

СРПСКО КРИСТАЛОГРАФСКО ДРУШТВО

SERBIAN CRYSTALLOGRAPHIC SOCIETY

**V КОНФЕРЕНЦИЈА  
СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА  
Изводи радова**

**V CONFERENCE  
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Abstracts**

БЕОГРАД - BELGRADE  
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**PLENARY LECTURES**

**ПЛЕНАРНА ПРЕДАВАЊА**

## Chemical bonding study in carbyne compounds using the electron deformation density method.

Anne Spasojević-de Biré and Nguyen Quy Dao

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### **Abstract.**

Joint experimental and theoretical electron density deformation methods have lead to a better understanding of the chemical bondings in carbyne compounds. In particular, the nature of the triple chromium - carbon bond has been determined. Conjugation and hyper conjugation effects have also been evidenced. Recently the linearity of the  $W \equiv C - H$  moiety has been established from neutron diffraction results.

### **Izvod.**

Zajednički eksperimentalan i teoretski elektron čvrstoće deformacije metoda je vodio za bolje poznavanje od hemijske veze u "carbyne" spoj. Narocito, karakter od trojne hrom - ugljenik veze je bio definisan. Konjugacija i iperkonjugacija efekti su bili isto istaknuti. Nedavno, linearost od  $W \equiv C - H$  deo, je postavio preko nucleari difrakt rezultata.

The carbynic complexes have been discovered in 1973 by E. O. Fischer [1]. Their originality consists in a triple bond between a transition metal and a carbon atom, which makes them very unstable, sensitive to moisture, air and temperature. In relation with this very specific structural character, the chemical bonding in this family of compounds requires special attention in order to understand a new and important area of organometallic chemistry. As a matter of fact, carbyne complexes have been recognized as precursors in the synthesis of organometallic products which take part into catalytic reactions. Our goal was to investigate the electronic deformation density of two members of this family: the *trans*-chlorotetracarbonyl phenylmethylidyne (**I**) and its methylitic analog (**II**) (figure 1); the neutron structure of  $BrW(\equiv CH)[(P(CD_3)_3)_2(C_2H_2)]_2$  (**III**) was determined (figure 2). In order to obtain informations of interest to the chemist on topics such backdonation, conjugation or hyperconjugation effects [2].

### **1. Density deformation studies of (**I**) and (**II**).**

The joint multipole model refinement and *ab initio* CASSCF study has given to important chemical informations concerning carbyne complexes. The carbyne bond has been characterized by an ellipsoïd of density accumulation originating in the carbon atom facing a depopulated metal orbital. A qualitative resemblance with the density pattern of the carbon

monoxyde interaction was noticed, indicating that both types of interaction can be rationalized in terms of  $\sigma$  donation and  $\pi$  backdonation. The density ellipsoïd associated with the carbynic bond, relatively smooth and more extended toward the  $\pi$  bonding regions, is in keeping with the unbalanced character of the electron flows, more important for the  $\pi$  backdonation than for the  $\sigma$  donation, eventually leading to a large negative net charge for the carbynic carbon. This backdonation interaction gives the carbon atom an electronic configuration close to  $\sigma^2\pi^2$  and then formally corresponding to a negatively charged carbon. The backdonation seems to be even stronger, though anisotropic, in the phenylcarbyne compound, in relation with a conjugation effect between the phenyl ring and the metal-carbon triple bond (figure 3). A weaker hyperconjugation effect was noticed in the methyl complex. The experimental investigations on the charge density agree with the evidence obtained from vibrational spectroscopy that two conformers of the methylcarbyne, eclipsed and non-eclipsed, do coexist in the crystal at 100 K. The hypothesis of an electronic, intramolecular effect originating in the methyl group of (II) and responsible for the observed breakdown of the  $C_{4v}$  symmetry in the  $\text{Cr}(\text{CO})_4$  moiety was ruled out from an analysis of the CASSCF wave function, and from both the theoretical and the modelized X-M deformation maps. Finally, the experimental and theoretical orbital  $d$  populations are in good agreement for the methyl complex and confirm the homopolar character of the metal-carbyne interactions (especially for the  $\pi$  bonds) as compared to the similar metal-carbonyl couplings.

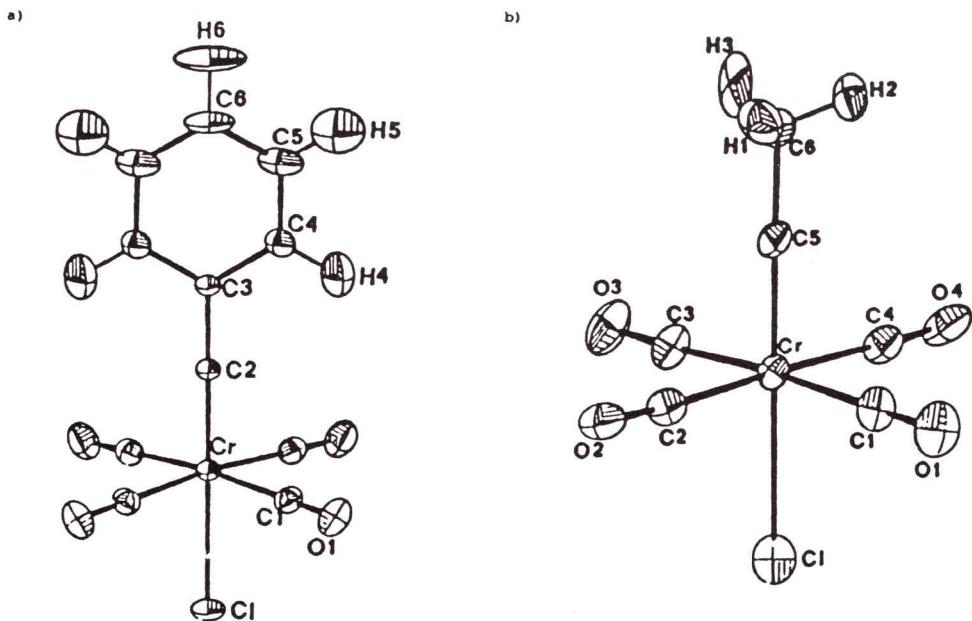


Figure 1. Molecular structure. a) phenylcarbyne complex (I); b) methylcarbyne complex (II).

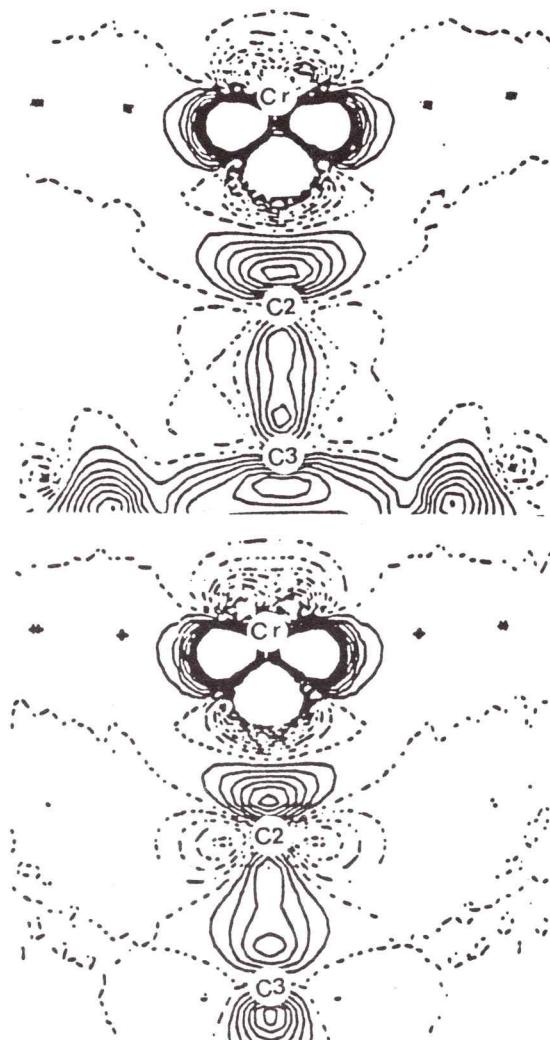


Figure 2. Conjugation effect in (I) a) experimental static deformation map in the plane containing the phenyl ring; b) in the plane perpendicular to the phenyl ring (contours  $0.1 \text{ e} \cdot \text{\AA}^{-3}$ ).

## 2. Neutron diffraction study of (III).

Churchill *et al* was the first to obtain the crystallization of a simply methylidyne complexes ( $R = H$ ). From 1981 to nowaday, only six species has been characterised from diffraction studies. These molecules adopt a pseudo octahedral structure. For the complexes whose position of the terminal hydrogen was determined, the value of the  $M \equiv C - H$  angle seems significantly differ from  $180^\circ$ , contrary to the results obtained for the other carbyne complexes. Unfortunately, all the structural results obtained for the methylidyne compounds came from X-ray experiments which does not allow a good precision for the hydrogen position

determination. Furthermore, some of these compounds display a positional disorder of the *cis* or *trans* ligand. In order to obtain more precise results, we have undertaken the structure resolution of the partially deuterated complexe (III) from a neutron diffraction experiment performed on a four-circle spectrometer at low temperature.

The general features of the structure can be briefly described as following: i) The metal lies in a pseudooctahedral environment. ii) The  $W \equiv C$  bond distance is one of the shortest distance reported. iii) In a first approximation the four phosphorous atoms are situated on the equatorial plane. The intra P - W - P angles ( $\langle P - W - P = 81.1(3)^\circ \rangle$ ) differ significantly from the inter P - W - P angle ( $\langle P - W - P = 98.5(3)^\circ \rangle$ ) as observed for other similar complexes. This dmpe ligand bent toward the bromium atom ( $\langle C1 - W - P = 93.4(2)^\circ \rangle$ ). This is in agreement with the Kostić and Fenske calculations which have demonstrated that the phosphorous ligand are oriented towards the groups with the weakest  $\pi$ -acceptor, as already observed experimentally for other carbyne complexes. iv) The most significant result of this work, is the first precise determination of the  $W \equiv C - H$  bond angle ( $178.1(9)^\circ$ ).

Therefore this study [3] demonstrates clearly for the first time the linearity of the  $W \equiv C - H$  group in this series of compound.

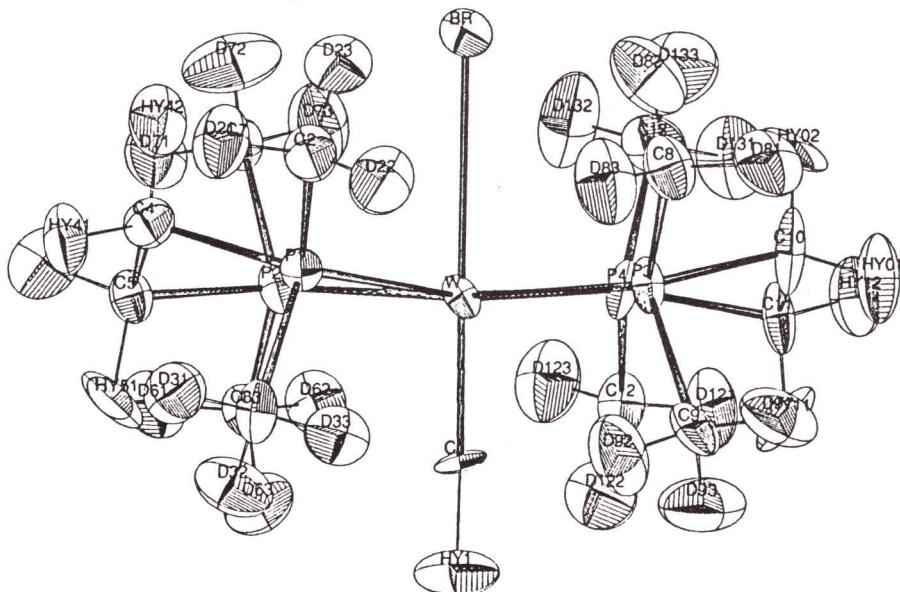


Figure 3. Molecular structure of methyldyne complex (III).

- [1] E. O. Fischer, "Nobel Vortrag", *Angew. Chem.*, **1974**, 86, 651
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## CRYSTAL STRUCTURES OF METAL UREA COMPLEXES

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Urea,  $\text{CO}(\text{NH}_2)_2$ , ( $\text{Ur}$ ) is of interest for researchers, because it is able to form both clathrates and complexes with metal salts. Some of the latter exhibit biological activity; they can serve as models for metal – ion binding in biological systems. In addition, the availability of great number of structural data makes it possible to reveal some crystal-chemical regularities.

The lecture is primarily concerned with complexes of non-transition metals. Structural features of urea complexes are considered depending on the metal cation and anion nature. Considerable attention is given to mixed complexes containing two different metals.

In complexes with alkali metals, urea molecules often bridge two metal atoms. In  $\text{Li}_2\text{SO}_4 \cdot 3\text{Ur}$  and  $\text{NaCl} \cdot \text{Ur}$  structures metal atoms are coordinated by both urea molecules and anions. However, in  $\text{LiI} \cdot 2\text{Ur}$  structure  $\text{I}^-$  anions are not involved in coordination. All these crystals are built of infinite chains linked to one another *via* hydrogen bonds.

In complexes of other metals, urea molecule, as a rule, acts as monodentate ligand coordinating metal atom through oxygen atom.

