOMS. A computer program for Displaying Atomic Structures.*, Hidden valley Rd, Kingston, TN 37663, USA.
[2] Hollabaugh, C.L., and Foit, F.F., Jr., *American Mineralogist* (1984), 69, 725-732.

СТРУКТУРА МОНОКРИСТАЛА СФЕНА ИЗ НАНОСА РЕКЕ ЛЕШНИЦЕ НА ЦЕРУ

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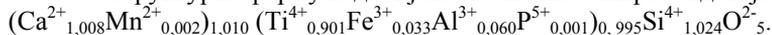
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Нанос реке Лешнице из којег су издвојени кристали сфена за анализу састоји се из великог броја минерала различите гранулације. Сфен је нађен у фракцији величине зрна од 0,25 mm до 0,5 mm у асоцијацији са гранатима, апатитом, каситеритом, цирконом и другим минералима.

Издвојени сфен је анализиран различитим методама. Измерена је густина методом пикнометра, одређена боја тристимулусном колориметријом, снимљен ИС-спектар, а затим урађена хемијска анализа методом микросонде и на крају одређена кристална структура сфена методом рендгенске дифракције са монокристала. Структура је утачњена у просторним групама $C2/c$ и $P2_1/c$, а затим трансформисана у нове просторне групе $A2/a$ и $P2_1/a$. За графички приказ структуре коришћен је програм *ATOMS* [1].

Добијени експериментални резултати су упоређени са литературним подацима сфена из Грисома [1], управо због сличности у хемизму. Растојања Ti-O, Si-O, Ca-O у просторној групи $A2/a$ показују добра слагања са литературним подацима, док са просторном групом $P2_1/a$ то није случај због непостојања померања Ti из геометријског центра у октаедру. На основу статистичких показатеља квалитета утачњавања (R-вредности, Goof, заостала електронска густина на диферентној Fo-Fc мапи), за испитивани сфен је прихваћена струкура описана у просторној групи $P2_1/a$.

Структурна формула добијена из анализе микросондом је:



[1] Dowty, E. (1994) *ATOMS. A computer program for Displaying Atomic Structures.*, Hidden valley Rd, Kingston, TN 37663, USA.

[2] Hollabaugh, C.L., and Foit, F.F., Jr., *American Mineralogist* (1984), 69, 725-732.

POLYMERIC MANGANESE(II) COMPLEX WITH PHTHALATE IONS

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The title coordination polymer, $[\text{Mn}(\text{pht})]_n$, where pht is dianion of phthalic (1,2-benzenedicarboxylic) acid was hydrothermally synthesized in a Teflon-lined steel autoclave ($T = 458 \text{ K}$, 3 days) starting from an aqueous suspension containing $\text{Mn}(\text{NO}_3)_2$ and phthalic acid. Relatively simple chemical formula of the obtained complex is in total contrast to its fascinating crystal structure (see below).

Only one half of pht ion belongs to the asymmetric unit and each COO group is bonded to three Mn(II) ions: O2 atom acts as mono-bridge, while O1 atom is coordinated to one Mn(II) ion. Since overall pht ion also chelates one central atom, it does not bridge six but only five Mn(II) ions. In this way, thick layers, which are oriented parallel to *ac*-plane and interconnected by van der Waals forces only, are formed (Figure 1). These layers can be divided in A and B sublayers with BAB sequence. The sublayer A is made of Mn(II) coordination polyhedra, while sublayer B consists of the pht aromatic rings.

All aromatic rings (sublayers B) are parallel to each other and to the (403) plane. The shortest C...C distance within sublayers B is $3.71(1) \text{ \AA}$ and weak face-to-face π - π interactions could be expected. However, aromatic rings from adjacent sublayers B are too far and oriented in a zigzag manner, so there is no possibility for π - π interactions.

Mn(II) ions are in a very deformed octahedral environment consisting of two O1 and four O2 atoms from five pht ions. According to the shortest Mn–Mn distance of only $3.486(1) \text{ \AA}$ in four-membered Mn1/O2/Mn1/O2 ring, the compound probably possess strong magnetic interactions.

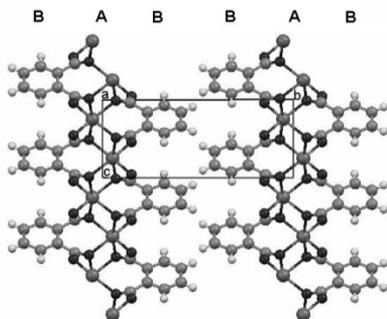


Figure 1. Crystal packing along *a*-axis showing A and B sublayers.

Crystal data:

$\text{C}_{16}\text{H}_8\text{Mn}_2\text{O}_8$, $M_r = 438.10$, monoclinic, space group $P2_1/n$, $a = 4.6729(9)$, $b = 13.657(3)$, $c = 6.0217(12) \text{ \AA}$, $\beta = 108.45(3)^\circ$, $V = 364.54(12) \text{ \AA}^3$, $Z = 1$, $F(000) = 218$, $\rho_x = 1.996 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 1.780 \text{ mm}^{-1}$.

The refinement on F^2 (68 parameters) yielded $R_1 = 0.021$, $wR_2 = 0.053$, $S = 1.11$ for all data, and $R_1 = 0.020$ for 860 observed reflections with $I \geq 2\sigma(I)$.

POLIMERNI MANGAN(II)-KOMPLEKS SA FTALAT-JONIMA

J. Rogan, D. Poletić

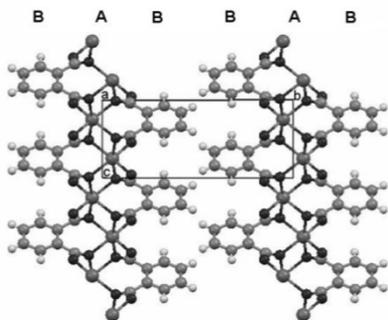
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Navedeni koordinacioni polimer, $[\text{Mn}(\text{pht})]_n$, gde je pht dianjon ftalne (1,2-benzendikarboksilne) kiseline je hidrotermalno sintetizovan u čeličnom autoklavu sa teflonskom posudom ($T = 458 \text{ K}$, 3 dana) polazeći od vodene suspenzije koja sadrži $\text{Mn}(\text{NO}_3)_2$ i ftalnu kiselinu. Relativno jednostavna hemijska formula dobijenog kompleksa u potpunosti je suprotnosti sa fascinantom kristalnom strukturom (videti ispod).

Samo pola pht-jona pripada asimetričnoj jedinici i svaka COO^- -grupa vezana je za tri Mn(II)-jona: atom O2 je mono-most, dok je atom O1 koordiniran za jedan Mn(II)-jon. Pošto je celokupni pht-jon još helatno vezan za jedan centralni atom, on ne premošćava šest nego samo pet Mn(II)-jona. Na ovaj način se formiraju debeli slojevi koji su orijentisani paralelno *ac*-ravni i povezani jedino van der Valsovim silama (Slika 1). Ovi slojevi mogu se podeliti na A i B podslojeve sa redosledom BAB. Podsloj A čine Mn(II)-poliedri, dok je podsloj B izgrađen od aromatičnih prstenova pht-jona.

Svi aromatični prstenovi (podsloj B) su paralelni međusobno i (403) ravni. Najkraće C...C rastojanje u podslojevima B iznosi $3,71(1) \text{ \AA}$ i mogu se očekivati slabe „face-to-face” π - π interakcije. Međutim, aromatični prstenovi iz susjednih podslojeva B su previše udaljeni i orijentisani su na cik-cak način, pa ne postoji mogućnost za π - π interakcije.

Joni Mn(II) se nalaze u vrlo deformisanom oktaedarskom okruženju koje čine dva atoma O1 i četiri atoma O2 iz pet pht-jona. Pošto najkraće Mn-Mn rastojanje iznosi samo $3,486(1) \text{ \AA}$ u četvoročlanom prstenu Mn1/O2/Mn1/O2, u jedinjenju verovatno postoje jake magnetne interakcije.



Slika 1. Kristalno pakovanje duž *a*-ose sa obeleženim A i B podslojevima.

Kristalografski podaci:

$\text{C}_{16}\text{H}_8\text{Mn}_2\text{O}_8$, $M_r = 438,10$, monoklinični sistem, prostorna grupa $P2_1/n$,
 $a = 4,6729(9)$, $b = 13,657(3)$,
 $c = 6,0217(12) \text{ \AA}$, $\beta = 108,45(3)^\circ$,
 $V = 364,54(12) \text{ \AA}^3$, $Z = 1$, $F(000) = 218$,
 $\rho_x = 1,996 \text{ g cm}^{-3}$,
 $\mu(\text{Mo K}\alpha) = 1,780 \text{ mm}^{-1}$. Utačnjavanje sa F^2 (68 parametara) dalo je $R_1 = 0,021$, $wR_2 = 0,053$, $S = 1,11$ za sve podatke, i $R_1 = 0,020$ za 860 refleksija sa $I \geq 2\sigma(I)$.

SYNTHESIS AND MODIFICATION OF NANOMATERIALS: CHANGES IN CHARACTERISTICS OF BRUSHITE DEPENDING ON THE PARTICLE SIZE

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Brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, a calcium phosphate mineral, crystallizes in the monoclinic crystal system, space group *Ia*. Brushite has a layered structure, in which the layers are held by the water molecules *via* hydrogen bonds. In nature, brushite can be found in caves, phosphate deposits and soils. Brushite has a wide range of applications. It is a major component of the toothpaste due to its abrasive properties. It is also used as remediation media and in waste water treatment.

The main objective of this preliminary study was to determine the properties of brushite in regards to its grain size. Characterization was performed on samples obtained by precipitation from the solution, and further characterization of modified nanomaterials prepared by grinding in the vibrating mill.

Material preparation was performed by titration of the solution $(\text{CH}_3\text{COO})_2\text{Ca} \cdot \text{H}_2\text{O}$ with the solution $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, under constant stirring, with an initial pH = 5 and temperature around 60 °C.