For alkaline-earth metals, a number of complexes of various composition was obtained depending on the component ratio in solution.  $\text{MgBr}_2$  forms  $[\text{Mg}\text{Ur}_4(\text{H}_2\text{O})_2]\text{Br}_2$  and  $[\text{Mg}\text{Ur}_6]\text{Br}_2 \cdot 4\text{Ur}$  crystals. Both structures contain octahedral complex cations.  $\text{Ca}(\text{NO}_3)_2$  forms  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{Ur}$  and  $\text{Ca}(\text{NO}_3)_2\text{Ur} \cdot 3\text{H}_2\text{O}$  complexes. In the former, Ca atoms has octahedral coordination involving 4 Ur molecules and 2 monodentate  $\text{NO}_3^-$  groups. In the latter,  $\text{NO}_3^-$  groups are bidentate, and coordination number of Ca atom is 8, coordination polyhedron is intermediate between dodecahedron and square antiprism. These structures contain discrete complexes. Isolated octahedral complex is found also in the structure of  $\text{Ca}(\text{N}_3)_2 \cdot \text{Ur}_4$ , whereas  $\text{Sr}(\text{N}_3)_2 \cdot \text{Ur}$  has a layer structure: azide anion is tridentate; one of its terminal atoms coordinates two Sr atoms, and another coordinates one Sr atom. Urea molecule bridges two Sr atoms, which coordination numbers reach 8 (distorted square antiprism).

Zinc and cadmium complexes are of interest.  $\text{ZnSO}_4$  and  $\text{Zn}(\text{NO}_3)_2$  form typical octahedral  $[\text{Zn}\text{Ur}_6]^{2+}$  complexes; anions do not participate in metal coordination. At the same time,  $\text{ZnCl}_2$  and  $\text{Zn}(\text{CH}_3\text{COO})_2$  form molecular complexes of  $\text{ZnX}_2\text{Ur}_2$  composition.

A tendency of Zn atom to coordinate Cl atoms manifests itself in presence of other metal atoms. In  $\text{ZnCl}_2 \cdot \text{MnCl}_2 \cdot 5\text{Ur} \cdot \text{H}_2\text{O}$  a complete separation of ligands occurs: all urea molecules are bonded to Mn atoms, and all Cl atoms are bonded to Zn atoms. The formula of the complex may be written as  $[\text{Mn}\text{Ur}_5(\text{H}_2\text{O})][\text{ZnCl}_4]$ .

The ligand separation is observed also in the structure of  $\text{ZnCl}_2 \cdot \text{CrCl}_3 \cdot 6\text{Ur} \cdot 2\text{H}_2\text{O}$ . However, in this crystal Zn atom can not use all Cl atoms, and one of them remains uncoordinated. The formula of the compound is:  $[\text{Cr}_5\text{Ur}_6][\text{ZnCl}_4]\text{Cl} \cdot 2\text{H}_2\text{O}$ .

Complex of different composition was also obtained:  $2\text{ZnCl}_2 \cdot \text{CrCl}_3 \cdot 7\text{Ur}$ . In this structure, on the contrary, Cl atoms are deficient to form two  $[\text{ZnCl}_4]^{2-}$  anions. As a result, the crystal contains two types of anions and has a formula  $[\text{CrUr}_6][\text{ZnCl}_4][\text{ZnCl}_3\text{Ur}]$ .

Although Cd belongs to the same group of Periodic system of elements, its crystal-chemical behavior is quite different.

$\text{CdCl}_2 \cdot 2\text{Ur}$  crystal is not molecular, but is built of chains formed by bridging Cl atoms. Cd atom has octahedral coordination ( $4\text{Cl} + 2\text{Ur}$ ).  $\text{CdCl}_2 \cdot \text{Ur}$  crystal contains similar chains, but one of Cl atoms acts as triple bridge connecting them into double chains.

In  $\text{CdI}_2 \cdot 2\text{Ur}$  crystal the separation of ligands is observed. The structure consists of octahedral complex  $[\text{CdUr}_6]^{2+}$  cations and chain  $[\text{CdI}_3]_\infty$  anions with tetrahedral Cd coordination.

So, a great variety of structural types is observed in metal urea complexes. Their geometric characteristics are also discussed in the lecture. Some properties of crystals are considered.

## Neutron Diffraction as a Tool in Crystal Structure Determination.

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Scientific research in various domains concerning the structure of matter has been of keen interest in chemistry, physics and biology for many years. the largest quantity of information has been derived, of course, from X-ray crystallography. However beginning in the 1960's neutron diffraction techniques have become to an increasing extent an important complement and in some cases a necessity for a successful structural investigation. The neutron diffraction technique as a tool for crystal structure determination is closely related to the more familiar X-ray diffraction technique. It is therefore natural that the similarities and differences between the X-ray and neutron diffraction technique are pointed out and that comparisons are made between the two techniques. This is further justified since a neutron diffraction study is seldom or never carried out until a careful X-ray study has been made. The reasons are twofold: an unknown structure is generally solved more easily from X-ray data, and the cost of a neutron diffraction study is at least hundred times that of an X-ray study. This, of course, represents a serious limitation when combined with the fact that the size of the single crystals or the amount of powder needed for neutron diffraction must be one to ten thousand times larger. However the advantages of neutron diffraction can be summarised as follows:

- ◆ Light and heavy atoms can usually be determined with the same precision which is not the case with X-rays where the scattering power depends on the number of electrons in each atom.
- ◆ Elements with adjacent atomic numbers can be separately identified as neutron are scattered by the nuclei. The scattering power is not strictly related to the atomic size but to the nuclear energy levels.
- ◆ Due to these differences in energy levels, isotopes of an element have often very different scattering powers. An isotopic substitution can thus drastically change the scattering conditions in a crystal.
- ◆ Atomic positional and displacement (thermal) parameters are not affected by bonding or lone-pair electrons.
- ◆ Unique information about the magnetic structure can be derived as the uncharged neutron has a magnetic moment which can interact with the permanent magnetic moments of atoms with unpaired electrons.
- ◆ Equipment for high and low temperatures and pressures can easily be designed as materials such as aluminium and quartz glass are nearly transparent for neutrons . Metal alloys with a scattering power close to zero can be used for sample holders.

After a short introduction of the basic properties of the neutron and its consequences for crystal structure work in general, the main lecture will be focused on the study of some magnetic structures.

**ORAL PRESENTATIONS**

**САОПШТЕЊА**

SYNTHESIS AND STRUCTURE OF MANGANESE(II) COMPLEX  
WITH 1,2-PROPANEDIAMINETETRAACETIC ACID

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In reaction of  $MnCO_3$  and 1,2-propane diaminetetraacetic acid ( $H_4^{1,2\text{-pdta}}$ ) a new complex of Mn(II) was prepared for which the structure was determined by X-ray analysis.

Colorless prismatic crystals were obtained by slowly evaporation of water solution. The complex crystallizes in the space group  $P2_1/n$  of the monoclinic crystal system with  $a = 1.0993(2)$  nm,  $b = 1.4092(2)$  nm,  $c = 1.1753(1)$  nm,  $V = 1.8097(3)$  nm<sup>3</sup>,  $\beta = 96.302(9)^\circ$ ,  $Z = 4$ . The cell unit is  $NbF_7^{2-}$  type containing seven-coordinated Mn(II) ion with  $H_2^{1,2\text{-pdta}}$  ion acting as a hexadentate ligand and one water molecule. The  $C_2$  axis (in approximation) going through oxygen of coordinated water molecule, central Mn(II) ion and middle-point C-C bond of the diamine "backbone" ring bisects the N1-Mn-N2 bong angle, making the two glycinate (R rings) (as well as the G rings) nearly identical.

SINTEZA I STRUKTURA MANGAN(II) KOMPLEKSA SA  
1,2-PROPAN-DIAMIN-TETRASIRĆETNOM KISELINOM

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U reakciji  $MnCO_3$  i 1,2-propan-diamin-tetrasirćetne kiseline ( $H_4^{1,2\text{-pdta}}$ ) nagrađen je novi kompleks mangana(II) čija je struktura odredjena na bazi rendgenske strukturne analize.

Bezbojni prizmatični kristali dobiveni su laganim uparavanjem vodenog rastvora a pripadaju prostornoj grupi  $P2_1/n$  monokliničnog sistema sa  $a = 1,0993(2)$  nm,  $b = 1,4092(2)$  nm,  $c = 1,1753(1)$  nm,  $V = 1,8097(3)$  nm<sup>3</sup>,  $\beta = 96,302(9)^0$ ,  $Z = 4$ . Osnovna celija je tipa  $NbF_7^{2-}$  jona i sadrži heptakoordinovani Mn(II) jon sa  $H_2^{1,2\text{-pdta}}$  jonom kao heksadentatnim ligandom i jednim molekulom vode.  $C_2$  osa simetrije, koja prolazi kroz atom kiseonika koordinovane vode, jon mangana i sredinu C-C veze ledjnog diaminskog prstena, polovi N1-Mn-N2 ugao veze čineći dva R glicinska prstena (kao i G prstenove) približno ekvivalentnim.

## Di-Rubidium Hexaaquacobalt(II) Tetra(Hydrogen Phthalate) Tetrahydrate

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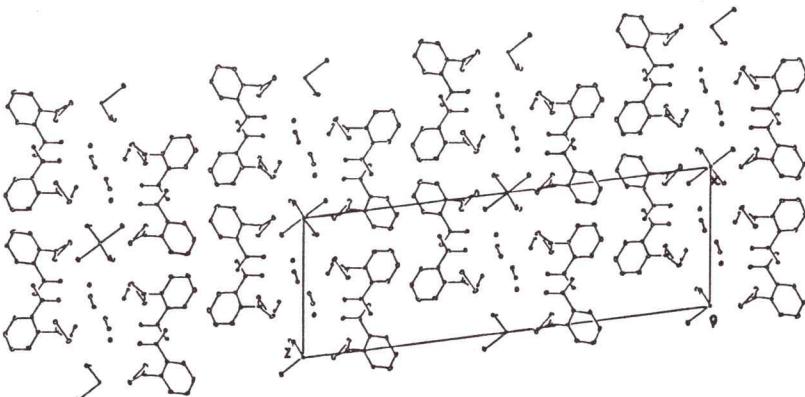
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This work is part of our studies of the transition metal complexes containing anions of 1,2-benzenedicarboxylic (phthalic, H<sub>2</sub>pht) acid.

An attempt to prepare Co(II) complex analogous to Rb<sub>2</sub>[Cu(pht)<sub>2</sub>]·2H<sub>2</sub>O yielded the title compound with formula Rb<sub>2</sub>[Co(H<sub>2</sub>O)<sub>6</sub>](Hpht)<sub>4</sub>·4H<sub>2</sub>O. The complex is isostructural with K<sub>2</sub>[Ni(H<sub>2</sub>O)<sub>6</sub>](Hpht)<sub>4</sub>·4H<sub>2</sub>O described previously by Biagini Cingi and coworkers <sup>1</sup>.

*Crystal and experimental data.* Formula C<sub>32</sub>H<sub>40</sub>CoO<sub>26</sub>Rb<sub>2</sub>, M<sub>r</sub> = 1070.52, monoclinic system, space group P2<sub>1</sub>/c, a = 10.322(2), b = 6.856(2), c = 30.070(4) Å, β = 97.34(14) °, V = 2109.6 (8) Å<sup>3</sup>, Z = 2, ρ<sub>x</sub> = 1.68 g cm<sup>-3</sup>, μ(Cu Kα) = 2.79 mm<sup>-1</sup>, F(000) = 1082, λ = 0.71073 Å. The structure has been solved by Patterson and Fourier methods and refined to R = 11.2 %, for 2535 reflections with F > 4σ(F) and 276 parameters.



The structure consists of double chains of hydrogen phthalate anions parallel to x axes, octahedral [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> cations, Rb<sup>+</sup> ions and water molecules. The Co–O<sub>w</sub> distances range from 2.063 to 2.131 Å, whereas angles in coordination polyhedron are close to 90 °.

Both independent Hpht ions have similar conformations, bond distances and angles. The chains of Hpht ions are held together by van der Waals contacts. On the other side, there is a system of hydrogen bonds including O atoms from Hpht ions, coordinated water molecules and water of crystallization, which is partially disordered.

There are no short intramolecular hydrogen bonds found in some other compounds containing Hpht ions.

<sup>1</sup> M. Biagini Cingi, A.M. Manotti Lanfredi and A. Tiripicchio, *Acta Cryst.*, C40, 56, (1984).

## Di-Rubidijum-Heksavakobalt(II)-Tetra(hidrogenftalat)-Tetrahidrat

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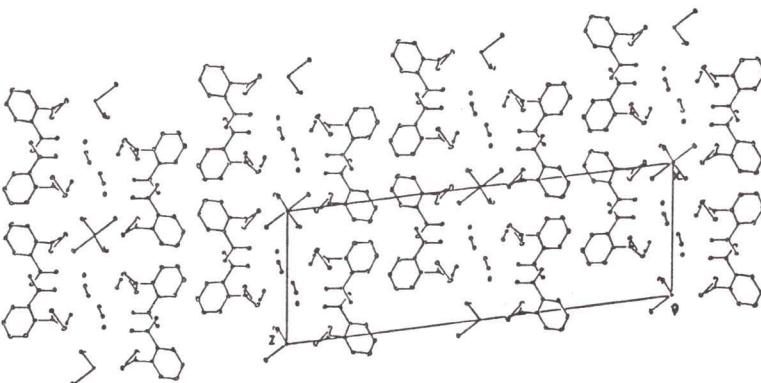
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Ovaj rad je deo naših istraživanja na kompleksima prelaznih metala koji sadrže anjone 1,2-benzendikarboksilne (ftalne, H<sub>2</sub>pht) kiseline.

Tokom pokušaja sinteze Co(II)-kompleksa koji bi bio analogan jedinjenju Rb<sub>2</sub>[Cu(pht)<sub>2</sub>]·2H<sub>2</sub>O nastalo je jedinjenje formule Rb<sub>2</sub>[Co(H<sub>2</sub>O)<sub>6</sub>](Hpht)<sub>4</sub>·4H<sub>2</sub>O, čiji je naziv dat u naslovu. Kompleks je izostrukturan sa K<sub>2</sub>[Ni(H<sub>2</sub>O)<sub>6</sub>](Hpht)<sub>4</sub>·4H<sub>2</sub>O, koji su ranije opisali Biagini Cingi i saradnici <sup>1</sup>.

*Kristalni i eksperimentalni podaci.* Formula C<sub>32</sub>H<sub>40</sub>CoO<sub>26</sub>Rb<sub>2</sub>, M<sub>r</sub> = 1070,52, monoklinični sistem, prostorna grupa P2<sub>1</sub>/c, a = 10,322(2), b = 6,856(2), c = 30,070(4) Å, β = 97,34(14) °, V = 2109,6 (8) Å<sup>3</sup>, Z = 2, ρ<sub>x</sub> = 1,68 g cm<sup>-3</sup>, μ(Cu Kα) = 2,79 mm<sup>-1</sup>, F(000) = 1082, λ = 0,71073 Å. Struktura je rešena Patersonovom i Furijevom sintezom i utačenjena do R = 11,2 %, za 2535 refleksija sa F > 4σ(F) i 276 parametara.



Struktura se sastoji od dvostrukih lanaca hidrogenftalat anjona paralelnih sa x-osi, oktaedarskih [Co(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> katjona, jona Rb<sup>+</sup> i molekula vode. Rastojanja Co–O<sub>w</sub> iznose između 2,061 i 2,131 Å, dok su uglovi u koordinacionom poliedru bliski 90 °.

Dva kristalografski nezavisna Hpht-jona imaju slične konformacije, uglove i veze. Lanci Hpht-jona su međusobno povezani Van der Valsovim silama. S druge strane postoji sistem vodoničnih veza u čijem stvaranju učestvuju O-atomi Hpht-jona, koordinirana voda i voda kristalne rešetke (koja je delom statistički raspoređena).

U ovoj strukturi ne postoje kratke intramolekulske vodonične veze kakve su nadene kod nekih drugih jedinjenja koja sadrže Hpht-jone.

<sup>1</sup> M. Biagini Cingi, A.M. Manotti Lanfredi and A. Tiripicchio, *Acta Cryst.*, C40, 56, (1984).

## POTASSIUM 3-DITHIOCARBOXY-3-AZA-5-AMINO-PENTANOATE DIHYDRATE

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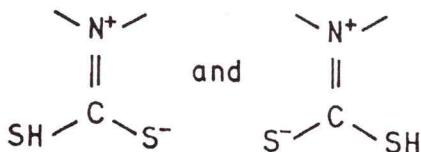
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Potassium 3-dithiocarboxy-3-aza-amino-pentanoate  $K^+(DAAP^-)$  has been obtained by the reaction of ethylidene- $N,N'$ -diacetatedihydroxychloride and corresponding amount of carbon disulfide in presence of potassium-hidroxide on room temperature. Product has been recrystallized from hot water. Characterization of the compound has been performed by micro analysis, IR and PMR spectroscopy, and its crystal and molecular structure determined on the basis of X-ray crystal structure analysis.

**Crystal data:**  $KS_2O_4N_2C_5H_{13}$ ,  $Mr=268.40$ , monoclinic, space group  $P2/c$ ,  $a=13.8156(12)$ ,  $b=6.9473(17)$ ,  $c=12.4225(14)\text{ \AA}$ ,  $\beta=111.661(9)^\circ$ ,  $Z=4$ ,  $V=1108.1(8)\text{ \AA}^3$ ,  $d_c=1.609\text{ Mgm}^{-3}$ ,  $d_0=1.606\text{ Mgm}^{-3}$ ,  $\lambda(MoK_\alpha)=0.71073\text{ \AA}$ ,  $\mu(MoK_\alpha)=0.83\text{ mm}^{-1}$ ,  $F(000)=560$ ,  $T=293\text{ K}$ , ENRAF-NONIUS CAD-4 DIFFRACTOMETER.

The structure was solved by direct methods (MULTAN) and difference Fourier synthesis and refined by full-matrix least squares to  $R=0.039$ ,  $R_w=0.041$ ,  $S=0.957$  on the basis of  $No=2030$  independent reflections, satisfying  $I \geq 3\sigma(I)$  criterion. Number of variables  $N_v=144$ . Structure is built up from  $K^+$ , DAAP $^-$  ions and molecules of water, connected by Coulomb forces and hydrogen bonds.

The most interesting feature of the structure is the state in which  $NCS_2$  group of DAAP $^-$  exists. On the basis of X-ray crystal structure analysis it is found that this group resonates between two forms:



with equal occupation of each of them in the crystal. There are some important facts speaking on behalf of this finding:

1. N-C bond length is slightly longer than N=C distance, but it is far away from single N-C bond.
2. C-S distances are very close to each other and N-C-S and S-C-S angles are very near to  $120^\circ$ .
3. In the final  $\Delta F$  synthesis there is no evidence of maxima in vicinity of S atoms which would correspond to S-H distance.

## KALIJUM 3-DITIOKARBOKSI-3-AZA-5-AMINO-PENTANOAT DIHIDRAT

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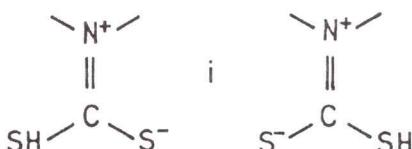
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Kalijum 3-ditioksi-3-aza-5-amino-pentanoat  $\text{K}^+(\text{DAAP})$  dobijen je reakcijom etilendiamin-N,N'-di-acetata-dihidrohlorida i odgovarajuće količine ugljen disulfida u prisustvu kalijum-hidroksida na sobnoj temperaturi. Sirovi proizvod je prekristalisan iz tople vode. Karakterizacija dobijenog jedinjenja izvršena je mikro analizom, IC i PMR spektroskopijom, a molekulska i kristalna struktura odredjene su rendgenostrukturnom analizom.

**Kristalografski podaci:**  $\text{KS}_2\text{O}_4\text{N}_2\text{C}_5\text{H}_{13}$ ,  $Mr=268,40$ , monoklinični, prostorna grupa  $P2_1/c$ ,  $a=13,8156(12)$ ,  $b=6,9473(17)$ ,  $c=12,4225(14)\text{\AA}$ ,  $\beta=111,661(9)^\circ$ ,  $Z=4$ ,  $V=1108,1(8)\text{\AA}^3$ ,  $d_c=1,609 \text{ Mgm}^{-3}$ ,  $d_o=1,606 \text{ Mgm}^{-3}$ ,  $\lambda(\text{MoK}_\alpha)=0,71073\text{\AA}$ ,  $\mu(\text{MoK}_\alpha)=0,83 \text{ mm}^{-1}$ ,  $F(000)=560$ ,  $T=293 \text{ K}$ , ENRAF-NONIUS CAD-4 DIFRAKTOMETAR.

Struktura je rešena direktnim metodama (MULTAN) i diferentnom Fourierovom sintezom i utačnjena metodom najmanjih kvadrata do  $R=0,039$ ,  $R_w=0,041$ ,  $S=0,957$  korišćenjem  $No=2030$  nezavisnih refleksija sa  $I \geq 3\sigma(I)$ , dok je broj parametara bio  $N_v=144$ . Struktura se sastoji od  $\text{K}^+$  i  $\text{DAAP}^-$  jona i molekula vode, vezanih međusobno Coulomb-ovim silama i vodoničnim vezama.

Najinteresantniji strukturni podatak dobijen iz strukturne analize je razrešenje stanja u kome se nalazi  $\text{NCS}_2$  grupa u  $\text{DAAP}^-$  anjonu. Na osnovu rendgenostrukturne analize utvrđeno je da ova grupa rezonira izmedju formi,



gde su one podjednako populisane u kristalu.  
Tome idu u prilog sledeće činjenice:

1. N-C veza ( $\sim 1,34 \text{ \AA}$ ) je nešto duža od dvostrukе N=C veze, ali je znatno kraća od jednostrukе N-C veze.
2. S-C veze su praktično jednakih dužina, a uglovi N-C-S i S-C-S vrlo su bliski uglu od  $120^\circ$ .
3. U konačnoj  $\Delta F$  mapi nije zapaženo prisustvo maksimuma u blizini S atoma koja bi odgovaralo zbiru atomskih radijusa S i H atoma.

**DIAQUA-2',2'''-(2,6-PYRIDINDIYL DIETHYLIDENE)-  
-DIOXAMOHYDRAZIDE COBALT(II) HEXAHYDRATE**

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For the first time complexes containing singly- and doubly-deprotonated ligand H<sub>2</sub>L=2',2'''-(2,6-pyridindiyl diethylidene)-dioxamohydrazide belonging to the class of planar pentadentates have been synthesized. As shown the geometry of pentagonal bipyramide found in previously synthesized [Co(H<sub>2</sub>L)(H<sub>2</sub>O)(MeOH)J](ClO<sub>4</sub>)<sub>2</sub><sup>1</sup> complex where the ligand appears in its neutral form has been preserved in doubly-deprotonated complex, as well.

**Crystal data:** *Crystal system triclinic, M<sub>r</sub>=534.35, a=8.947(1), b=10.474(1), c=13.846(1) Å, α=107.79(2), β=94.12(2), γ=69.93(2), space group P\bar{I}, V=1129.5(5) Å<sup>3</sup>, Z=2, d<sub>x</sub> = 1.57 Mg·m<sup>-3</sup>, F(000)=558, λ<sub>MoKα</sub>=0.71073 Å, μ(MoK<sub>α</sub>)=0.83 mm<sup>-1</sup>, 1° ≤ θ ≤ 29°, ω/2θ scanning, T=293 K, CAD-4 automated diffractometer.*

**Remaining relevant data:** number of measured intensities 4319, number of independent reflexions with  $I \geq 3\sigma(I)$  used for crystal structure determination 3421, number of parameters refined 451 (all H atoms were isotropically refined), R=0.038, R<sub>w</sub>=0.039, S=0.87.

The crystal structure was solved by heavy-atom methods and refined by full-matrix least squares.

The coordination polyhedron around cobalt is pentagonal bipyramidal with N<sub>3</sub>O<sub>2</sub> donor set of atoms in the basal plane. Axial positions are occupied by water oxygen atoms. The coordinated polydentate ligand is planar. The planarity of the ligand is conditioned by the existence of four condensed chelate rings. Coordinated to the metal molecules of water as well as crystalline water molecules are included in complex and extended hydrogen bonding network.

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<sup>1</sup>K. Andjelković, I. Ivanović, B. Prelesnik, V. Leovac and D. Poleti, Polyhedron, in press

**DIAKVA-2',2'''-(2,6-PIRIDINDIILDIELTILIDEN)-DIOKSAMOHIDRAZIDKOBALT(II)  
HEKSAHIDRAT**

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Po prvi put su sintetisani kompleksi Co(II) sa jedanput i dvaput deprotovanim ligandom  $H_2L = 2',2'''-(2,6\text{-piridindiildieltiliden})\text{-dioksamohidrazid}$  iz klase planarnih pentadentata, pri čemu je oko Co(II) sačuvana geometrija pentagonalne bipiramide prisutna kod prethodno sintetisanog kompleksa  $[Co(H_2L)(H_2O)(MeOH)](ClO_4)_2^1$  u kojem se ligand javlja u neutralnoj formi.

**Kristalografski podaci:** *Triklinični sistem,  $M_r=534,35$ ,  $a=8,947(1)$ ,  $b=10,474(1)$ ,  $c=13,846(1)\text{\AA}$ ,  $\alpha=107,79(2)$ ,  $\beta=94,12(2)$ ,  $\gamma=69,93(2)$ , prostorna grupa  $P\bar{1}$ ,  $V=1129,5(5)\text{\AA}^3$ ,  $Z=2$ ,  $d_x = 1,57 \text{ Mg}\cdot\text{m}^{-3}$ ,  $F(000)=558$ ,  $\lambda_{MoK\alpha}=0,71073\text{\AA}$ ,  $\mu(MoK\alpha)=0,83 \text{ mm}^{-1}$ ,  $1^\circ \leq \theta \leq 29^\circ$ ,  $\omega/2\theta$  skening,  $T=293 \text{ K}$ , CAD-4 automatski difraktometar.*

**Ostali relevantni podaci:** broj izmerenih intenziteta 4319, broj nezavisnih refleksija sa  $I \geq 3\sigma(I)$  korišćenih u rendgenostruktturnoj analizi 3421, broj utaćnjavanih parametara 451 (svi vodonikovi atomi izotropno),  $R=0,038$ ,  $R_w=0,039$ ,  $S=0,87$ . Struktura je rešena metodom teškog atoma i utaćnjena metodom najmanjih kvadrata sa punom matricom.

Koordinacioni polieder oko kobalta je pentagonalna bipiramida sa  $N_3O_2$  donorskim setom atoma u bazalnoj ravni, dok su aksijalni položaj i zauzeti atomima kiseonika iz koordinovanih voda. Koordinovani polidentatni ligand je planaran. Njegova planarnost je uslovljena postojanjem četiri petočlana fuzionisana helatna prstena. Koordinovane i kristalne vode grade razgranatnu i kompleksnu mrežu vodoničnih veza.

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<sup>1</sup>K. Andjelković, I. Ivanović, B. Prelesnik, V. Leovac and D. Poleti, Polyhedron, in press

***Cis- and Trans-Influence in Pt Complexes.***  
**Crystal Structure of Diiodo(1,4-dithiane)platinum(II)**

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The present work is part of an investigation aiming to correlate kinetic, thermodynamic and structural properties of square-planar complexes of palladium(II) and platinum(II) containing sulphur-donor ligands. The *trans*-influence,<sup>1,2</sup> expressed as the extend to which a ligand L in a metal complex lengthens or shortens a bond M-X *trans* to itself<sup>2</sup>, is expected to run approximately parallel to the *trans*-effect of L, as displayed by the substitution rate of X<sup>3</sup>. In order to study further the affinity of Pt to S in different types of ligands we have synthesized and determined the crystal structures of Diiodo(1,4-dithiane)platinum(II).