Material was analyzed by X-ray powder diffraction and Raman spectroscopy.

Crystallite size was modified by grinding in vibrating mill. The sample was ground five times for 2.5 minutes and analyzed by X-ray powder diffraction each time between grinding. Particle size was determined from the X-ray diffraction patterns by using Scherer equation. Milling in the vibrating mill leads to an increase in temperature and reduction in the particle size. Due to a temperature increase, there is a phase transformation of brushite in monetite (CaHPO_4) after 5 min of grinding.

SINTEZA I MODIFIKACIJA NANOMATERIJALA: PROMENE OSOBINA BRUŠITA U ZAVISNOSTI OD VELIČINE ČESTICA

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Brušit, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, je mineral iz grupe kalcijum fosfata. Kristališe monoklinočno u prostornoj grupi *Ia*. Struktura brušita je slojevita u kojoj molekuli vode povezuju susedne slojeve vodoničnim vezama. U prirodi se nalazi u pećinama, ležištima fosfora i u zemljištima. Brušit ima širok spektar primene, pri čemu predstavlja glavnu komponentu u proizvodnji pasti za zube jer ima abrazivna svojstva, a koristi se i kao medijum u procesima remedijacije i za prečišćavanje otpadnih voda.

Glavni cilj ovog preliminarnog istraživanja bilo je određivanje osobina brušita zavisno od veličine čestica. Ispitivani su uzorci brušita koji su sintetisani precipitacijom iz rastvora, a zatim, mlevenjem u vibracionom mlinu, modifikovani do nanometarskih dimenzija.

Materijal je pripreman mokrim hemijskim postupkom, titracijom rastvora $(\text{CH}_3\text{COO})_2\text{Ca} \cdot \text{H}_2\text{O}$ rastvorom $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. Postupak je rađen uz konstantno mešanje, sa početnom vrednošću $\text{pH} = 5$ na oko 60°C .

Dobijeni materijal prvo je analiziran metodom rendgenske difrakcije na polikristalnom materijalu i pomoću Ramanske spektroskopije.

Veličina kristalita je modifikovana mlevenjem materijala u vibracionom mlinu pet puta po 2,5 minuta pri čemu su, nakon svakog koraka, prikupljeni difrakcioni podaci iz kojih je uz pomoć Šererove jednačine određena promena veličine kristalita. Dobijeni rezultati su pokazali da mlevenjem u vibracionom mlinu usled trenja dolazi do povećanja temperature i smanjenja čestica. Posle 5 minuta mlevenja usled porasta temperature dolazi do fazne transformacije i prelaska brušita u monetit, CaHPO_4 .

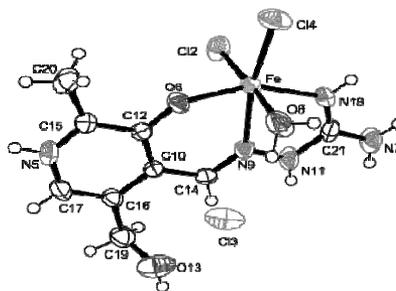
STRUCTURAL CHARACTERIZATION OF THE FIRST IRON(III) COMPLEX WITH PYRIDOXALAMINO GUANIDINE

M. M. Lalović, V. M. Leovac, Lj. S. Vojinović-Ješić, V. I. Češljević, M. V. Rodić

*Faculty of Sciences, Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia;
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Here we present the structure of the first iron(III) complex with pyridoxalaminoguanidine (PLAG), of the coordination formula $[\text{Fe}(\text{PLAG})\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$. The ligand is coordinated as a usual tridentate, ONN coordination mode in zwitter-ionic form, *via* oxygen atom of phenolic hydroxyl and nitrogen atoms of azomethine and guanido groups. The Fe(III) is situated in a slightly deformed octahedral environment achieved by tridentate coordination of the chelate ligand and one chloride ion in equatorial plane and the other chloride ion and one water molecule in axial positions. In this complex O-ligand of the chelate ligand is closer to the central ion, compared to both N-ligands, as it was expected, based on characterization of previously obtained complexes [1, 2]. Central ion is shifted from the basal plane of the coordination polyhedra towards the axial chlorido-ligand (0.152 Å). Coordinated ligand deviates from planarity and that can be described by the values of dihedral angles between mean planes of pyridine ring, five- and six-membered metallocycles, which are 7.56 and 1.58°, respectively. The six-membered metallocycle is in “screw-boat” conformation, while the other two rings are planar. The crystal structure of the complex is stabilized by an extended network of inter- and intra-molecular hydrogen bonds. It can be mentioned that all possible hydrogen donors are involved in hydrogen-bonding, except H atom from coordinated N atom of the guanido-group.

Crystal data: $\text{FeC}_9\text{H}_{15}\text{N}_5\text{O}_3\text{Cl}_3$,
 $M_r = 403.46$, orthorhombic, space group
 $P2_12_12_1$, $a = 7.351(5)$, $b = 8.489(5)$,
 $c = 25.047(5)$ Å, $V = 1563.0(14)$ Å³,
 $D_{\text{cal}} = 1.715$ g cm⁻³, $Z = 4$, $F(000) = 820$,
 $\mu(\text{MoK}\alpha) = 1.493$ mm⁻¹. The refinement on F^2
(199 parameters) yielded $R_1 = 0.0479$,
 $wR_2 = 0.0744$, $S = 0.937$, for all data, and
 $R_1 = 0.034$ for 2717 reflections with $I \geq 2\sigma(I)$.



- [1] V. M. Leovac, M. D. Joksović, V. Divjaković, Lj. S. Jovanović, Ž. Šaranović, A. Pevec, J. Inorg. Biochem., 101 (2007) 1094.
[2] V. M. Leovac, Lj. S. Vojinović-Ješić, V. I. Češljević, S. B. Novaković, G. A. Bogdanović, Acta Cryst., C65 (2009) 337.

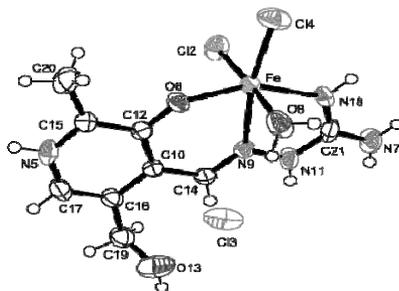
STRUKTURNA KARAKTERIZACIJA PRVOG KOMPLEKSA GVOŽĐA(III) SA PIRIDOKSALAMINOGVANIDINOM

M. M. Lalović, V. M. Leovac, Lj. S. Vojinović-Ješić, V. I. Češljević, M. V. Rodić

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U ovom radu opisana je struktura prvog kompleksa piridoksalaminogvanidina (PLAG) sa gvožđem(III), koordinacione formule $[\text{Fe}(\text{PLAG})\text{Cl}_2(\text{H}_2\text{O})]\text{Cl}$. Nađen je uobičajen, tridentatni ONN način koordinacije PLAG u zwitter-jonskoj formi, preko atoma kiseonika fenolnog hidroksila i atoma azota azometinske i gvanido-grupe. Atom gvožđa se nalazi u blago deformisanom oktaedarskom okruženju, koje je realizovano tridentatnom koordinacijom helatnog liganda i jednog hloridnog jona u ekvatorijalnoj ravni i koordinacijom drugog hloridnog jona i molekula vode u aksijalnim položajima. Interesantno je napomenuti da se u ovom kompleksu O-ligand helatnog liganda nalazi na kraćem rastojanju od centralnog jona, nego dva N-ligatora, kao što je nađeno i za ranije okarakterisane komplekse [1, 2]. Centralni jon je pomeren iz bazalne ravni koordinacionog poliedra ka hlorido-ligandu u aksijalnom položaju za 0,152 Å. Koordinovani ligand odstupa od planarnosti, što se može iskazati vrednostima diedarskih uglova između srednjih ravni piridinskog prstena i petočlanog, odnosno šestočlanog metalocikla, koji iznose 7,56 i 1,58°, respektivno. Šestočlani metalocikl zauzima konformaciju „uvijene lađe”, dok su ostala dva prstena planarni. Kristalna struktura kompleksa stabilizovana je mrežom inter- i intramolekulskih vodoničnih veza. Treba reći da svi potencijalni donorski atomi vodonika učestvuju u građenju vodoničnih veza, sa izuzetkom atoma vodonika vezanog za koordinovani atom azota gvanido-grupe.

Kristalografski podaci: $\text{FeC}_9\text{H}_{15}\text{N}_5\text{O}_3\text{Cl}_3$, $M_r = 403,46$, ortorombični sistem, prostorna grupa $P2_12_12_1$, $a = 7,351(5)$, $b = 8,489(5)$, $c = 25,047(5)$ Å, $V = 1563,0(14)$ Å³, $D_{\text{cal}} = 1,715$ g cm⁻³, $Z = 4$, $F(000) = 820$, $\mu(\text{MoK}\alpha) = 1,493$ mm⁻¹. Utačnjavanje sa F^2 (199 parametara) dalo je $R_1 = 0,0479$, $wR_2 = 0,0744$, $S = 0,937$, za sve podatke, i $R_1 = 0,034$ za 2717 refleksija sa $I \geq 2\sigma(I)$.



- [1] V. M. Leovac, M. D. Joksović, V. Divjaković, Lj. S. Jovanović, Ž. Šaranović, A. Pevec, *J. Inorg. Biochem.*, **101** (2007), 1094.
[2] V. M. Leovac, Lj. S. Vojinović-Ješić, V. I. Češljević, S. B. Novaković, G. A. Bogdanović, *Acta Cryst.* **C65** (2009) 337.