Diiodo(1,4-dithiane)platinum(II), [Pt(C<sub>4</sub>H<sub>8</sub>S<sub>2</sub>)I<sub>2</sub>], M<sub>r</sub> = 569.13, tetragonal, P4<sub>3</sub>2<sub>1</sub>2,  $a = 8.985(1)$ ,  $c = 12.286(2)$  Å, V = 991.9(2) Å<sup>3</sup>, Z = 4,  $D_X = 3.811$  Mg · m<sup>-3</sup>, MoKα,  $\lambda = 0.7107$  Å,  $\mu = 20.79$  mm<sup>-1</sup>, F(000) = 992, T = 293 K, R = 0.0249 for 965 unique reflections with I > 2σ(I). The coordination around Pt is square-planar with a maximal deviation of 0.0007 Å (S) from the least-square plane through PtI<sub>2</sub>S<sub>2</sub>. Pt bonds to two iodides in *cis* position and to the two sulphurs of the cyclic dithioether, 1,4-dithiane, which acts as a chelating ligand. The acceptor-donor distances are Pt-I = 2.6026(7) and Pt-S = 2.277(3). The boat conformation of 1,4-dithiane is adopted. Normal distances and angles are found with the 1,4-dithiane ring. The crystal is built up from discrete complexes. The shortest Pt-Pt distance is 6.2154(6) Å.

<sup>1</sup>Pidock, A., Richards, R. E. and Venanzi, L. M. *J. Chem. Soc. A* (1966) 1707.

<sup>2</sup>Mason, R. and Towl, D. C. *J. Chem. Soc. A* (1970) 1601.

<sup>3</sup>Oskarsson, Å, Norén, B., Svensson, C. and Elding, L. I. *Acta Crystallogr., Sect. B* 46 (1990) 748.

## *Cis- i Trans-uticaj u kompleksima platine.* **Kristalna struktura Dijodo(1,4-ditian)platina(II)**

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Ovaj rad je deo ranije započetih istraživanja u iznalaženja korelacije između kinetičkih, termodinamičkih i strukturnih svojstava kvadratno-planarnih kompleksa paladijuma(II) i platine(II). Pokazano je da male promene u strukturi kompleksnog jedinjenja znatno utiču na brzinu supstitucije. Kod kompleksa platine(II) razlikujemo dva efekta: Kinetički *trans*-efekat, koji se odnosi na brzinu hemijskih reakcija, recimo pri izučavanju supstitionih reakcija i *trans*-uticaj, koji opisuje prome u dužini veza u kristalu. Odnosno, *trans*-uticaj<sup>1,2</sup> nekog liganda L odražava se na dužinu veze drugog liganda X, koji se nalazi u *trans* položaju u odnosu na L, a veza M-X može biti duža ili kraća u poređenju sa referentnom X-M-X.<sup>3</sup> U cilju izučavanja i kvantitativnog merenja *trans*-uticaja sumpor-vezivnih liganada u kompleksima Pt(II), sintetisali smo i odredili strukturu dijodo(1,4-ditian) platina(II) kompleksa.

Struktura kristala, dijodo(1,4-ditian)platina(II), [Pt(C<sub>4</sub>H<sub>8</sub>S<sub>2</sub>)I<sub>2</sub>], određena je difrakcijom x-zraka (Mo K $\alpha$ ,  $\lambda = 0,7107 \text{ \AA}$ ) na sobnoj temperaturi pomoću CAD-4 difraktometra. Nađeni su sledeći parametri: tetragonal, P4<sub>3</sub>2<sub>1</sub>2,  $a = 8,985(1)$ ,  $c = 12,286(2) \text{ \AA}$ ,  $V = 991,9(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 3,811 \text{ Mg}\cdot\text{m}^{-3}$ ,  $\mu = 20,79 \text{ mm}^{-1}$ ,  $F(000) = 992$ ,  $R = 0,0249$  za 965 refleksija sa  $I > 2\sigma(I)$ . Koordinacija oko Pt je kvadratno-planarna. Dva jodo liganda se nalaze u *cis* položaju, a druga dva mesta u koordinaciji zauzimaju dva sumpora iz 1,4-ditiana, koji je bidentatni ligand. Dužina veze Pt-I iznosi 2,6026(7)  $\text{\AA}$ , a dužina veze Pt-S 2,277(3)  $\text{\AA}$ . Prilikom koordinacije molekul 1,4-ditiana zauzima konformaciju lađe. Najkrađe rastojanje Pt-Pt iznosi 6,2154(6)  $\text{\AA}$ .

<sup>1</sup>Pidock, A., Richards, R. E. and Venanzi, L. M. *J. Chem. Soc. A* (1966) 1707.

<sup>2</sup>Mason, R. and Towl, D. C. *J. Chem. Soc. A* (1970) 1601.

<sup>3</sup>Oskarsson, Á., Norén, B., Svensson, C. and Elding, L. I. *Acta Crystallogr. Sect. B* 46 (1990) 748.

## STRUCTURE OF (2-ACETYL PYRIDINE S-METHYLISOTHIOSEMICARBAZONE) AQUA-SULPHATO COPPER(II) MONOHYDRATE

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The reaction of warm ethanolic solution of 2-acetylpyridine S-methylisothiocarbazonhydrogen-iodide with warm aqueous solution of copper(II)-sulphate-pentahydrate resulted in the formation of green monocrystals of  $[\text{CuSO}_4(\text{HL})\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$  ( $\text{HL}$  = neutral form of 2-acetylpyridine-S-methylisothiocarbazole).

Monocrystal of the complex was examined by X-ray diffraction. Reflection intensities were collected by a CAD-4 diffractometer using MoK<sub>α</sub> radiation. Unit cell parameters are  $a=8.846(1)$ ,  $b=17.138(1)$ ,  $c=10.410(1)\text{\AA}$ ,  $\beta=107.72(1)^\circ$ ,  $V=1503.3(2)\text{\AA}^3$ ,  $Z=4$ ,  $D_c=1.785\text{ Mg m}^{-3}$ , space group  $P2_{1}h$ . The structure was solved using program SHELXS 86 and refined by SHELXL 93 to the final R factor  $R=0.0315$  for 6604 independent reflections [ $I>2\sigma(I)$ ] and  $R_w=0.085$  for all data (7117) and 206 parameters. Largest difference peak and hole are  $0.396$  and  $-0.731\text{ e\AA}^{-3}$ , respectively.

Cu(II) ion has a distorted square pyramidal environment. The central metal ion is coordinated by three nitrogen atoms from neutral organic ligand and oxygen atom from one lattice water molecule, which form an approximately planar square. Cu(II) is axially coordinated with oxygen atom from SO<sub>4</sub>-group.

It is important to note, that although there exist two water molecules per crystal unit cell, with only one of them being coordinated, both of the molecules are released during the heating up to 110°C.

## STRUKTURA (2-ACETILPIRIDIN S-METILIZOTIOSEMIKARBAZON)-AKVA-SULFATO BAKAR(II)-MONOHIDRATA

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Reakcijom toplog etanolnog rastvora 2-acetylpiridin-S-metilizotiosemikarbazona hidrogen-jodida i vodenog rastvora bakar(II)-sulfata-pentahidrata dobiveni su zeleni monokristali kompleksa sastava  $[\text{CuSO}_4(\text{HL})\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$  ( $\text{HL}$  = nautralna forma 2-acetylpiridin-S-metilizotiosemikarbazona).

Monokristalni uzorak je ispitana metodom difrakcije x-zraka. Intenziteti refleksija su sakupljeni automatskim difraktometrom CAD-4 korišćenjem  $\text{MoK}_{\alpha}$  zračenja. Parametri elementarne ćelije su:  $a=8,845(1)$ ,  $b=17,138(1)$ ,  $c=10,410(1)$  Å,  $\beta=107,72(1)^\circ$ ,  $V=1503,3(2)$  Å<sup>3</sup>,  $Z=4$ ,  $D_c=1,785$  Mgm<sup>-3</sup> a prostorna grupa je  $P2_{1h}$ . Struktura je rešena korišćenjem programa SHELXS 86 i utaćnjena sa SHELXL 93 do konačnog R faktora  $R=0,0315$  za 6604 nezavisnih refleksija [ $I>2\sigma(I)$ ] i  $R_w=0,085$  za sve refleksije (7117) a za 206 parametara. U diferentnoj Fourier-ovoj mapi dobijeni su maksimum i minimum elektronske gustine od 0,396 i -0,731 eÅ<sup>-3</sup>, respektivno.

Jon Cu(II) se nalazi u deformisanom kvadratno-piramidalnom okruženju. Centralni jon metala je koordinovan sa tri atoma azota neutralnog organskog liganda i atomom kiseonika iz jednog molekula kristalne vode, koji formiraju osnovu piramide, dok se u aksijalnom položaju nalazi atom kiseonika  $\text{SO}_4^{2-}$  grupe.

Važno je primetiti da iako u elementarnoj ćeliji kristala postoje dva molekula vode, od kojih je samo jedan u koordinaciji, oba molekula se udaljavaju zagrevanjem do 110 °C .

THE SINGLE CRYSTAL STRUCTURE AND CATION DISTRIBUTION IN SOLID  
SOLUTION  $(\text{Al}_{1-x}\text{Cr}_x)(\text{H}_2\text{O})_6(\text{NO}_3)_3 \times 3\text{H}_2\text{O}$

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The structure of solid solution  $(\text{Al}_{1-x}\text{Cr}_x)(\text{H}_2\text{O})_6(\text{NO}_3)_3 \times 3(\text{H}_2\text{O})$  ( $x \approx 0.25$ ) was determined using the methods of X-ray diffraction. Starting from the isostructural compounds hexaaquaaluminium (chromium) nitrate(III) trihydrate [1,2], a saturated aqueous solution was prepared with mass ratio of the components 75 : 25. Highly hygroscopic single crystals of the solid solution were obtained by the slow evaporation at room temperature and atmospheric pressure.

Reflection intensities were collected on the automatic diffractometer using MoK<sub>α</sub> radiation. Unit cell parameters:  $a=13.882(9)$ ,  $b=9.612(4)$ ,  $c=10.918(5)\text{\AA}$ ,  $\beta=95.43(4)^\circ$ ,  $V=1450(6)\text{\AA}^3$ ,  $M_r=381.39$ ,  $D_x=1.746 \text{ Mgm}^{-3}$  and the space group P2<sub>1</sub>/c indicate to isomorphism and probably isostructuralism with component compounds. The strucuture of the solid solution was refined starting from the structure of hexaaquaaluminium nitrate trihydrate using the program SHELXL 93 with the variable value of the position factor of Al and Cr atoms, begining from 0.75 and 0.25 respectively (molar ratio was 0.762 : 0.238). The final results ( $R=0.038$ , for 3245 reflections with  $F_o > 4\sigma(F_o)$ ,  $n_p=279$ ,  $R_w=0.117$ ,  $S=0.948$ ,  $(\Delta/\sigma)_{\max}=0.002$ ,  $\Delta\rho_{\max}=0.34\text{e}/\text{\AA}^3$ ,  $\Delta\rho_{\min}=-0.27\text{e}/\text{\AA}^3$ ) confirm the isostructurality. The distribution of the cations Al and Cr in the special position (0,0,0, 1/2,0,1/2) shows from the final values of position factors  $K1(\text{Al})=0.388(2)$ ,  $K1(\text{Cr})=0.112(2)$ ,  $K2(\text{Al})=0.267(2)$ ,  $K2(\text{Cr})=0.233(2)$  that the total relative abundance of Al cations with respect to Cr cations is 0.655(2) : 0.345(2). Preferential occupation of the position 2 by Cr ions indicates that at the room temperature the structure is bellow the point of statistical ordering.

[1] D.Lazar, B.Ribar, B.Prelesnik:Redeterminantion of the Structure of Hexaaquaaluminium(III)nitrate trihydrate, Acta Cryst.C47, 2282-2285, (1991)

[2] D.Lazar, B.Ribar, V.Divjaković, Cs.Meszaros:Structure of Hexaaqua chromium(III)nitrate trihydrate, Acta Cryst.C47,1060-1062,(1991).

## KRISTALNA STRUKTURA I DISTRIBUCUJA KATJONA U ČVRSTOM RASTVORU $(\text{Al}_{1-x}\text{Cr}_x)(\text{H}_2\text{O})_6(\text{NO}_3)_3 \times 3\text{H}_2\text{O}$

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Kristalna struktura čvrstog rastvora  $(\text{Al}_{1-x}\text{Cr}_x)(\text{H}_2\text{O})_6(\text{NO}_3)_3 \times 3(\text{H}_2\text{O})$  ( $x \approx 0.25$ ) određena je metodom difrakcije x-zraka na monokristalu. Polazeći od izostruktturnih jedinjenja heksaakvaluminijum(hromo)nitrata(III) trihidrata [1,2] napravljeni su zasićeni vodeni rastvori u masenom odnosu komponenti 75 : 25. Laganim isparavanjem na sobnoj temperaturi i atmosferskom pritisku dobijeni su monokristali čvrstog rastvora.

Veoma higroskopni kristali premazani lakom snimljeni su automatskim difraktometrom korišćenjem  $\text{MoK}_\alpha$  radijacije. Kristalografski parametri :  $a=13,882(9)$ ,  $b=9,612(4)$ ,  $c=10,918(5)\text{\AA}$ ,  $\beta=95,43(4)^\circ$ ,  $V=1450(6)\text{\AA}^3$ ,  $M_r=381,39$ ,  $D_x=1,746 \text{ Mgm}^{-3}$  i prostorna grupa  $P2_1/c$  ukazuju na izomorfizam i mogući izostrukturalizam sa kristalima polaznih komponenti. Struktura je rešena direktnom metodom korišćenjem programa SHELXS 86. Položaji nevodoničnih atoma odgovaraju koordinatama odgovarajućih atoma polaznih komponenti. Struktura je utvrđena (SHELXL93) sa promenljivom vrednošću okupacionog faktora za atome Al i Cr polazeći od vrednosti 0,75 i 0,25 (molarni odnos je 0,762 : 0,238). Konačni rezultati ( $R=0,038$ , za 3245 refleksija sa  $F_o > 4\sigma(F_o)$ ,  $n_p=279$ ,  $R_w=0,117$ ,  $S=0,948$ ,  $(\Delta/\sigma)_{\max}=0,002$ ,  $\Delta\rho_{\max}=0,34\text{e}/\text{\AA}^3$ ,  $\Delta\rho_{\min}=-0,27\text{e}/\text{\AA}^3$ ) potvrđuju izostrukturalnost sa polaznim jedinjenjima.

Distribucija katjona Al i Cr u specijalnim položajima (0,0,0, 1/2,0,1/2) vidi se iz konačnih vrednosti pozicionih faktora.  $K1(\text{Al})=0,388(2)$ ,  $K1(\text{Cr})=0,112(2)$ ,  $K2(\text{Al})=0,267(2)$ ,  $K2(\text{Cr})=0,233(2)$  koje pokazuju da je relativni odnos katjona Al i Cr  $0,655(2) : 0,345(2)$ . Preferentna okupacija pozicije 2 jonima Cr ukazuje da je struktura na sobnoj temperaturi ispod tačke statističke uređenosti.

- [1] D.Lazar, B.Ribar, B.Prelesnik: Redetermination of the Structure of Hexaaquaaluminium(III)nitrate trihydrate, Acta Cryst.C47,2282-2285 (1991)
- [2] D.Lazar, B.Ribar, V.Divjaković, Cs.Meszaros: Structure of Hexaaqua chromium(III)nitrate trihydrate, Acta Cryst.C47,1060-1062,(1991).

## *Synchrotron "in sity" high temperature investigation of hexacelsian $\alpha \rightleftharpoons \beta$ inversion*

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Temperature induced phase transformation of heksacelsian, synthesized<sup>(1,2)</sup> from Ba(LTA) and Ba(FAU) zeolites is structurally investigated by the x-ray diffraction from polycrystalline materials. Diffraction of monochromatic x-rays ( $\lambda = 1.1153 \text{ \AA}$ ) formed in synchrotron source are obtained on X7B, NSLS, Brookhaven National Laboratory, USA. Instrument is equipped with INEL CPS90 position sensitive detector and high temperature x-ray camera. Specimens are annealed during one hour from room temperature to 700°C. Diffraction data are collected at approximately every two minute. For structure analysis Rietveld technique and computing program Fullprof<sup>(3)</sup> are applied. Crystal structures are refined in space groups  $P\bar{3}$ , Immm and  $P6_3/mcm$ . Crystal structure of hexacelsian<sub>LTA</sub> with ordered Si and Al distribution is refined in space group  $P\bar{3}$  while crystal structure of hexacelsian<sub>FAU</sub> with disordered Si and Al distribution is refined in space groups Immm and  $P6_3/mcm$ .

Results of structural analysis are in agreement with DSC measurements<sup>(2)</sup>. These results indicate that phase transition of first order exists in the heksacelsian<sub>LTA</sub> sample at T~310°C. On the other hand heksacelsian<sub>FAU</sub> does not show  $\alpha \rightleftharpoons \beta$  phase transformation in the investigated temperature range.

### References:

- <sup>(1)</sup>Kremenović, A., "Kristalne strukture  $MAl_2Si_2O_8$  ( $M = Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}$ ) faza sintetizovanih procesom termalne transformacije LTA i FAU zeolita", master degree thesis, University of Belgrade, 1995
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## *Sinhrotronska "in sity" visokotemperaturna ispitivanja transformacije $\alpha \rightleftharpoons \beta$ heksacelzijan*

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Temperaturno indukovana fazna transformacija heksacelzijana, koji je sintetisan<sup>(1,2)</sup> iz Ba(LTA) i Ba(FAU) zeolita, strukturno je ispitana pomoću difrakcije rendgenskih zraka sa polikristalnih materijala. Difrakcija monohromatskih rendgenskih zraka ( $\lambda = 1,1153 \text{ \AA}$ ), primarno nastalih u sinhrotronskom izvoru, izvedena je pomoću instrumenta X7B, NSLS, Brookhaven National Laboratory, USA. Instrument je bio opremljen detektorom INEL CPS90 i visokotemperaturnom rendgenskom komorom. Uzorci su zagrevani u toku jednog sata u temperaturnom opsegu od sobne temperature do  $700^\circ\text{C}$ . Difrakcioni podaci su prikupljeni približno na svaka 2 minuta. Za strukturu analizu primenjena je Ritveldova tehnika i kompjuterski program Fullprof<sup>(3)</sup>. Kristalne strukture su utaćnjavane u prostornim grupama  $P\bar{3}$ , Immm i  $P6_3/mcm$ . Kristalna struktura heksacelzijana<sub>LTA</sub> koju karakteriše uređena raspodela Si i Al utaćnjena je u prostornoj grupi  $P\bar{3}$  dok je struktura heksacelzijana<sub>FAU</sub> koju karakteriše neuredena raspodela Si i Al utaćnjena u prostornim grupama Immm i  $P6_3/mcm$ .

Rezultati strukturne analize su u dobroj saglasnosti sa DSC merenjima<sup>(2)</sup> i ukazuju na postojanje faznog prelaza prvog reda u uzorku heksacelzijana<sub>LTA</sub> na  $T \sim 310^\circ\text{C}$ . Nasuprot tome u uzorku heksacelzijana<sub>FAU</sub> fazna transformacija  $\alpha \rightleftharpoons \beta$  izostaje.

### **Literatura:**

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## *Crystal structure of body centered anorthite*

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Crystal structure of body centered anorthite is refined from the x-ray diffraction data from polycrystalline material. Specimen is obtained by quenching of Ca(LTA) zeolite from 1700°C (annealed for one hour) to room temperature<sup>(1)</sup>. Structure is refined in the space group  $I\bar{1}$ . Unit cell parameters<sup>1</sup> are:  $a = 8.180(2)$ ,  $b = 12.860(3)$ ,  $c = 14.167(3)$  Å,  $\alpha = 93.21(1)$ ,  $\beta = 115.65(1)$ ,  $\gamma = 91.09(1)$ °. Agreement factors of refined structure are:  $R_{\text{exp}} = 7.09$ ,  $R_p = 10.04$ ,  $R_{\text{wp}} = 12.73$ ,  $R_B = 5.56$ ,  $R_F = 2.09$ , GOF = 1.42. Rietveld method and computer program LHPM-8<sup>(2)</sup> are used for the refinement procedure. Starting structural model is the same as given by Ghose et al.<sup>(3)</sup>. Due to the complexity of structural model hard constrain were used. The results of applied constrains are the same values to the isotropic temperature factors for the same atoms or ions.

On the basis of well agreement between examined and starting model it is deduced that specimen of quenched anorthite is characterized by the disorder of Si and Al. That is confirmed with the value of ordering parameter ( $Q_{\text{OD}} = 0.807$ ) which is defined in Landau theory of phase transitions<sup>(4)</sup>.

### References:

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- <sup>(2)</sup> Lengauer, C.L., HILL, A Computer Program for Rietveld Analysis. PC-Implementation of LHPM-8, Version 93.06, University of Vienna, Institute of Mineralogy and Crystallography, Vienna, Austria, (1993).
- <sup>(3)</sup> Ghose,S., McMullan, R.K., Webwe, H.P., Zeits für Kristall., 204, 215 (1993)
- <sup>(4)</sup> Carpenter, M.A., Angel, R.J., Finger,L.W., Contrib. Mineral. Petrol., 104, 471 (1990).
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<sup>1</sup> Standard deviations of unit cell parameters are multiplied with factor SCOR = 2.920<sup>(5)</sup>.

## Kristalna struktura zapreminske centriranog anortita

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Kristalna struktura zapreminske centriranog anortita utičnjena je iz podataka koji su dobijeni difrakcijom rendgenskih zraka sa polikristalnog uzorka. Uzorak je dobijen naglim hladnjem Ca(LTA) zeolita koji je prethodno zagrejan na temperaturi od 1700°C u toku jednog sata<sup>(1)</sup>. Struktura je utičnjena u prostornoj grupi  $I\bar{1}$ . Parametri jedinične celije<sup>1</sup> su:  $a = 8,180(2)$ ,  $b = 12,860(3)$ ,  $c = 14,167(3)$  Å,  $\alpha = 93,21(1)$ ,  $\beta = 115,65(1)$ ,  $\gamma = 91,09(1)$ °. Faktori slaganja utičnjene modela su:  $R_{exp} = 7,09$ ,  $R_p = 10,04$ ,  $R_{wp} = 12,73$ ,  $R_B = 5,56$ ,  $R_F = 2,09$ , GOF = 1,42. Prilikom utičnjavanja primenjena je Rietveldova metoda i kompjuterski program LHPM-8<sup>(2)</sup>. Početni model strukture dali su Ghose i dr.<sup>(3)</sup>. Zbog kompleksnosti strukturnog modela prilikom utičnjavanja primljeno je ograničenje koje se odnosi na jednakost izotropnih temperaturnih faktora odgovarajućih atoma ili jona. Na osnovu dobrog slaganja ispitivanog i početnog modela može se zaključiti da ispitivani uzorak anortita karakteriše neuređeno stanje raspodele Si i Al. Neuređenost raspodele Si i Al potvrđena je na osnovu izračunate vrednosti parametra uređenosti ( $Q_{OD} = 0,807$ ) koji je definisan preko Landauove teorije faznih prelaza<sup>(4)</sup>.

### Literatura:

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<sup>(5)</sup> Berar,J.F., Lelann, P., J.Appl.Cryst., 24, 1 (1991).

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<sup>1</sup> Standardne devijacije parametara jedinične celije date u zagradama pomnožene su faktorom SCOR = 2,920<sup>(5)</sup>.

*The crystal structures of  $Y_3Fe_5O_{12}$ ,  $Y_3Fe_4AlO_{12}$ ,  
 $Y_3Fe_3Al_2O_{12}$ ,  $Y_3Fe_2Al_3O_{12}$  and  $Y_3FeAl_4O_{12}$*

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*The samples  $Y_3Fe_5O_{12}$ ,  $Y_3Fe_4AlO_{12}$ ,  $Y_3Fe_3Al_2O_{12}$ ,  $Y_3Fe_2Al_3O_{12}$  and  $Y_3FeAl_4O_{12}$  were obtained starting from coprecipitation of hydroxides from corresponding nitrates. The hydroxides were subsequently fired at temperature of  $950^{\circ}C$  and samples of the mentioned compounds were obtained. The samples were pressed under the pressure of  $1.5\text{ t/cm}^2$  and refired at  $1350^{\circ}C$  in order to get samples of higher density.*

*The x-ray diffraction experiment was done at powder diffractometer Philips with Ni filtered  $CuK_{\alpha 1}$  and  $CuK_{\alpha 2}$  radiation. The diffraction patterns were taken in  $2\theta$  region  $15-115^{\circ}$ , with  $0.02^{\circ}$  step and exposition of 5s per step. It was found that all the samples crystallize in the garnet structure type, in the space group Ia3d. The structures were refined by the full profile Rietveld's method, by using software package FULLPROF. The ionic scattering factors were assumed in the refinements.*

*In the garnet structure yttrium ion occupy dodecahedral 24c position, aluminum and iron ions occupy tetrahedral and octahedral positions 24d and 16a, respectively, oxygen ion occupies general 96h position. It was found that distribution of Al and Fe cations in octahedral and tetrahedral positions is preferential. The coefficient of distribution varies between 0.31 for  $Y_3Fe_4AlO_{12}$  and 0.49 for  $Y_3Fe_2Al_3O_{12}$ . The cation-anion distances in octahedra and in tetrahedra point to the different nature of the chemical bonds in octahedra and tetrahedra.*

## *Kristalne strukture $Y_3Fe_5O_{12}$ , $Y_3Fe_4AlO_{12}$ , $Y_3Fe_3Al_2O_{12}$ , $Y_3Fe_2Al_3O_{12}$ i $Y_3FeAl_4O_{12}$*

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*Uzorci  $Y_3Fe_5O_{12}$ ,  $Y_3Fe_4AlO_{12}$ ,  $Y_3Fe_3Al_2O_{12}$ ,  $Y_3Fe_2Al_3O_{12}$  i  
 $Y_3FeAl_4O_{12}$  dobijeni su polazeci od zajedničkog taloženja hidroksida iz  
 odgovarajućih nitrata. Ovi hidroksidi su zatim žareni na temperaturi  $950^{\circ}C$   
 nakon čega su dobijeni pomenuti uzorci. Uzorci su zatim presovani pod  
 pritiskom  $1,5 \text{ t/cm}^2$  i ponovo žareni na temperaturi  $1350^{\circ}C$  čime su  
 dobijeni uzorci veće gustine.*

*Svi uzorci su snimljeni na difraktometru za polikristale Philips sa  
 $CuK_{\alpha 1}$  i  $CuK_{\alpha 2}$  zračenjem i Ni filterom. Difraktogrami su snimljeni u 20  
 rasponu  $15-115^{\circ}$ , sa korakom  $0,02^{\circ}$  i vremenom ekspozicije 5s po koraku.  
 Utvrđeno je da svi uzorci kristališu u struktturnom tipu granata, prostorna  
 grupa  $Ia3d$ . Strukture su utaćnjene punom profilnom Rietveld-ovom  
 metodom, koristeći programski paket FULLPROF. Pri utaćnjavanju su  
 pretpostavljeni jonski faktori rascjemanja.*

*U strukturi granata ion itrijuma zauzima dodekaedarski položaj  $24c$ ,  
 joni aluminijuma i gvožda tetraedarske i oktaedarske položaje  $24d$  i  $16a$ ,  
 respektivno, a jon kiseonika opšti  $96h$  položaj. Utvrđeno je da u svim  
 uzorcima dolazi do preferentne raspodele katjona Al i Fe u oktaedarskom  
 i tetraedarskom položaju. Koeficijent raspodele varira između 0,31 za  
 $Y_3Fe_4AlO_{12}$  i 0,49 za  $Y_3Fe_2Al_3O_{12}$ . Katjon-anjon rastojanja u oktaedru i  
 tetraedru ukazuju na razliku prirode hemijske veze u oktaedru i tetraedru.*

**CRYSTAL STRUCTURES OF  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ ,  $\text{Gd}_3\text{Fe}_4\text{AlO}_{12}$ ,  $\text{Gd}_3\text{Fe}_3\text{Al}_2\text{O}_{12}$** 

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**ABSTRACT**

The samples  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ ,  $\text{Gd}_3\text{Fe}_4\text{AlO}_{12}$  and  $\text{Gd}_3\text{Fe}_3\text{Al}_2\text{O}_{12}$  were obtained by ceramic technology. The oxides  $\text{Gd}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  were mixed in appropriate stoichiometric ratios, milled in powder and pressed under the pressure of 1.5 t/cm<sup>2</sup>.