STRUCTURAL ANALYSIS AND ANTICONVULSANT ACTIVITY OF SOME 3,5-DISUBSTITUTED-5-PHENYLHYDANTOINS

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Conformational analysis of a large number of anticonvulsant drugs containing aromatic substituents led to a proposal that the correct orientation of the aromatic rings could be the most important structural requirement for the activity [1,2]. Considering the importance of hydantoin (imidazolidine-2,4-dione) derivatives in the therapy of epilepsy, three 3,5-disubstituted-5-phenylhydantoins were synthesized (**1–3**, Figure 1) and their structures were determined by X-ray structure analysis. The compounds were designed as equilipophilic derivatives, which differ in distribution of the lipophilic elements of molecular structure. The phenyl ring orientation, relative to the hydantoin ring was constrained by the steric effects of R₁. The anticonvulsant potency of the investigated compounds was evaluated in pentylenetetrazole test. The compound **3**, bearing small methyl group as R₁ and bulky *n*-butyl group as R₂, showed to be the most active, but it exerted an additional sedative effect.

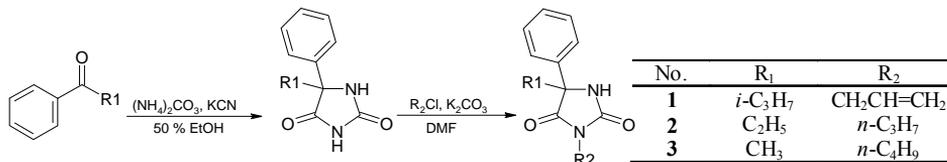


Figure 1. Synthesis of 3,5-disubstituted-5-phenylhydantoins (**1–3**)

In all cases, crystal packing is governed by hydrogen N–H...O bonds. Thus, the chains along *b*-axis are formed in **1** and **3**. The chains in **3** are stacked in a 3D framework holding by weak π - π interactions (at 3.80 Å). In **2**, hydrogen bonds between neighboring molecules form centrosymmetric dimmers along *b*-axis.

Crystal data: (**1**) C₁₅H₁₈N₂O₂, *M_r* = 258.31, orthorhombic, space group *Pbca*, *a* = 16.3379(6), *b* = 6.2509(2), *c* = 28.3984(18) Å, *V* = 2900.2(2) Å³, *R*₁ = 0.073 for 2056 observed reflections with *I* ≥ 2σ(*I*); (**2**) C₁₄H₁₈N₂O₂, *M_r* = 246.30, monoclinic, space group *P2₁/c*, *a* = 7.7724(10), *b* = 20.220(3), *c* = 8.6004(11) Å, β = 90.045(12)°, *V* = 1351.6(3) Å³, *R*₁ = 0.064 for 1698 observed reflections with *I* ≥ 2σ(*I*); (**3**) C₁₄H₁₈N₂O₂, *M_r* = 246.30, monoclinic, space group *P2₁/c*, *a* = 14.748(2), *b* = 8.4420(11), *c* = 11.0540(13) Å, β = 94.583(14)°, *V* = 1371.9(3) Å³, *R*₁ = 0.073 for 1598 observed reflections with *I* ≥ 2σ(*I*).

[1] N. Camerman, A. Camerman, *J. Am. Chem. Soc.* 94 (1972) 8553-8556.

[2] W. J. Brouillette, G. B. Brown, T. M. DeLory, G. Liang, *J. Pharm. Sci.* 79 (1990) 871-874.

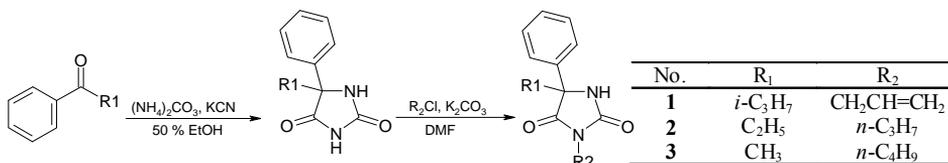
STRUKTURNA ANALIZA I ANTIKONVULZIVNA AKTIVNOST 3,5-DISUPSTITUISANIH-5-FENILHIDANTOINA

N. Trišović^a, B. Božić^a, T. Timić^b, J. Rogan^a, D. Poletić^a, M. Savić^b, G. Ušćumlić^a

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Konformaciona analiza velikog broja antikonvulzivnih lekova, koji sadrže aromatične supstituente, ukazala je da odgovarajuća orijentacija aromatičnih prstenova može da bude najvažniji strukturni preduslov za aktivnost [1,2]. Uzimajući u obzir značaj derivata hidantoina (imidazolidin-2,4-diona) u terapiji epilepsije, sintetizovana su tri 3,5-disupstituisana-5-fenilhidantoina (**1–3**, Slika 1) i njihove strukture određene su rendgenskom strukturnom analizom. Jedinjenja su zamišljena kao derivati jednake lipofilnosti, koji se razlikuju po raspodeli lipofilnih elemenata. Orijetacija fenilnog prstena, u odnosu na hidantoinski prsten, ograničena je sternim efektom grupe R₁. Antikonvulzivna aktivnost proučavanih jedinjenja procenjena je pentilentetrazolskim testom. Jedinjenje **3**, koje sadrži malu metil-grupu kao R₁ i veliku *n*-butil-grupu kao R₂, pokazalo se kao najaktivnije, ali je ispoljilo dodatni sedativni efekat.



Slika 1. Sinteza 3,5-disupstituisanih-5-fenilhidantoina (**1–3**)

U svim slučajevima, kristalno pakovanje je određeno N–H...O vodoničnim vezama. Na taj način, lanci se formiraju duž *b*-ose kod **1** i **3**. Lanci su trodimenzionalno umreženi preko slabih π - π interakcija (na rastojanju 3,80 Å) kod jedinjenja **3**. Kod **2**, vodonične veze između susjednih molekula obrazuju centrosimetrične dimere duž *b*-ose.

Kristalografski podaci: (**1**) C₁₅H₁₈N₂O₂, M_r = 258,31, rombični sistem, *Pbca*, *a* = 16,3379(6), *b* = 6,2509(2), *c* = 28,3984(18) Å, *V* = 2900,2(2) Å³, R₁ = 0,073 za 2056 refleksija sa *I* ≥ 2σ(*I*); (**2**) C₁₄H₁₈N₂O₂, M_r = 246,30, monoklinični sistem, *P2₁/c*, *a* = 7,7724(10), *b* = 20,220(3), *c* = 8,6004(11) Å, β = 90,045(12)°, *V* = 1351,6(3) Å³, R₁ = 0,064 za 1698 refleksija sa *I* ≥ 2σ(*I*); (**3**) C₁₄H₁₈N₂O₂, M_r = 246,30, monoklinični sistem, *P2₁/c*, *a* = 14,748(2), *b* = 8,4420(11), *c* = 11,0540(13) Å, β = 94,583(14)°, *V* = 1371,9(3) Å³, R₁ = 0,073 za 1598 refleksija sa *I* ≥ 2σ(*I*).

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HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURE OF MICROPOROUS $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{ZnPO}_4)_2$

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A new microporous compound, $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{ZnPO}_4)_2$, was synthesized under hydrothermal conditions, from a mixture of $5\text{ZnO} \cdot 2\text{CO}_3 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$ and one drop of ethylenediamine. The mixture was transferred into Teflon vessels and filled to approximately 70 % of its volume with distilled water. The initial pH of the mixture was 9. Finally it was enclosed into stainless steel autoclave and heated under autogeneous pressure to 160 °C, held at this temperature for 72 h and cooled to room temperature over a period of 96 h. The pH of supernatant solution was 7. The resulting product was filtered, washed thoroughly with distilled water and dried in air at room temperature. The title compound crystallized as prismatic colorless transparent crystals (yield ca. 50 %) together with uninvestigated white powder.

The structure was solved using single-crystal X-ray diffraction data (CCD detector, MoK α radiation, 25 °C, $\theta_{\text{max}} = 26.35^\circ$). The compound crystallizes in orthorhombic space group *Pcca* (54). *Crystal data*: $a = 14.712(2)$, $b = 8.9440(18)$, $c = 14.712(2)$ Å, $V = 1935.9(6)$ Å³, $Z = 8$. The refinement on F^2 with 156 parameters and 1990 unique reflections yielded $R_1 = 0.0280$, $wR_2 = 0.0716$ and $R_1 = 0.0234$ for 1764 observed reflections with $I \geq 2\sigma(I)$.

The investigated compound has a zeolite-type topology and it is very similar to $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{ZnAsO}_4)_2$ (UCSB-3) [1] and $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{GaGeO}_4)_2$ (UCSB-3GaGe) [2]. The framework consists of strictly alternating ZnO_4 and PO_4 tetrahedral units forming 4-, 6-, and 8-membered rings and has 3-dimensional, orthogonal 8-membered ring channels.

There are two different diprotonated ethylenediammonium cations, H_2en^{2+} (en = ethylenediamine), both located at the center of 8-membered ring channels. The H_2en^{2+} situated in the 8-membered ring channel along [100] is ordered, while both C atoms in another H_2en^{2+} situated in the 8-membered ring channel along [001] are positionally disordered. The ordered nitrogen atoms are found in special positions, whereas carbon atoms are placed in two split sites with 50 % occupation. The ordering of N atoms is a result of hydrogen bonding between framework oxygen atoms and terminal NH_3^+ groups of the H_2en^{2+} .

[1] X. Bu, P. Feng, T. Gier, G. Stucky, *J. Solid State Chem.*, 136 (1998), 210-215.

[2] X. Bu, P. Feng, T. Gier, D. Zhao, G. Stucky, *J. Am. Chem. Soc.*, 120 (1998), 13389-13397.

HIDROTERMALNA SINTEZA I KRISTALNA STRUKTURA MIKROPOROZNOG $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{ZnPO}_4)_2$

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Novo mikroporozno jedinjenje, $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{ZnPO}_4)_2$, dobijeno je hidrotermalnom sintezom kao proizvod reakcije između $5\text{ZnO}\cdot 2\text{CO}_3\cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$ i jedne kapi etilendiamina. Mešavina je prebačena u teflonski sud i pomešana sa vodom do približno 70 % zapremine suda; početna pH vrednost mešavine bila je 9. Potom je sud zatvoren u čelični autoklav i zagrevan je pod autogenim pritiskom na 160 °C, zadržan na toj temperaturi 72 h, a potom hlađen do sobne temperature 96 h; pH matičnog rastvora bio je 7. Rezultujući proizvod je filtriran, ispran destilovanom vodom i sušen na sobnoj temperaturi. Dobijeni su bezbojni providni prizmatični kristali (oko 50 %) zajedno sa neispitivanim belim prahom.