Then the mixtures were fired at temperature of 1600 K for 7 hours. After presintering process cooled samples were milled again, and refired at 1600 K during 10 hours period.

Diffraction patterns were taken in  $2\theta$  region  $15^\circ$ - $115^\circ$ , at powder diffractometer Philips with Ni filtered  $\text{CuK}_{\alpha 1,2}$  radiation. All the samples crystallize in the garnet structure type, in the space group Ia3d. The structure refinement was provided by the Ritveld's profile method by using software package DBWS 9006PS with ionic scattering factors assumed.

In the unit cell, gadolinium ion occupies 24c position with dodecahedral surrounding, while iron (or aluminium) ions occupie two different positions: 24d with tetrahedral, and 16a with octahedral surrounding. It was found that in  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$  exists preferential distribution of iron in 16a position with relatively high coefficient of preferential distribution  $K=3.7$ ,while in the case of  $\text{Gd}_3\text{Fe}_4\text{AlO}_{12}$ , this coefficient is bigger and equals 5.3 . Furthermore, it was found that cell parameter increase with iron concentration, while magnetic measurements showed that Curie point also depends on it.

## KRISTALNE STUKTURE $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ , $\text{Gd}_3\text{Fe}_4\text{AlO}_{12}$ , $\text{Gd}_3\text{Fe}_3\text{Al}_2\text{O}_{12}$

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### IZVOD

Uzorci  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ ,  $\text{Gd}_3\text{Fe}_4\text{AlO}_{12}$ ,  $\text{Gd}_3\text{Fe}_3\text{Al}_2\text{O}_{12}$  dobijeni su keramičkom tehnologijom. Polazni oksidi  $\text{Gd}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  su pomešani u odgovarajućim stehiometrijskim odnosima, samleveni u prah i presovani pod pritiskom od  $1.5 \text{ t/cm}^2$ . Zatim su žareni na temperaturi od  $1600 \text{ K}$  u trajanju od 7 sati. posle završenog predsinterovanja, ohlađeni uzorci su ponovo samleveni, presovani i žareni na  $1600 \text{ K}$  u trajanju od 10 sati.

Difraktogrami su snimljeni u  $2\theta$  rasponu  $15^\circ$ - $115^\circ$ , na difraktometru za polikristale Philips sa  $\text{CuK}_{\alpha 1,2}$  zračenjem i Ni filterom. Svi dobijeni uzorci kristališu u struktornom tipu granata, u prostornoj grupi Ia3d. Utačnjavanje strukture vršeno je profilnom Ritveld-ovom metodom pomoću programskog paketa DBWS 9006PS, sa pretpostavljenim jonskim faktorima rasejanja.

Jon gadolinijuma u jediničnoj celiji zauzima položaj 24c sa dodekaedarskim okruženjem, dok joni gvožđa (ili aluminijuma) zauzimaju dva različita položaja: 24d sa tetraedarskim i 16a sa oktaedarskim okruženjem. Utvrđeno je da u  $\text{Gd}_3\text{Fe}_3\text{Al}_2\text{O}_{12}$  postoji preferentna raspodela gvožđa u položaju 16a sa relativno visokim koeficijentom preferentne distribucije  $K=3,7$  dok je za  $\text{Gd}_3\text{Fe}_4\text{AlO}_{12}$  ovaj koeficijent veći i iznosi 5,3. Takođe je utvrđeno da konstanta rešetke linearno raste sa koncentracijom gvožđa, dok su magnetna merenja pokazala da od nje zavisi položaj Kirijeve tačke.

## THE STRUCTURE OF USNIC ACID 11-[(1-NAPHTHOYL)HYDRAZONE]

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Four new condensation derivates of usnic acid with hydrazides of  $\alpha$ -naphthoic and caprylic acid, semioxamazide and thiosemicarbazide have been synthesized. These compounds were characterized by microanalysis, IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and mass spectrometry. The derivative of usnic acid and hydrazide of  $\alpha$ -naphthoic acid (UANH) has been obtained in form of single crystals and its molecular structure predicted on the basis of mentioned investigations. The molecular structure was confirmed by X-ray crystal structure analysis and its crystal structure was determined too.

**Crystal data for UANH· $C_2H_5OH$  ( $C_{31}H_{29}N_2O_8$ ) :**  $Mr=558.59$ , monoclinic, space group  $P2_1$ ,  $a=7.7365(7)$ ,  $b=19.639(2)$ ,  $c=9.4150(15)$  Å,  $\beta=100.830(11)^\circ$ ,  $Z=2$ ,  $V=1405.0(4)$  Å $^3$ ,  $d_c=1.320$  Mgm $^{-3}$ ,  $\mu(\text{MoK}_\alpha)=0.897$  mm $^{-1}$ ,  $F=(000)=588$ ,  $T=295$  K, ENRAF-NONIUS CAD-4 SINGLE CRYSTAL DIFFRACTOMETER.

The structure has been solved by direct methods (MULTAN) and refined by the full-matrix least squares to  $R=0.055$ ,  $R_w=0.052$ ,  $S=0.852$ , using  $No=1941$  independent reflections having  $2\leq\theta\leq30^\circ$  and  $I\geq2\sigma(I)$ . Number of variables was  $N_v=369$ .

The crystal structure consists of UANH and ethanol molecules in ratio 1:1. The packing in the crystal is controlled by Van der Waals forces and intermolecular hydrogen bonds of O-H...O and N-H...O type. The oxygen atom belonging to ethanol appears as donor in O-H...O bond and as acceptor in N-H...O bond. Molecules of ethanol are located in sandwiches between UANH molecules. It is a surprising fact that "mean planes" through atoms of UANH are perpendicular to the  $b$  crystallographic axis, since this axis is the longest one in the unit cell. No clear reasons of such a packing of molecules could be recognised. The geometry of UANH molecules is controlled by the role which different atoms play in molecular skeleton (type of bonds, angles between bonds etc). Unexpected bond distances and interbond angles were not registered in the molecule. It is a very important fact that there are two nearly linear and short intramolecular hydrogen bonds ( $\sim 2.50$  Å) connecting neighbouring hydroxylic and carbonyl groups.

## STRUKTURA 11-[(1-NAFTOIL)HIDRAZONA] USNINSKE KISELINE

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Sintetisana su četiri nova kondenzaciona derivata usninske kiseline sa hidrazidima  $\alpha$ -naftojeve i kaprilne kiseline kao i sa semioksamazidom i tiosemikarbazidom. Ova jedinjenja okarakterisana su mikroanalizom, IC,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  i masenom spektroskopijom. Derivat usninske kiseline i hidrazida  $\alpha$ -naftojeve kiseline (UANH) dobijen je u obliku monokristala. Pretpostavljena molekulska struktura ovog derivata potvrđena je rendgenostrukturnom analizom.

**Kristalografski podaci za UANH:**  $C_2H_5OH$  ( $C_3H_{29}N_2O_8$ ) :  $Mr=558,59$ , monoklinični, prostorna grupa  $P2_1$ ,  $a=7,7365(7)$ ,  $b=19,639(2)$ ,  $c=9,4150(15)\text{\AA}$ ,  $\beta=100,830(11)^\circ$ ,  $Z=2$ ,  $V=1405,0(4)\text{\AA}^3$ ,  $d_x=1,320 \text{ Mgm}^{-3}$ ,  $\mu(\text{MoK}_\alpha)=0,897 \text{ mm}^{-1}$ ,  $F(000)=588$ ,  $T=295 \text{ K}$ .

Struktura je rešena direktnim metodama (MULTAN) i utačnjena metodom najmanjih kvadrata do  $R=0,055$ ,  $R_w=0,052$ ,  $S=0,89$ , iz  $S=0,852$ , korišćenjem  $No=1941$  nezavisne refleksije sa  $I \geq 2\sigma(I)$  za  $N_v=369$  nezavisnih parametara i ugaoni opseg  $2 \leq \theta \leq 30^\circ$ .

Kristalna struktura sastoji se od molekula UANH i molekula etanola u odnosu 1:1. Pakovanje u kristalu kontrolisano je Van der Waalsovim silama i intermolekularnim vodoničnim vezama O-H...O i N-H...O tipa. Kiseonikov atom iz etanola pojavljuje se kao donor u O-H...O vezi i kao akceptor u N-H...O vezi. Molekuli etanola nalaze se u sendvičima izmedju UANH molekula. Veoma iznenadjujuća je činjenica da su "srednje ravni" povučene kroz UANH molekule normalne na kristalografsku  $b$  osu koja je i najduža osa u jediničnoj celiji.

Geometrija samog molekula kontrolisana je ulogom koju igraju pojedini atomi u molekulu i u tom smislu nema neočekivanih medjuatomskih rastojanja i uglova izmedju veza. Važna je međutim činjenica da postoje dve intramolekularne jake O-H...O vodonične veze izmedju kiseonikovih atoma iz hidroksilnih i karbonilnih grupa, koje su skoro linearne i čija su O...O rastojanja oko  $2,50 \text{ \AA}$ .

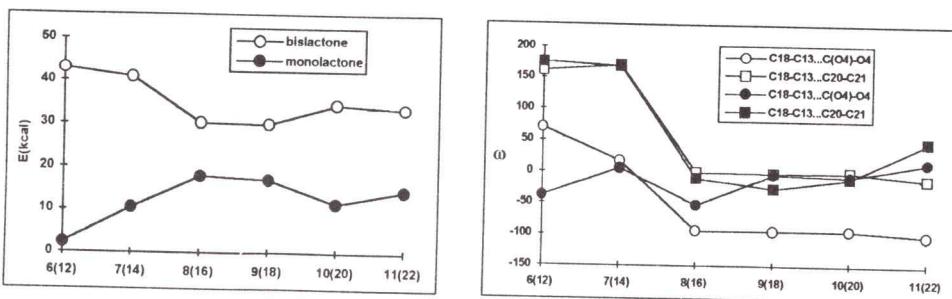
## STUDY OF MONO- AND BISLACTONE RING FORMATION OF DEOXYCHOLIC ACID AND ITS NOR AND HOMO DERIVATIVES

*Slobodanka Stanković, Dušan Lazar, Ksenija Kuhajda and Dušan Miljković*

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The formation of  $3\alpha$ -acetoxy- $5\beta$ -cholano-bislactone (from 3-O-acetyl-deoxycholic acid) was described in our earlier paper (1). In order to study further the lactonization processes in similar compounds, we have examined the chemical and structural features of  $3\alpha$ -acetoxy-*24-nor*- $5\beta$ -cholano- $12\alpha,24$ -lactone. The structure was determined by X-ray diffraction. Contrary to our earlier finding, in this case the monolactonization process occurred exclusively.

The molecules with 7-membered monolactone rings are related by twofold screw axis lying parallel to the c-axis, resembling molecules with 16-membered bislactone rings which possess the pseudo twofold axis as an element of symmetry.



Energetical examinations, applied to similar molecules containing 6- to 11-membered monolactone and 12- to 22-membered bislactone rings (obtained by modeling), are summarized in graphs. The relative energy minimum values, obtained by MMX calculations, show a dramatic change between molecules with 7- and 8-membered monolactone and, consequently, 14- and 16-membered bislactone rings, which is in full agreement with our experimental results.

The change of energy is followed by a complete change in torsion angles, which define the orientations of C21 methyl groups and carbonyl oxygen O4. The bislactone rings with 16 and more members provide enough room for two methyl groups, and they are pointing towards the center of the ring. Consequently, the  $\alpha$ -oriented O4 atoms in 12- and 14-membered rings become  $\beta$ -oriented in 16- and more membered rings.

(1) S. Stanković *et al.*, *J.Mol.Struc.*, 221 (1990), 271-282.

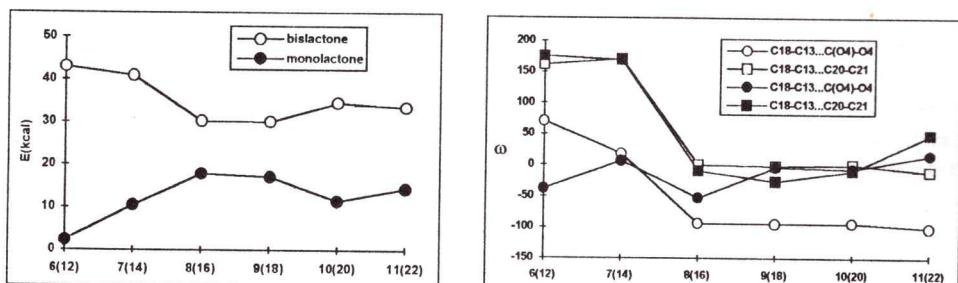
## ENERGETSKA ISPITIVANJA FORMIRANJA MONO- I BIS-LAKTONSKOG PRSTENA U JEDINJENJIMA DEZOKSIHOLNE KISELINE

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Formiranje bislaktonskog prstena u  $3\alpha$ -acetoksi- $5\beta$ -holano-bislaktonu (iz 3-O-acetyldezoksiholne kiseline) opisano je u našem prethodnom radu (1). U cilju daljeg proučavanja procesa laktonizacije u sličnim jedinjenjima, ispitivanci su strukturne i hemijske osobine  $3\alpha$ -acetoksi-24-nor- $5\beta$ -holano-12 $\alpha$ ,24-laktona. Struktura je određena difrakcijom x-zraka na monokristalu. Suprotno našim očekivanjima, u ovom slučaju došlo je do formiranja isključivo monolaktonskog prstena.