Eksperimentalni podaci su prikupljeni na difraktometru za monokristale (CCD detektor, $\text{MoK}\alpha$ rendgensko zračenje, 25°C, $\theta_{\text{max}} = 26,35^\circ$). $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)[\text{Zn}(\text{PO}_4)_2]$ kristališe rombično u prostornoj grupi *Pcca* (54). Jedinčna ćelija: $a = 14,712(2)$, $b = 8,9440(18)$, $c = 14,712(2)$ Å, $V = 1935,9(6)$ Å³, $Z = 8$. Utačnjavanjem 156 parametara dobijene su sledeće vrednosti *R*-faktora: $R_1 = 0,0280$, $wR_2 = 0,0716$ za svih 1990 refleksija i $R_1 = 0,0234$ za 1764 refleksija sa $I \geq 2\sigma(I)$.

Ispitivano jedinjenje ima topologiju zeolita i veoma je slično sa $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{ZnAsO}_4)_2$ (UCSB-3) [1] i $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{GaGeO}_4)_2$ (UCSB-3GaGe) [2]. Cinkofosfatnu mrežu čine naizmenični ZnO_4 i PO_4 tetraedri koji formiraju 4-, 6-, i 8-člane prstenove i trodimenzionalne ortogonalne kanale sa poprečnim presekom izgrađenim od 8-članog tetraedarskog prstena.

U strukturi se javljaju dva različita katjona etilendiamonijuma, H_2en^{2+} , oba smeštena u centrima kanala. H_2en^{2+} u kanalu duž [100] je uređen, dok u drugom H_2en^{2+} , smeštenom u kanalu duž [001], oba atoma ugljenika poziciono su neuređena. Atomi azota su u specijalnim položajima, dok je svaki atom ugljenika podeljen u dva položaja sa 50 % zauzeća. Uređenje atoma azota je rezultat vodoničnih veza između mrežnih atoma kiseonika i NH_3^+ grupa iz H_2en^{2+} .

[1] X. Bu, P. Feng, T. Gier, G. Stucky, *J. Solid State Chem.*, 136 (1998), 210-215.

[2] X. Bu, P. Feng, T. Gier, D. Zhao, G. Stucky, *J. Am. Chem. Soc.*, 120 (1998), 13389-13397.

CRYSTAL STRUCTURE OF $\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$

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There are many reports on divalent metal vanadates synthesized by high temperature solid-state reactions. However, hydrothermal methods are proved to be effective for the synthesis of single crystals of new vanadium compounds [1,2 and references therein].

$\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$ was synthesised under hydrothermal conditions from the mixture of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, Co powder, V_2O_5 and H_2O using Teflon-lined stainless steel autoclave ($T = 423 \text{ K}$, 9 d). It crystallized as transparent light pink needle-like crystals up to 0.17 mm in length together with uninvestigated powder. It represents a new structure type and the first compound synthesized in the four component $\text{BaO-CoO-V}_2\text{O}_5\text{-H}_2\text{O}$ system.

The crystal structure of $\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$ was determined by single-crystal X-ray diffraction (298 K, $\text{MoK}\alpha$, $2\theta_{\text{max}} = 60^\circ$): space group $R\bar{3}m$ ($a = 5.9210(8)$, $c = 21.0160(42) \text{ \AA}$, $V = 638.07(18) \text{ \AA}^3$, $Z = 3$). The refinement (24 free parameters) yielded $R_1(F) = 0.0191$, $wR_2(F^2) = 0.0599$ for the 222 unique reflections; for the 215 ‘observed’ reflections with $F_o^2 \geq 4\sigma(F_o^2)$, $R_1(F)$ is 0.0184 [3].

The crystal structure of $\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$ represents a new layered structure that is built up from two kinds of interconnected sheets, Co octahedral sheets with short Co–Co distances of 2.9605(4) Å and barium vanadate polyhedral-tetrahedral sheets, which alternate along the *c*-axis. The Co octahedral sheets with six-membered octahedral rings are formed by edge sharing of $[\text{CoO}_4(\text{OH})_2]$ octahedra. The Co–O distances vary from 1.945(2) to 2.161(2) Å. The BaO_{12} is an anticuboctahedron with six shorter [2.824(3) Å] and six longer [3.4186(5) Å] distances. $\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$ is topologically closely related to minerals vesignieite, $\text{BaCu}_3(\text{VO}_4)_2(\text{OH})_2$ [4] and bayldonite, $\text{PbCu}_3(\text{AsO}_4)_2(\text{OH})_2$ [5]. The H atom is located near the O3. The O3 atom, which is bonded to three Co atoms is highly undersaturated (3 Co atoms contribute to the bond valence sum by 1.53 v.u.), indicating that O3 acts as a hydrogen bond donor. The acceptor of the hydrogen bond is the O1 atom [$\text{O3} \cdots \text{O1} = 2.596(3) \text{ \AA}$], which is also highly charge deficient (1.61 v.u. from one V atom and three Ba atoms).

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- [1] T. Đorđević, Lj. Karanović, E. Tillmanns, *Crys.Res. Technol.*, 43 (2008), 1202-1209.
- [2] T. Đorđević, J. Stojanović and Lj. Karanović, *Acta Cryst.*, E66 (2010), i 79.
- [3] G. M. Sheldrick, SHELX-97, a program for the solution and refinement of crystal structures. University of Göttingen, Germany (1997).
- [4] Zh. Ma, R. He and X. Zhu, *Acta Geologica Scandinavica*, 4 (1991), 145-151.
- [5] C. Ghose and C. Wang, *Acta Cryst.*, B35 (1979), 819-823.

KRISTALNA STRUKTURA $\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$

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Vanadati divalentnih metala uglavnom se sintetišu metodom visokotemperaturnih reakcija u čvrstom stanju. Ipak, iako ne često primenjivana, hidrotermalna sinteza se pokazala kao efikasna metoda za sintezu monokristala okso-soli vanadijuma [1, 2 i tamo citirane reference].

$\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$ je sintetisan hidrotermalnom metodom. Smeša $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, praha Co, V_2O_5 i H_2O stavljena je u teflonski sud i zagrevana je u autoklavu od nerđajućeg čelika ($T = 423$ K, 9 dana). $\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$ je iskristalisao u vidu prozračnih, svetloružičastih igličastih kristala dužine do 0,17 mm zajedno sa neispitanim praškastim materijalom. On predstavlja kako prvi vanadat u sistemu $\text{BaO}-\text{CoO}-\text{V}_2\text{O}_5-\text{H}_2\text{O}$, tako i novi strukturni tip.

Kristalna struktura $\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$ rešena je direktnim metodama korišćenjem podataka dobijenih rendgenskom difrakcijom sa monokristala (298 K, $\text{MoK}\alpha$, $2\theta_{\text{max}} = 60^\circ$): prostorna grupa $R\bar{3}m$ ($a = 5,9210(8)$, $c = 21,0160(42)$ Å, $V = 638,07(18)$ Å³, $Z = 3$). Utačnjavanje 24 slobodna parametra dalo je sledeće vrednosti: $R_1(F) = 0,0191$, $wR_2(F^2) = 0,0599$ za 222 jedinstvene refleksije; za 215 posmatranih refleksija sa $F_o^2 \geq 4\sigma(F_o^2)$, $R_1(F)$ je 0,0184 [3].

$\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$ predstavlja novi tip strukture koji se sastoji od dve vrste slojeva koji se naizmenično smenjuju duž c -ose. Prvi sloj je izgrađen od CoO_6 oktaedara sa kratkim Co-Co rastojanjima od 2,9605(4) Å, a drugi je izgrađen od međusobno povezanih Ba poliedara i VO_4 tetraedara. U prvom sloju, $[\text{CoO}_4(\text{OH})_2]$ oktaedri povezani su preko iverica u šestočlane prstenove. Co-O rastojanja variraju od 1,945(2) do 2,161(2) Å. BaO_{12} je antikuboktaedar sa šest kraćih [2,824(3) Å] i šest dužih [3,4186(5) Å] rastojanja. $\text{BaCo}_3(\text{VO}_4)_2(\text{OH})_2$ je topološki veoma sličan mineralima vesignieitom, $\text{BaCu}_3(\text{VO}_4)_2(\text{OH})_2$ [4] i baidonitom, $\text{PbCu}_3(\text{AsO}_4)_2(\text{OH})_2$ [5]. Atom vodonika lokalizovan je na Furijeovoj mapi u blizini kiseonika O3 ($\Sigma s = 1,53$ v.u. od 3 atoma Co). Akceptor vodonične veze je kiseonik O1 [$\text{O3} \cdots \text{O1} = 2,596(3)$ Å], koji takođe pokazuje manjak naelektrisanja dobijenog od susednih jona (1,61 v.u. od jednog atoma V i tri atoma Ba).

Prvi autor se zahvaljuje austrijskom fondu za nauku (FWF) (projekat T300-N19).

- [1] T. Đorđević, Lj. Karanović, E. Tillmanns, *Crys.Res. Technol.*, 43 (2008), 1202-1209.
- [2] T. Đorđević, J. Stojanović and Lj. Karanović, *Acta Cryst.*, E66 (2010), i79.
- [3] G. M. Sheldrick, SHELX-97, a program for the solution and refinement of crystal structures. University of Göttingen, Germany (1997).
- [4] Zh. Ma, R. He and X. Zhu, *Acta Geologica Sinica*, 4 (1991), 145-151.
- [5] C. Ghose and C. Wang, *Acta Cryst.*, B35 (1979), 819-823

THE COMPLEX OF Ni(II) WITH 3,5-DIMETHYL-1H-PYRAZOLE-1-CARBOXAMIDIUM NITRATE

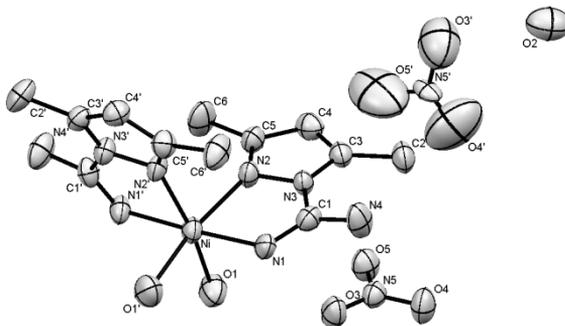
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Pyrazole derivatives, beside of their various practical applicability are known of their rich coordination modes [1, 2]. Lots of them and their complexes with transition metals are used as active components of pharmaceuticals (analgetics, antireumatics, antipiretics) [3]. Other pyrazole based compounds are used in industry as materials for thin film production [4], as catalysts [5] or ionophores [6]. Some of pyrazole based complexes are suitable for modeling metabolic processes [7].

In this paper a new complex of nickel(II) with 3,5-dimethyl-1H-pyrazole-1-carboxamidinium nitrate (*dpca*·HNO₃) of formula [Ni(*dpca*)₂(H₂O)₂](NO₃)₂·H₂O is described. The octahedral geometry in this complex around Ni(II) is established by bidentate coordination of two *dpca* ligands and two molecules of water in *cis*-position while the corresponding *trans*-*dpca* complex is already described [8]. The complex cation is formed by coordination of the ligand by N2 atom of the pyrazole ring and N1 atom of the substituent and two water molecules being in *cis* positions (see figure). The electroneutrality of the complex is accomplished by two nitrate contraions. The compound crystallizes with one water molecule. *Trans*-angles of 177.2° (N1–Ni–N1'), 168.3° (N2–Ni–O1') and 168.3° (N2'–Ni–O1) refer to a slightly deformed structure.



- [1] Rabindranath Mukherjee, *Coordination Chemistry Reviews*, 203 (2000) 151–218
- [2] Ahmed A. Mohamed, *Coordination Chemistry Reviews*, 254 (2010) 1918–1947
- [3] S. A. M. El-Hawash, E. S. A. M. Badawey, I. M. El-Ashmawey, *European Journal of Medicinal Chemistry*, 41 (2006) 155–165
- [4] C. Yélamos, K. R. Gust, A. G. Baboul, M. J. Heeg, H. B. Schlegel, C. H. Winter, *Inorganic Chemistry*, 40 (2001) 6451–6462
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- [8] Ž. K. Jaćimović, V. M. Leovac, K. Mészáros Szécsényi, I. Radosavljević Evans, J. A. K. Howard, *Acta Crystallographica Section C*, 3C60 (2004) m467–m470

KOMPLEKS Ni(II) SA 3,5-DIMETIL-1H-PIRAZOL-1-KARBOKSAMIDINIJUM NITRATOM

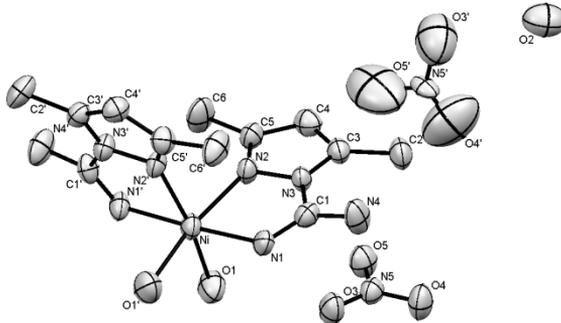
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Derivati pirazola su pored raznovrsne praktične primene poznati i po bogatoj koordinacionoj hemiji [1, 2]. Neki derivati i njihovi kompleksi sa prelaznim metalima se koriste kao aktivne komponente lekova (analgetici, antireumatici, antipiretici) [3], dok se drugi primenjuju u industriji kao materijal za tanke filmove [4], katalizatori [5], jonofore [6]. Takođe su neka kompleksna jedinjenja na bazi pirazola pogodna kao model sistemi za izučavanje nekih metaboličkih procesa [7].

U radu je prikazan novi kompleks nikla(II) sa 3,5-dimetil-1H-pirazol-1-karbonsamidinijum nitratom (*dpca*-HNO₃) formule [Ni(*dpca*)₂(H₂O)₂](NO₃)₂·H₂O. Oktaedarsko okruženje u ovom kompleksu Ni(II) se ostvaruje bidentatnom koordinacijom dva molekula *dpca* i dva molekula vode u *cis*-položajima dok je odgovarajući *trans-dpca* kompleks Ni(II) već opisan u literaturi [8]. Kompleksni katjon nikla(II) nastaje koordinacijom liganda preko N2 atoma pirazolskog prstena i N1 atoma supstituenta i dva molekula vode. Elektroneutralnost kompleksa se postiže nitratnim kontrajonima. *Trans*-uglovi od 177,2° (N1–Ni–N1'), 168,3° (N2–Ni–O1') i 168,3° (N2'–Ni–O1) ukazuju na blagu deformaciju strukture.



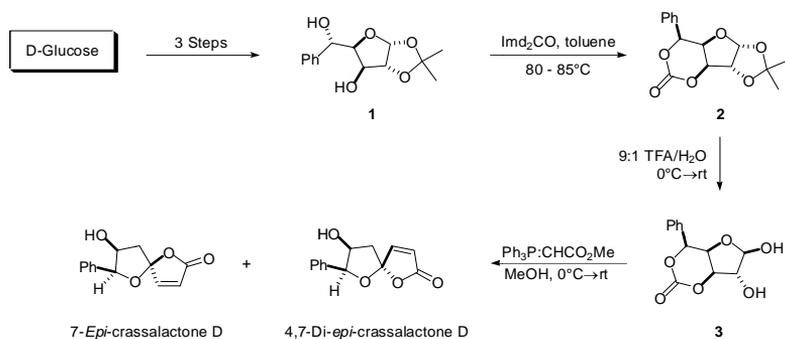
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- [5] A. Dehestani, A. Wu, R. Hayoun, W. Kaminsky, J. M. Mayer, *Inorganica Chimica Acta* 362 (2009) 4534–4538
- [6] A. K. Singh, V. Aggarwal, U. P. Singh, S. Mehtab, *Talanta* 77 (2008) 718–726
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CRYSTAL AND MOLECULAR STRUCTURE OF 7-EPI- AND 4, 7-DI-EPI-CRASSALACTONE D

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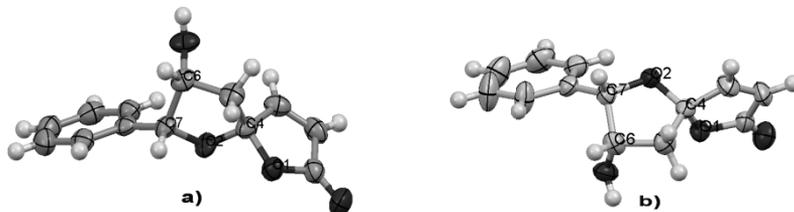
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Naturally occurring antitumour styryl-lactone [1] Crassalactone D, was used as a parent compound for the design of 7-*epi*- and 4,7-di-*epi*-crassalactone D. Both of these stereoisomers were synthesized starting from D-glucose in six steps (Scheme 1).



Scheme 1.

Both compounds crystallize in the same orthorhombic space group $P2_12_12_1$ with approximately equal volume of elementary cells. Based on measured diffraction intensities, initial structures were determined by direct method (SIR-92) and then anisotropic refined by least square methods (SHELXL-97). Hydrogen atoms were located in geometrically optimal positions which finally resulted in sufficiently reliable agreement between measured and calculated structure factors.



(a) Molecular structure of 4,7-di-*epi*-crassalactone D and (b) 7-*epi*-crassalactone D

Hydrogen bonds (2.85-2.90 Å) established between neighboring molecules in each of these crystal lattices are directed along one of the unit cell edges, forming in this way chainlike supramolecular structures. The chains are laterally interconnected by weak Van der Waals interactions.

[1] P. Tuchinda, B. Munyoo, M. Pohmakotr, P. Thinapong, S. Sophasan, T. Santisuk, V. Reutrakul, *J. Nat. Prod.* **2006**, *69*, 1728.

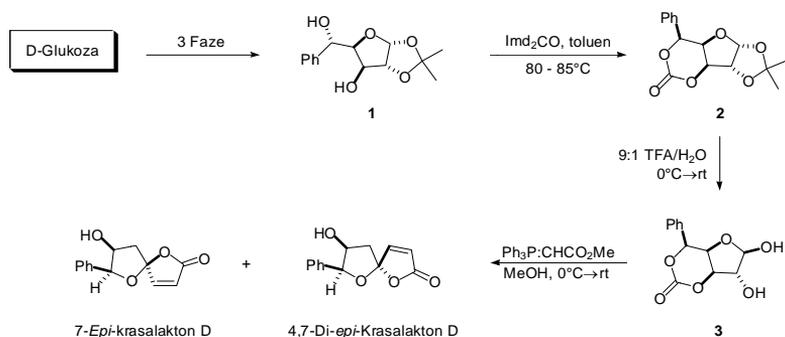
KRISTALNA I MOLEKULSKA STRUKTURA 7-EPI- I 4,7-DI-EPI-KRASALAKTONA D

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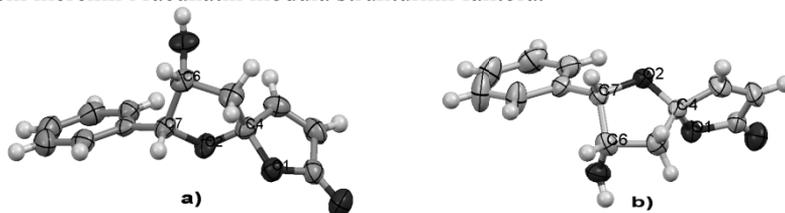
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Krasalakton D, prirodni stiril-lakton[1] koji pokazuje značajnu biološku aktivnost, poslužio je kao “lead compound” za dizajn 7-*epi*- i 4,7-di-*epi*-krasalaktona D. Ova dva epimera su sintetisana iz D-glukoze u šest sintetskih faza (shema 1).