Molekuli su međusobno povezani osom uvrтанja drugog reda koja leži paralelno  $c$ -osi. Ako se posmatra duž  $c$ -ose, par ovih molekula ima sličnost sa molekulom jedinjenja (1), čiji 16-člani bislaktonski prsten poseduje pseudoosu simetrije drugog reda.



Rezultati energetskih ispitivanja, primenjenih na ove i slične molekule koji sadrže 6- do 11-člane monolaktonske i 12- do 22-člane bislaktonske prstene (koji su dobijeni modeliranjem), sumirani su na grafiku. Vrednosti minimuma energije, dobijene MMX proračunima, značajno se menjaju između molekula sa 7-članim i 8-članim laktonskim prstenom i, sledstveno, 14-članim i 16-članim bislaktonskim prstenom, što je u saglasnosti sa dosadašnjim eksperimentalnim rezultatima.

Promena energije je praćena kompletном promenom vrednosti torzionih uglova (takođe prikazano grafički), koji definišu orijentaciju C21 metilnih grupa i karbonilnog kiseonika O4. Bislaktonski prsten sa 16 i više članova obezbeđuje dovoljno prostora za dve metilne grupe, pa su one orijentisane ka njegovom centru. Sledstveno tome,  $\alpha$ -orientisani O4 atomi u 12-članom i 14-članom prstenu postaju  $\beta$ -orientisani u prstenima sa 16 i više članova.

(1) S.Stanković et al., *J.Mol.Struc.*, 221(1990), 271-282.

STRUCTURE OF  $17\beta$ -BENZYL- $3\beta,17\alpha$ -DIHYDROXY-5-ANDROSTEN-16-ONE

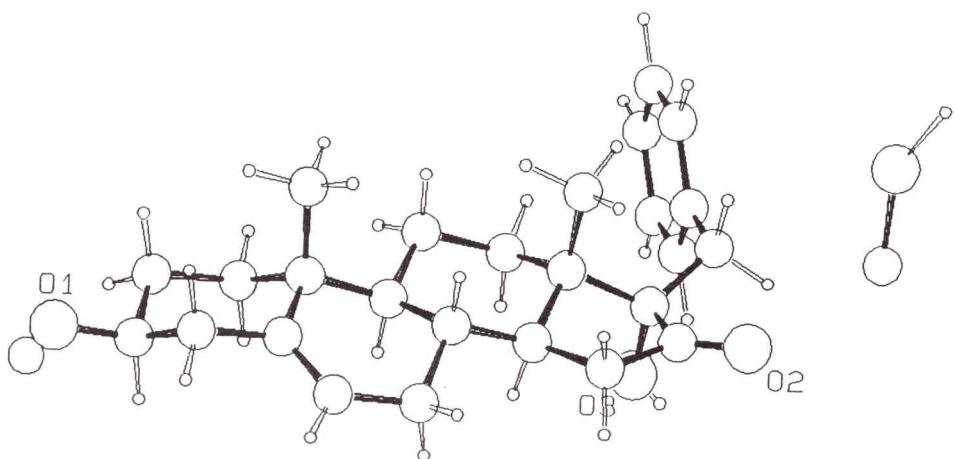
D. Lazar<sup>1</sup>, S. Stanković<sup>1</sup>, K. Gašić<sup>2</sup>, Lj. Medić-Mijačević<sup>2</sup>, E. Djurendić<sup>2</sup>

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In the series of newly synthesized androgens, potential antiandrogens, the structure of  $17\beta$ -benzyl- $3\beta,17\alpha$ -dihydroxy-5-androsten-16-one is determined. Beside its activity, this compound is interesting for examination the configuration changing of atom C17. Namely, in the compounds similar in the region of D (and C) ring, but with different C16-substituents, 17-benzyl and 17-hydroxy substituents exchange their positions depending on the C16-substituent: in the 16-keto substituted compounds 17-benzyl is  $\beta$ - and 17-hydroxy moiety  $\alpha$ -oriented. If atom C16 is not substituted or substituent is not keto oxygen, 17-benzyl is  $\alpha$ - and 17-hydroxy group  $\beta$ -oriented.

The title compound crystallizes in  $P2_1$ ,  $a = 11.960(2)$ ,  $b = 6.0989(5)$ ,  $c = 16.692(3)$  Å,  $\beta = 99.22(3)^\circ$ ,  $Z = 2$ ,  $V = 1201.8(3)$  Å<sup>3</sup>,  $F(000) = 460$ ,  $\mu = 0.61$  mm<sup>-1</sup>. Unit-cell parameters were obtained and reflections collected on the Enraf-Nonius CAD-4 diffractometer. The structure was solved by direct methods and refined to  $R = 0.05$  for 2088 observed reflections.

Conformational analysis and molecular-mechanical calculations were performed for molecule. The ring conformations are usual for this kind of compounds. The C17 atom has an unusual configuration ( $17\beta$ -benzyl,  $17\alpha$ -hydroxy), which could be explained by the presence of 16-keto oxygen. The molecule conformation practically remains unchanged during the energy minimization.



## STRUKTURA 17 $\beta$ -BENZIL-3 $\beta$ ,17 $\alpha$ -DIHIDROksi-5-ANDROSTEN-16-ONA

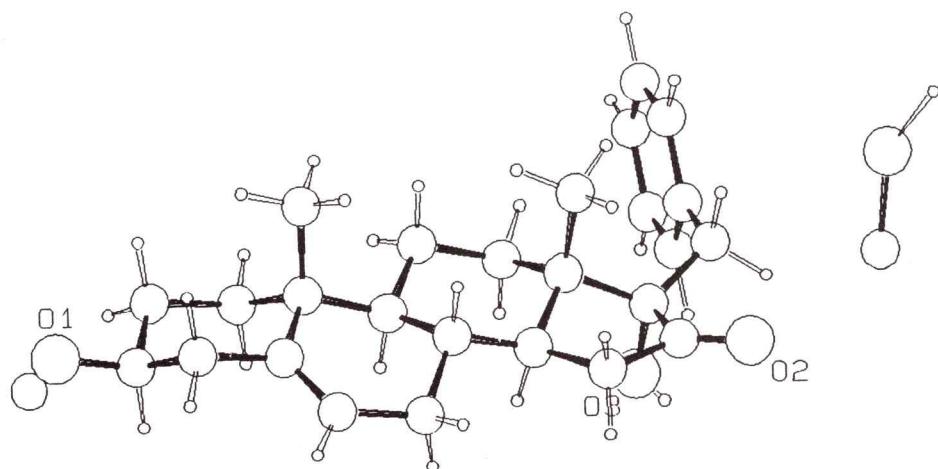
D. Lazar<sup>1</sup>, S. Stanković<sup>1</sup>, K. Gašić<sup>2</sup>, Lj. Medić-Mijačević<sup>2</sup>, E. Djurendić<sup>2</sup>

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U nizu novosintetizovanih androgena, potencijalnih antihormona, određena je struktura 17 $\beta$ -benzil-3 $\beta$ ,17 $\alpha$ -dihidroksi-5-androsten-16-onsa. Pored biološke aktivnosti, ovo jedinjenje je interesantno za proučavanje promene konfiguracije C17 atoma. Naime, primećeno je da kod jedinjenja sličnih u oblasti D (i C) prstena, ali sa različitim 16-supstituentima, 17-benzil i 17-hidroksi supstituenti zamenjuju mesta u zavisnosti od supstituenta atoma C16: kod jedinjenja kod kojih je atom C16 supstituisan keto kiseonikom 17-benzil je  $\beta$ -, a 17-hidroksi grupa  $\alpha$ -orientisan, a u slučaju da C16 nije supstituisan ili da je supstituent različit od keto kiseonika, 17-benzil je  $\alpha$ -, a 17-hidroksi grupa  $\beta$ -orientisana.

Jedinjenje kristališe u prostornoj grupi  $P2_1$ ,  $a = 11,960(2)$ ,  $b = 6,0989(5)$ ,  $c = 16,692 (3)$  Å,  $\beta = 99,22 (3)^\circ$ ,  $Z = 2$ ,  $V = 1201,8(3)$  Å<sup>3</sup>,  $F(000) = 460$ ,  $\mu = 0,61$  mm<sup>-1</sup>. Parametri su odredjeni i refleksi skupljeni Enraf-Noniusovim CAD-4 difraktometrom. Struktura je rešena direktnim metodama i utačnjena do  $R = 0,05$  za 2088 opserviranih refleksa.

Uradjeni su konformaciona analiza i molekularno-mehanički proračuni molekula. Konformacija prstenva molekula je uobičajena za ovu vrstu jedinjenja. C17 atom ima neobičnu konfiguraciju (17 $\beta$ -benzil, 17 $\alpha$ -hidroksi), što se može objasniti prisustvom 16-keto kiseonika. Konformacija molekula u toku minimizacije se ne menja značajno.



CRYSTAL AND MOLECULAR STRUCTURE OF TRITERPENE ISOMERS FROM  
*HIERACIUM PLUMULOSUM* A. KERNER, ASTERACEAE

A.Kapor<sup>1</sup>, B.Ribár<sup>1</sup>, Gy.Argay<sup>2</sup>, A.Kálmán<sup>2</sup>, S.Petrović<sup>3</sup>, M.Gorunović<sup>3</sup>

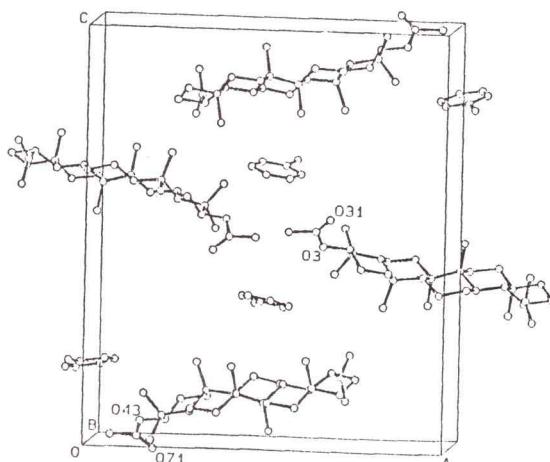
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<sup>3</sup> Pharmacognostic Institute, Pharmaceutical Faculty, Belgrade

The aim of the study was to investigate the natural product originating from the plant *Hieracium plumulosum* A. Kerner. Transparent monocrystals were obtained from purified chloroform extract of plant, after separating by the chromatography on silicagel column with the aid of toluene, washing by acetone and recrystallization from toluene. The monocrystals are highly unstable in the air - they turn white and process of their decomposition begins, which lasts 3-4 days depending on the sample size. As the preliminary part of the identification of the isolated product, IR, MS, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded.

Single crystal sample prepared in the capillary was examined using X-Ray diffraction method, with CuK<sub>α</sub> radiation. Reflection intensities were collected by CAD-4 diffractometer. Crystallographic parameters are : a=19.190(2), b=8.118(1), c=21.841(2) Å, β=90.29°, P2<sub>1</sub>, Z=4, D<sub>x</sub>=1.095 Mg m<sup>-3</sup> for bruto formula C<sub>32</sub>H<sub>52</sub>O<sub>2</sub> + C<sub>7</sub>H<sub>8</sub> and M<sub>r</sub>=560.84. Using programs SHELXS and SHELXL 93 the structure was solved by the direct method and refined up to R=0.0822 for 5122 independent reflections with F<sub>o</sub> > 4σ(F<sub>o</sub>) and N<sub>p</sub>=777, S=0.970. Besides two symmetry independent molecules A and B, the assumed presence of two types of both molecules with the same bruto formula, but differing in the position of double C=C bond in the substituent bonded to C19 was confirmed by detecting an oxygen atom O19 bonded to C19 and to C20 with occupation factor K=0.22 which is captured from the atmosphere. Hydrogen migrations takes place between the atoms C19 and C29 and the structure reflects the statistical distribution of two acetylated pentacyclic triterpene alcohols: lupeol-acetate(I) and its isomer(II), which is in agreement with the recorded spectra. There are also two toluene molecules incorporated into the crystal lattice. The presence of oxygen atoms O19 in the secund type of the molecule, explains the destruction of the double C19-C20 bond and the tendency of epoxide formation, which results in the crystal decomposition in the air.



## KRISTALNA I MOLEKULSKA STRUKTURA TRITERPENSIH IZOMERA IZ *HIERACIUM PLUMULOSUM* A.KERNER, ASTERACEAE

A.Kapor<sup>1</sup>, B.Ribár<sup>1</sup>, Gy.Argay<sup>2</sup>, A.Kálmán<sup>2</sup>, S.Petrović<sup>3</sup> i M.Gorunović<sup>3</sup>

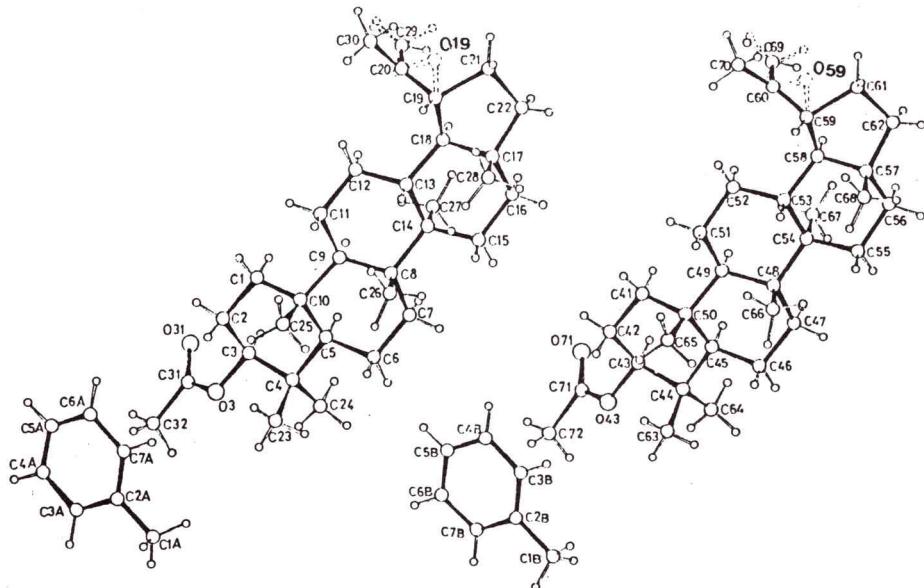
<sup>1</sup> Institut za fiziku, Prirodno-matematički fakultet, Novi Sad

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<sup>3</sup> Zavod za farmakognoziju, Farmaceutski fakultet, Beograd

Cilj istraživanja je bio određivanje strukture prirodnog produkta dobijenog iz biljke *Hieracium plumulosum* A. Kerner. Providni monokristali dobijeni su iz prečišćenog hloroformskog ekstrakta, razdvajanjem hromatografijom na stubu silikagela pomoću toluena a posle ispiranja acetonom i prekristalizacije iz toluena. Kristali su veoma nestabilni na vazduhu. U cilju identifikacije izolovanog proizvoda snimljeni su IR, MS,  $^1\text{H}$  NMR i  $^{13}\text{C}$  NMR spektri.