Shema 1.

Kristali oba jedinjenja pripadaju prostornoj grupi $P2_12_12_1$ sa periodama koje određuju približno podjednake zapremine elementarnih ćelija. Na osnovu izmerenih intenziteta difrakcije, polazni modeli struktura određeni su direktnom metodom (SIR-92), a zatim utajnavani metodom najmanjih kvadrata (SHELXL-97). Atomi vodonika su zadati u geometrijski optimalnim položajima što je na kraju rezultiralo dovoljno pouzdanim slaganjem merenih i računatih modula strukturnih faktora.



Slika 1. (a) Molekulska struktura 4,7-di-*epi*-krasalaktona D i (b) 7-*epi*-krasalaktona D

Vodonične veze (2,85 – 2,90 Å), koje se uspostavljaju između susjednih molekula u svakoj od ovih kristalnih rešetki imaju pravac jedne od ivica elementarne ćelije, formirajući tako lančaste nadmolekularne strukture.

[1] P. Tuchinda, B. Munyoo, M. Pohmakotr, P. Thinapong, S. Sophasan, T. Santisuk, V. Reutrakul, *J. Nat. Prod.* **2006**, 69, 1728.

CRYSTAL STRUCTURE OF BUILDING MATERIALS OF SIGNIFICANT ROMAN BUILDINGS AT THE ARCHEOLOGICAL SITES IN SERBIA

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This paper presents the analysis of the structure of samples of building materials from late antiquity and early medieval period, from the archaeological sites of the Republic of Serbia. Investigation was performed with optical microscopy and SEM, and chemical compositions were determined by EDS. Samples of roasted bricks were derived from archaeological sites: the Trajan Bridge at Iron Gate I (Figure a), the Viminacium by Kostolac (Figure B), Sarkamen in Negotin, Felix Romuliana and Fratenize by Zajecar. The aim of this paper is to prove the similarities and differences of building materials that were used in various Roman legions.

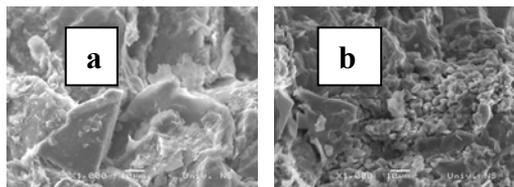


Figure a. SEM of brick of Trajan's bridge, Figure b. SEM of brick of Viminacium

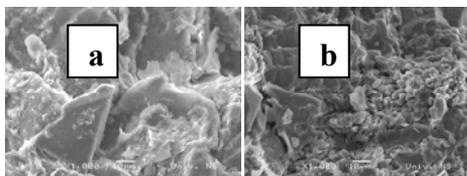
- [1] Kurzmann R., Soldier, *civilian and military brick production*, Oxford Journal of Archaeology, Vol. 24, Issue 4, p. 405-414, November 2005.

KRISTALNA STRUKTURA GRAĐEVINSKOG MATERIJALA ZNAČAJNIH RIMSKIH GRAĐEVINA SA ARHEOLOŠKIH LOKALITETA U SRBIJI

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U ovom radu su predstavljene analize struktura uzoraka građevinskih materijala iz doba kasne Antike i ranog srednjeg veka sa arheoloških lokaliteta Republike Srbije. Ispitivanja su radena metodama optičke mikroskopije i SEM, a hemijski sastavi su određeni metodom EDS. Uzorci pečene cigle su poreklom sa arheoloških lokaliteta: Trajanov most kod Đerdapa I (Slika a), Viminacium kod Kostolca (Slika b), Šarkamen kod Negotina, Feliks Romuliana i Fratenize kod Zaječara. Cilj ovoga rada je dokazivanje sličnosti i razlika građevinskih materijala koje su korišćene kod raznih rimskih Legija.



Slika a. SEM cigle iz Trajanovog mosta, Slika b. SEM cigle iz Viminaciuma

- [1] Kurzmann R., *Soldier, civilian and military brick production*, Oxford Journal of Archaeology, Vol. 24, Issue 4, p. 405-414, November 2005.

STRUCTURAL STUDIES ON DIFFERENT TYPES OF FERROELECTRIC LIQUID CRYSTALLINE SUBSTANCES

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Structural studies of different types of ferroelectric liquid crystalline substances have been reviewed. The discussion deals mainly with the structure of liquid crystals forming chiral ferroelectric mesophase, because after discovery of ferroelectricity in liquid crystals, the research on ferroelectric liquid crystals (FLC) has become one of the most attractive fields due to their technological application. On the basis of optical microscopy and X-ray diffraction data from unoriented samples we have identified the type and the temperature of the phase transitions and outlined the phase diagrams [1, 2, 3]. An analysis of the relation between molecular conformation and the different types of mesomorphic phase transitions has been performed. The layer spacing d and the average intermolecular distance D (i.e. the mean distance between neighboring molecules along and normal to their long axes, respectively) have been determined in all investigated phases using the Bragg law: $\lambda = 2x \sin \theta$, where the distance $x = (d \text{ or } D)$ has been calculated from the positions of the small angle or the large angle diffraction peak, respectively. A comparison of ferroelectric components has been made respect to the residual spontaneous polarization that depends on the density and order of molecular packaging in the smectic phase.

- [1] M. Stojanović, A. Bubnov, D. Ž. Obadović, V. Hamplova, M. Kašpar, M. Cvetinović, *Effect of the chiral chain length on structural and phase properties of ferroelectric liquid crystals*, Phase Transitions, 84 (2011) 380-390
- [2] D. Ž. Obadović, A. Vajda, M. Garić, A. Bubnov, V. Hamplova, M. Kašpar, K. Fodor-Csorba, *Thermal Analysis and X-ray Studies of Chiral Ferroelectric Liquid Crystalline Materials and their Binary Mixtures*, Journal of Thermal Analysis and Calorimetry, 82 (2005) 519-523
- [3] M. Stojanović, D. Z. Obadović, A. Bubnov, V. Hamplova, M. Kašpar, *X-ray and Dielectric Spectroscopy Studies Of Chiral Ferroelectric Liquid Crystals With Keto Group*, Sixth international conference of the Balkan Physical Union (2007)

STRUKTURNA ISPITIVANJA RAZLIČITIH TIPOVA FEROELEKTRIČNIH TEČNO-KRISTALNIH SUPSTANCI

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Izvršili smo strukturna ispitivanja različitih tipova feroelektričnih tečno-kristalnih supstanci. Pošto je nakon otkrića feroelektriciteta u tečnim kristalima istraživanje feroelektričnih tečnih kristala postalo jedno od najatraktivnijih polja zbog njihove tehnološke primene, diskutovali smo strukturu tečnih kristala koji formiraju hiralnu feroelektričnu mezofazu. Na osnovu optičke mikroskopije i rendgenskih difraktografskih podataka na neorijentisanim uzorcima, identifikovali smo tipove i temperature faznih prelaza i naznačili fazne dijagrame [1, 2, 3]. Analizirali smo vezu između konformacije molekula i različitosti tipova mezomorfni faznih prelaza. Rastojanje između slojeva d i prosečno intermolekularno rastojanje D (srednje rastojanje između susednih molekula duž normala na njihove duge ose) je određeno u svim ispitivanim fazama korišćenjem Bragovog zakona : $\lambda = 2x \sin \theta$, gde je rastojanje $x = (d \text{ or } D)$ izračunato na osnovu položaja difrakcionog pika na malom odnosno velikom uglu, respektivno. U odnosu na rezidualnu spontanu električnu polarizaciju koja zavisi od gustine i uređenja molekularnog pakovanja, uradili smo poređenja feroelektričnih komponenti.

- [1] M. Stojanović, A. Bubnov, D. Ž. Obadović, V. Hamplova, M. Kašpar, M. Cvetinoy , *Effect of the chiral chain length on structural and phase properties of ferroelectric liquid crystals* , Phase Transitions, 84 (2011) 380-390
- [2] D. Ž. Obadović, A. Vajda, M. Garić, A. Bubnov, V. Hamplova, M. Kašpar, K. Fodor-Csorba ,*Thermal Analysis and X-ray Studies of Chiral Ferroelectric Liquid Crystalline Materials and their Binary Mixtures*, Journal of Thermal Analysis and Calorimetry, 82 (2005) 519-523
- [3] M. Stojanović, D. Z. Obadović, A. Bubnov, V. Hamplova, M. Kašpar , *X-ray and Dielectric Spectroscopy Studies Of Chiral Ferroelectric Liquid Crystals With Keto Group* , Sixth international conference of the Balkan Physical Union (2007)

SYNTHESIS AND CRYSTAL STRUCTURE OF 2-HYDROXYMETHILEN-17-OXA-D-HOMOANDROST-4-ENE-3,16-DIONE

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In order to study antiproliferative activity, new compound 2-hydroxymethilen-17-oxa-D-homoandrost-4-ene-3,16-dione was synthesized in several synthetic steps, starting from dehydroepiandrosterone.

Crystallographic data for compound were collected at room temperature on an Oxford Diffraction Gemini S system using Mo K α radiation ($\lambda = 0.7107$ Å). The program suite CrysAlis^{Pro} [1] was used for data collection, semi-empirical absorption correction and data reduction. Structure was solved with direct methods using SIR97 [2] and was refined by full-matrix least-squares methods on F² with SHELXL-97 [3]. The compound (C₂₀H₂₆O₄) crystallizes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters $a = 9.012(5)$, $b = 11.633(5)$, $c = 16.355(5)$ Å, and $Z = 4$, $\rho_x = 1.28$ g cm⁻³, $\mu = 0.09$ mm⁻¹. The final R factor is 0.056 for 2757 independent reflections and 240 parameters.

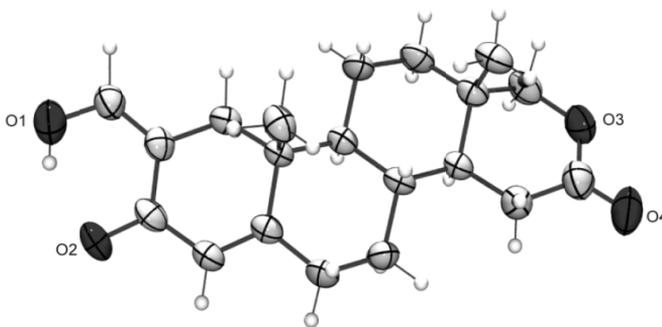


Figure 1. A view of the molecular structure of C₂₀H₂₆O₄

The financial support of the Provincial Secretariat for Science and Technological Development (Grant No. 114-451-1987/2011-01) is gratefully acknowledged.

- [1] CrysAlisPro Software system; Oxford Diffraction Ltd., vers. 171.32 Oxford, UK, 2007.
- [2] Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G., Spagna, R. *J. Appl. Cryst.* 1999, 32, 115-119.
- [3] Sheldrick, G. M. (1997). SHELX97. University of Göttingen, Germany

SINTEZA I KRISTALNA STRUKTURA 2-HIDROKSIMETILEN-17-OKSA-D-HOMOANDROST-4-EN-3,16-DIONA

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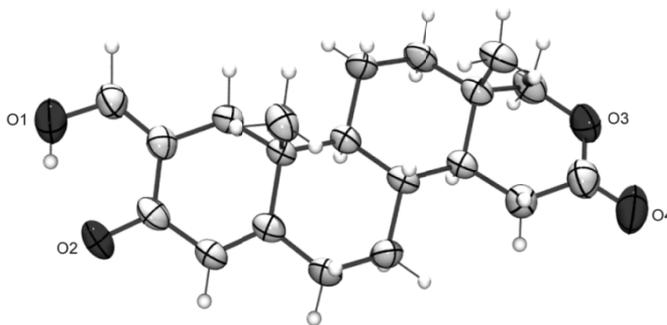
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U cilju ispitivanja biološke aktivnosti, novo jedinjenje 2-hidroksimetilen-17-oksa-D-homoandrost-4-en-3,16-dion je dobijeno u višefaznoj sintezi, polazeći od dehidroepiandrosterona.

Kristalografski podaci za novosintetisano jedinjenje su prikupljeni na sobnoj temperaturi na Oxford Diffraction Gemini S difraktometru uz upotrebu Mo K α zračenja ($\lambda = 0,7107 \text{ \AA}$). Programski paket CrysAlis^{Pro} [1] upotrebljen je za prikupljanje, semi-empirijsku korekciju na apsorpciju i redukciju podataka. Struktura je rešena uz pomoć direktnih metoda upotrebom SIR97 [2] programa i utačnjena upotrebom SHELXL-97 programa [3]. Jedinjenje kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije: $a = 9,012(5)$, $b = 11,633(5)$, $c = 16,355(5) \text{ \AA}$, $I Z = 4$, $\rho_x = 1,28 \text{ g cm}^{-3}$, $\mu = 0,09 \text{ mm}^{-1}$. Konačna vrednost R faktora je 0,056 za 2757 nezavisnih refleksija i 240 parametara.



Slika 1. Prikaz molekulske strukture C₂₀H₂₆O₄

Autori se zahvaljuju Pokrajinskom sekretarijatu za nauku i tehnološki razvoj za finansijsku pomoć (broj projekta 114-451-1987/2011-01).

[1] CrysAlisPro Software system; Oxford Diffraction Ltd., vers. 171.32 Oxford, UK, 2007.

[2] Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G., Spagna, R. J. Appl. Cryst. 1999, 32, 115-119.

[3] Sheldrick, G. M. (1997). SHELX97. University of Göttingen, Germany

CRYSTALLOGRAPHIC AND QUANTUM-CHEMISTRY ANALYSIS OF THE INTERACTIONS BETWEEN BENZENE MOLECULES WITH MUTUALPARALLEL ORIENTATION

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Aromatic-aromatic interactions are one of the most important noncovalent interactions and occur in various systems, from biomolecules to crystals.

Data in the crystal structures from the Cambridge Structural Database (CSD) were searched for interactions between two parallel benzene molecules. We consider that an interaction occurs if the distance between centers of the benzene rings is shorter than 6.0 Å, while the normal distance of ring planes (R) is shorter than 4.0 Å. 1824 contacts of benzene molecules were found. The results of statistical analysis show that unexpectedly large numbers of contacts are located at large offset distances. The distribution of *r* values, shown in Figure 1(a), reveals that most of contacts (58%) have the offset distances in the range 4.5-5.5 Å.

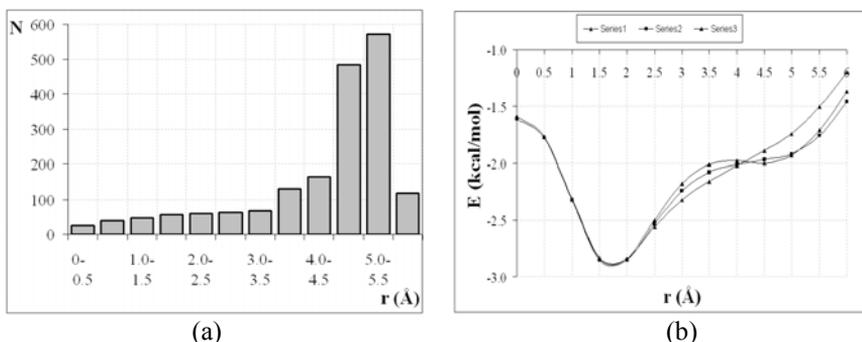


Figure 1.(a) Histogram of the distribution of *r* values (b) The calculated interaction energies (ΔE) for three different geometries of benzene molecules plotted as a function of *r* value

In order to determine whether the interactions between benzene molecules with the large offset values is attractive, and not just the consequence of packing in the crystal structures, the interaction energies for a number of benzene/benzene model systems were calculated using B2PLYP method and the def2-TZVP basis set. The normal (*R*) and the offset (*r*) distances were systematically varied while the monomer geometries were kept rigid. The calculated minimum energies (ΔE) of interaction with different *R* normal distances are plotted in Figure 1(b), as a function of *r* value. Figure reveals that even at long offsets of 4.0 Å, interaction is substantially strong (approximately 2.0 kcal/mol). This indicates that the parallel alignment interactions at the long offset distances are important.

KRISTALOGRAFSKA I KVANTNO-HEMIJSKA ANALIZA INTERAKCIJA IZMEĐU PARALELNO ORIJENTISANIH MOLEKULA BENZENA

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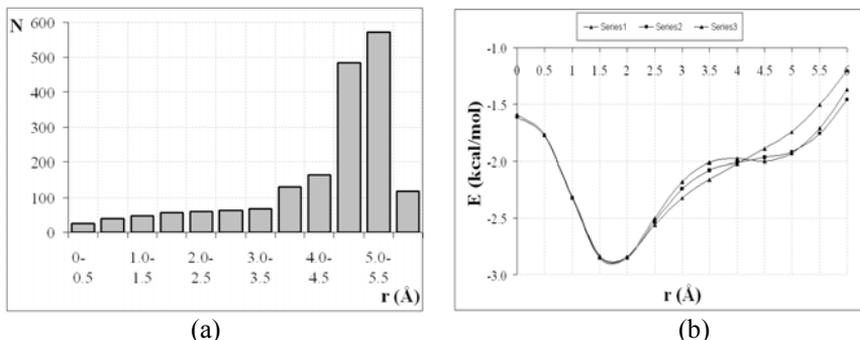
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Aromatično-aromatične interakcije su jedne od najvažnijih nekovalentnih interakcija u prirodi i nalaze se u raznim sistemima, od biomolekula do kristala.

Kembrička kristalografska banka podataka (CSD) je pretražena da bi se došlo do podataka o interakcijama između molekula benzena sa paralelnom orijentacijom. Smatra se da se interakcije javljaju ako je rastojanje između centara prstenova manje od 6,0 Å i ako je normalno rastojanje između ravni benzena manje od 4,0 Å. Pronađeno je 1824 kontakata između benzenovih prstenova. Rezultati statističke analize pokazuju neočekivano veliki broj kontakata sa velikim ofset vrednostima. Raspodela r vrednosti, prikazana na slici 1(a), pokazuje da većina kontakata (58%) ima ofset vrednost u intervalu od 4,5 do 5,5 Å.



Slika 1. (a) Histogram raspodele r vrednosti (b) Izračunate vrednosti energija (ΔE) za tri različite geometrije benzenovih molekula prikazana u funkciji r vrednosti

Da bi smo utvrdili da li je priroda interakcija između benzenovih molekula sa velikim ofset vrednostima privlačna, a ne samo posledica pakovanja u kristalnim strukturama, izračunate su energije interakcija za veći broj benzen/benzen model sistema koristeći def2-TZVP „basis set“ i B2PLYP metodu. Vrednosti normalnih rastojanja i ofseta su menjane dok su geometrije monomera ostajale iste. Dobijeni minimumi za različite R vrednosti su prikazane na slici 1 (b) za sve razmatrane r vrednosti. Sa slike se vidi da su interakcije, na ofset vrednostima većim od 4,0 Å relativno jake (energija je oko 2.0 kcal/mol). Ovo ukazuje da su interakcije između paralelnih molekula sa velikim ofset vrednostima značajne ali da pakovanje u kristalnim strukturama ima odlučujuću ulogu.

PARALLEL WATER/AROMATIC INTERACTIONS WITH LARGE OFFSET DISTANCES

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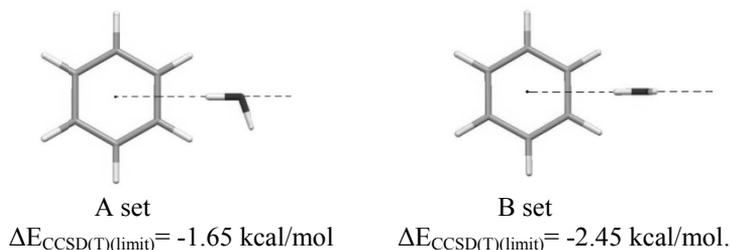
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Interaction of aromatic group with water molecule is the subject of extensive investigation, because aromatic molecules and groups appear in various systems, while the water molecule plays an essential role in nature. The most important property of water molecule is its hydrogen bond ability. Recently, we recognized the parallel water/aromatic interactions in crystal structures [1]. In spite of significantly stronger O-H/ π interactions, the parallel- alignment interaction occur quite frequently in crystal structures [2].

These new geometric features were discovered by analyzing crystal structures from the Cambridge Structural Database (CSD) and by high level *ab initio* calculations. Analysis of crystal structures revealed the existence of orientation where the whole water molecule (A set) or one of its O–H bonds (B set) is parallel to the aromatic ring plane. We unexpectedly observed that the most of parallel alignment interactions are not above C-H region of the aromatic ring, but for larger offset (horizontal displacement) distances.

In order to determine if the interactions with the large offset values are attractive, and not just the consequence of packing, the interaction energies for a number of water/benzene model systems are calculated. Attractive interaction energies, obtained from *ab initio* calculations, including coupled cluster electron correlation treatment (CCSD(T)) and complete basis set extrapolation, are significant and consistent with the observed crystal structures.

The most stable model system of all those considered has one O–H bond parallel to benzene ring at horizontal displacement of 2.6 Å (B set). This interaction is quite stronger than C-H/O interactions ($\Delta E_{\text{CCSD(T)}(\text{limit})} = -1.41$ kcal/mol), somewhat weaker than O-H/ π ($\Delta E_{\text{CCSD(T)}(\text{limit})} = -3.19$ kcal/mol) and comparable with the energy for the slipped-parallel benzene-benzene dimer ($\Delta E_{\text{CCSD(T)}(\text{limit})} = -2.45$ kcal/mol).



[1] B. Ostojić, G. Janjić, S. Zarić, *Chemical Communication*, 28 (2008), 6546-6548

[2] G. Janjić, D. Veljković, S. Zarić, *Crystal Growth & Design*, submitted.

INTERAKCIJE VODE I ARIL GRUPE SA PARALELNO ORIJENTACIJOM NA VELIKIM OFSET RASTOJANJIMA

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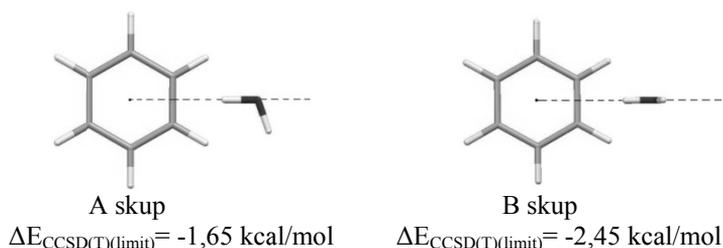
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Interakcije aromatičnih jedinjenja sa vodom predmet su opsežnih istraživanja, a razlog tome su zastupljenost aromatičnih jedinjenja u veoma različitim sistemima, kao i važna uloga vode u prirodi. Građenja vodoničnih veza je jedna od veoma bitnih osobina molekula vode. Interakcije vode i aril grupe, sa međusobno paralelnom orijentacijom, nedavno su otkrivene u kristalnim strukturama [1]. Uprkos znatno jačim OH/ π interakcijama, paralelne interakcije se ipak često javljaju u kristalnim strukturama [2].

Nova geometrija otkrivena je analizom kristalnih struktura iz Kembričke kristalografske banke (CSD) ali i na osnovu *ab initio* proračuna. Analizom kristalnih struktura utvrđeno je postojanje orijentacija, gde je ceo molekul vode (A skup) ili pak jedna njegova O-H grupa (B skup) paralelna sa ravni aromatičnog prstena. Neočekivano je utvrđeno da se kod najstabilnijih paralelnih orijentacija, O-H grupa ne nalazi iznad C-H regiona aromatičnog prstena, nego na većim ofset (horizontalno odstupanje) rastojanjima.

Da bi utvrdili da li su interakcija sa velikim ofset rastojanjima privlačnog karaktera, a ne samo posledica pakovanja u kristalnim strukturama, računata su energije interakcije na brojnim voda/benzen model sistemima. *Ab initio* proračunima, koji uključuju i proračune na CCSD(T) limitu, pokazano je da ove interakcije imaju privlačan karakter i da su njihove vrednosti u skladu sa podacima dobijenim analizom kristalnih struktura.

Kod najstabilnijeg model sistema samo jedna O-H grupa je paralelna sa ravni benzenovog prstena (B skup) i ima vrednost ofset rastojanja od 2,6 Å. Ove interakcije su se pokazale nešto jačim od C-H/O interakcija ($\Delta E_{\text{CCSD(T)}(\text{limit})} = -1,41$ kcal/mol), nešto slabija od O-H/ π ($\Delta E_{\text{CCSD(T)}(\text{limit})} = -3,19$ kcal/mol) i slične vrednosti kao energija za steking interakcije između dva smaknuta benzenova prstena ($\Delta E_{\text{CCSD(T)}(\text{limit})} = -2,45$ kcal/mol).



[1] B. Ostojić, G. Janjić, S. Zarić, *Chemical Communication*, 28 (2008), 6546-6548

[2] G. Janjić, D. Veljković, S. Zarić, *Crystal Growth & Design*, submitted.

STUDY OF INTERACTIONS BETWEEN NON-COORDINATED PYRIDINES MOLECULES

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Noncovalent interactions of π -systems, including stacking interactions, have been extensively studied in recent years. Stacking interactions are generally studied between aromatic organic molecules or fragments [1, 2]. The SCS-MP2/aug-cc-pVTZ calculations on pyridine molecules in sandwich, parallel-displaced and T-shaped geometries showed that the most stable configuration was parallel-displaced, and more than 1 kcal/mol over the most stable T-shaped pyridine.

Our study was based on the statistical analysis of crystal structures archived in the Cambridge Structural Database (CSD) and *ab initio* calculations. By searching CSD 334 contacts were found and 129 had parallel alignment. Among these 129 contacts 66 were stacking interactions. This indicates that parallel alignment is prevalent type of the orientation between pyridine molecules. The results of *ab initio* calculations are in an excellent agreement with results of CSD search. The most stable stacking geometry with the offset value of 1.3 Å and normal distance of 3.46 Å has interactions energy of -4.08 kcal/mol. The influence of hydrogen bonds on stacking interactions of pyridines were also analyzed. In the cases where pyridines form hydrogen bonds, energy of stacking interaction between two Py...H₂O complexes is -6.87 kcal/mol. The effect of crystal packing on the geometry of stacking interactions is pronounced, and when stacking interactions do not coexist with hydrogen bonds, this influence is more pronounced.

Analysis of the packing in crystal structures showed that stacking interactions form stacking dimers and chains. The reason for larger number of structures with stacking dimers is stronger interactions of pyridine molecules with environment than the stacking interactions.

- [1] B. D. Ostojić, G. V. Janjić, S. D. Zarić, *Chem. Comm.* 48 (2008) 6546-6548
[2] G. V. Janjić, D. Z. Veljković, S. D. Zarić, *Cryst. Growth Des.*, submitted

PROUČAVANJE INTERAKCIJA IZMEĐU NEKOORDINOVANIH PIRIDINSKIH MOLEKULA

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Nekovalentne interakcije π -sistema uključujući i steking interakcije su veoma mnogo proučavane tokom nekoliko poslednjih godina. Steking interakcije su najviše proučavane između aromatičnih organskih molekula ili fragmenata [1, 2]. SCS-MP2/aug-cc-pVTZ proračuni na molekulima piridina koji su u sendvič, paralelno-smaknutoj i T- oblik orijentaciji pokazuju da je najstabilnija paralelno-smaknuta orijentacija, čak više od 1 kcal/mol u odnosu na najstabilniji T- oblik.

Naša studija se zasnivala na statističkoj analizi kristalnih struktura iz kristalografske banke podataka (CSD) i *ab initio* proračunima. Pretragom banke je nađeno 334 kontakata od kojih je 129 bilo u paralelnoj orijentaciji. Ovi podaci ukazuju na dominantnost paralelne orijentacije piridina. Od 129 kontakata, u 66 je opažena steking interakcija. U ovom radu je izračunata energija najstabilnije steking orijentacije koja je iznosila -4,08 kcal/mol kada je offset vrednost 3 Å, a normalno rastojanje 3,46 Å. Naši rezultati *ab initio* proračuna su u veoma dobrom slaganju sa rezultatima pretrage CSD-a. Ovdje je takođe analiziran uticaj vodoničnog vezivanja piridina na jačinu steking interakcija. U slučaju gde piridini formiraju vodonične veze, energija steking interakcije između dva Py..H₂O kompleksa je -6,87 kcal/mol. Efekat pakovanja kristala veoma utiče na geometriju steking interakcija, a još je izraženiji u slučajevima kada steking interakcije ne postoje zajedno sa vodoničnim vezama.

Analiza kristalnih struktura je pokazala da piridini koji su u stekingu formiraju nizove i dimere. Razlog zbog kojeg veći broj struktura formira dimere je to što su interakcije piridina sa okolinom jače od steking interakcija.

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

[2] G. V. Janjić, D. Ž. Veljković, S. D. Zarić, *Cryst. Growth Des.*, submitted