Monokristalni uzorak prepariran u kapilari ispitana je metodom difrakcije x-zraka, korišćenjem CuK $\alpha$  radijacije. Intenziteti refleksa sakupljeni su na CAD-4 difraktometru. Kristalografski parametri su:  $a=19,190(2)$ ,  $b=8,118(1)$ ,  $c=21,841(2)\text{\AA}$ ,  $\beta=90,29^\circ$ ,  $P2_1$ ,  $Z=4$ ,  $D_x=1,095 \text{ Mgm}^{-3}$  za bruto formulu  $\text{C}_{32}\text{H}_{52}\text{O}_2 + \text{C}_7\text{H}_8$  i  $M_r=560.84$ . Korišćenjem programa SHELXS i SHELXL 93 rešena je struktura direktnim metodama i utačnjena do  $R=0,0822$  za 5122 refleksa sa  $F_o > 4\sigma(F_o)$  i  $N_p=777$ ,  $S=0,970$ . Pored dva simetrijski nezavisna molekula A i B, može se pretpostaviti i prisustvo dva izomera koji bi se razlikovali po položaju dvostrukе C=C veze u supstituentu vezanom za C19. Postojanje dvostrukе veze C19-C20 je posredno potvrđeno nalaženjem atoma kiseonika O19 sa okupacionim faktorom  $K=0,22$  koji se u kristal vezuje iz atmosfere sa tendencijom formiranja epoksida, što kao posledicu ima raspadanje kristala na vazduhu. Migracija vodonika se odvija između atoma C19 i C20 i struktura odražava statistički raspored dva acetilovana pentaciclična triterpenska alkohola: lupeol-acetata(I) i njegovog epoksidnog izomera(II), što je u skladu sa snimljenim spektrima. U kristalnu rešetu ugrađena su i dva molekula toluena.



## POTASSIUM SULPHATE AS A NATURAL PRODUCT

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In the process of alkaloid separation from medicinal herb *Corydalis ochroleuca* collected at Fruška Gora mountin, in various stages of the extraction, transparent colourless single crystals were obtained. Their structure was studied by X-ray diffraction method. One of the products was identified as *sinoacutine* [1], alkaloid of *morphinandienone* type, while the other product was identified as the β-form of potassium sulphate.

We shall describe here the results of the study of the second natural product. Using single crystal automatic diffractometer CAD-4, 467 independent reflections were recorded at T=293K using MoK<sub>α</sub> radiation. Following crystallographic parameters were obtained: a=7.455(4), b=5.746(4), c=10.045(4) Å, V=430.3(4) Å<sup>3</sup>, Z = 4, D<sub>x</sub> = 2.69 Mgm<sup>-3</sup> and space group Pnma. The structure was solved as β-K<sub>2</sub>SO<sub>4</sub> by the direct method (SHELXS86) and refined anisotropically (SHELXL93) up to final R factor R=0.0448 for 465 reflections ( $I > 2\sigma(I)$ ) for 41 parameters with S=1.662.

The comparison of the structure obtained with literature data, it was established that the structure of monocrystalline low-temperature phase of K<sub>2</sub>SO<sub>4</sub> was solved several times [2,3,4]. According to the last reference (R=0.051, N<sub>ref</sub>=854) one can notice good agreement of the coordinates and the geometry with solved structure. Somewhat better results of our measurements, lower value of R factor and lower values of the atomic displacement parameters probably reflect the better quality of the crystals leading to better quality of recorded reflection intensities.

Structural phase transition of potassium sulphate was noticed at 860 and 920 K. The structure of high-temperature α-form K<sub>2</sub>SO<sub>4</sub> was solved in 1980 [5] and indicates to the change of the symmetry of the crystal lattice. The structure of K<sub>2</sub>SO<sub>4</sub> at room temperature shows the layered distribution of K1 and K2 cations and anions (tetrahedra of SO<sub>4</sub> group) parallel to b c - plane. At elevated temperature the ions occupy special positions and change simmetry and space group.

- [1] B.Ribar,A.Kapor,O.Gašić,J.Kanyo, P.Engel; Acta Cryst C49, 978-980 (1993).
- [2] M.T.Robinson, J.Phys.Chem., 62, 925-928, (1958)
- [3] M.Gaultier, G.Pannetier, Bull.Soc.Chim.Fr., 105-112, (1968)
- [4] J.A.McGinnety, Acta Cryst., B28, 2845-2852, (1972)
- [5] M.Miyake, H.Morikawa, S.Iwai, Acta Cryst., B36, 532-536, (1980)

## KALIJUM SULFAT KAO PRIRODNI PRODUKT

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<sup>1</sup> DD Beočinska fabrika cementa, Beočin

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U procesu izdvajanja alkaloida iz lekovite biljke *Corydalis ochroleuca* sakupljene na Fruškoj Gori, u različitim stadijumima prečišćavanja dobijeni su bezbojni providni monokristali. Ispitana je njihova struktura metodom difrakcije x-zraka. Jedan od produkata je identifikovan kao *sinoacutine* [1] alkaloid tipa *morphinandienona*, dok je za drugi produkt utvrđeno da se radi o  $\beta$ -formi kalijum sulfata.

Ovde ćemo opisati rezultate ispitivanja drugog prirodnog produkta. Korišćenjem automatskog difraktometra za monokristale CAD-4, izmereno je 467 nezavisnih refleksija na temperaturi  $T=293\text{K}$  korišćenjem  $\text{MoK}_\alpha$  zračenja. Dobijeni su kristalografski parametri:  $a=7,455(4)$ ,  $b=5,746(4)$ ,  $c=10,045(4)\text{\AA}$ ,  $V=430,3(4)\text{\AA}^3$ ,  $Z=4$ ,  $D_x = 2,69 \text{ Mgm}^{-3}$  i prostorna grupa  $\text{Pnma}$ . Struktura je rešena kao  $\beta\text{-K}_2\text{SO}_4$  direktnom metodom (SHELXS86) i utvrđena anizotropno (SHELXL93) do konačnog R faktora  $R=0,0448$  za 465 refleksija ( $I>2\sigma(I)$ ) i 41 parametar sa  $S=1,662$ .

Poređenjem dobijene strukture sa literaturom, utvrđeno je da je struktura monokristala niskotemperaturske faze  $\text{K}_2\text{SO}_4$  više puta rešavana [2,3,4]. Na osnovu poslednje reference ( $R = 0,051$ ,  $N_{\text{ref}} = 864$ ) može se utvrditi dobro slaganje koordinata i geometrije sa rešenom strukturom. Nešto bolji rezultati naših merenja, niža vrednost R faktora i manje vrednosti termičkih parametara atoma, verovatno su odraz boljeg kvaliteta kristala, a samim tim i snimljenih intenziteta refleksija.

Strukturni fazni prelaz kalijum sulfata uočen je na 860 i 920 K. Struktura visokotemperaturske  $\alpha$ -forme  $\text{K}_2\text{SO}_4$  rešena je 1980 godine [5] i ukazuje na promenu simetrije kristalne rešetke. Poznavanje strukture  $\text{K}_2\text{SO}_4$  na sobnoj temperaturi pokazuje slojeviti raspored katjona K1 i K2 i anjona (tetraedara  $\text{SO}_4$  grupe) paralelno b c - ravni. Na povišenoj temperaturi joni zauzimaju specijalne položaje i menjaju simetriju i prostornu grupu.

- [1] B.Ribar,A.Kapor,O.Gašić,J.Kanyo, P.Engel; Acta Cryst C49, 978-980 (1993).
- [2] M.T.Robinson, J.Phys.Chem., 62, 925-928, (1958)
- [3] M.Gaultier, G.Pannetier, Bull.Soc.Chim.Fr., 105-112, (1968)
- [4] J.A.McGinnety, Acta Cryst., B28, 2845-2852, (1972)
- [5] M.Miyake, H.Morikawa, S.Iwai, Acta Cryst., B36, 532-536, (1980)

## REAL-SPACE CRYSTALLOGRAPHY IN Pt-Ru NANOPHASE PARTICLES

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The small size of the Pt-Ru particles, important in catalyst systems, causes serious limitations in microstructural characterization, that could be overcome by high resolution electron microscopy (HREM), especially for particle morphology studies, presence of faults, surface steps and facets, etc. The present study uses HREM in order to perform real-space crystallography on the Pt-Ru particles, since the reciprocal space crystallography on such a small particle of the size around 2 nm is practically impossible.

It has been found that some of Pt-Ru particle in an catalyst containing 20 % of metal mass and having ratio Pt:Ru=3:1, exhibits pronounced microfaceting on 111 and 200 type planes, forming so called cubo-octahedron shape particles, already observed in pure platinum particles<sup>[1]</sup>, of the size 10 to 20 nm. In addition to 111 and 200 facets (Fig.1. a and b), typical for FCC type particles, 113 facets, that are not typical of FCC metal nanocrystals, are also observed (Fig. 1. b).

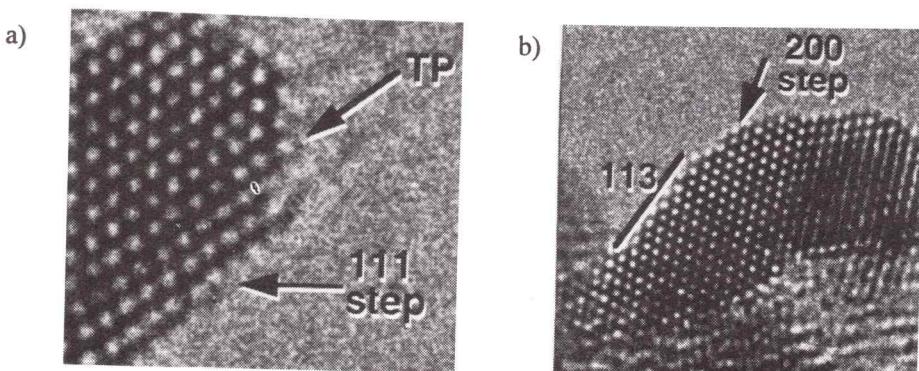


Fig. 1- High resolution electron micrographs of a twinned Pt-Ru particles

This facet does not appear to be accompanied by any relaxation in the interatomic spacing near the surface. Some of the particles appear to have twinned type structure with the same 111 twinning plane, as any other FCC system. Twinning, however is not commonplace. By internal calibration using pure Cu grid it has been found that this FCC unit cell has lattice parameter of 0.3902 nm, which is almost the same as in the pure Pt, e.g. 0.393 nm. Lattice constant measurements from HREM images or by electron diffraction do not have enough accuracy<sup>[2]</sup> to determine the amount of Ru into Pt, e.g. value of x in the formula  $Pt_{1-x}Ru_x$ . It is especially difficult when the difference in atomic radius is very small, as it is case of Ru and Pt where their radii are 0.189 nm and 0.183 nm, respectively.

#### References

- [1] J. M. Dominguez, M. J. Yacaman, J. of Catalysis, 64(1980)223-227.
- [2] T. Chojanacki, K. Krause, L. D. Schmidt, J. of Catalysis, 128(1991)161-185.

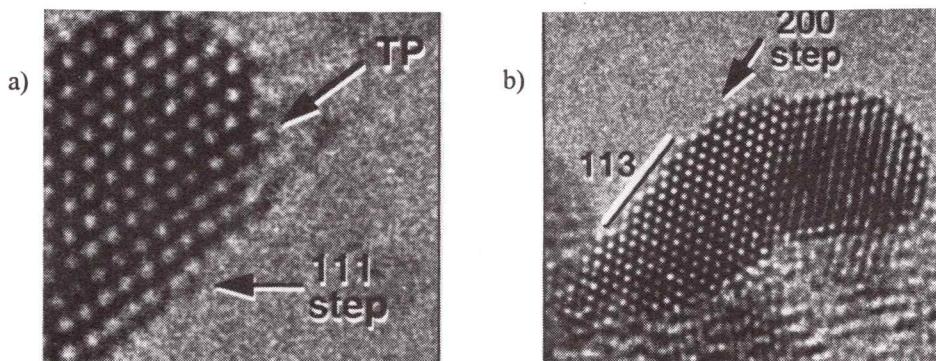
## KRISTALOGRAFIJA Pt-Ru NANOČESTICA U REALNOM PROSTORU

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Mala veličina Pt-Ru čestica, koje su važne u katalitičkim sistemima, predstavlja ozbiljno ograničenje u njihovoj mikrostruktурној karakterizaciji, koje može da bude prevaziđeno pomoću elektronske mikroskopije visoke rezolucije (HREM), posebno u izučavanju morfologije, prisustva grešaka, stepenica na površini kristala i faceta. U ovom radu korišćena je HREM metoda da bi se ispitala kristalografijska svojstva Pt-Ru čestica u realnom prostoru, s obzirom da je kristalografijska u recipročnom prostoru, na tako malim česticama veličine oko 2 nm, praktično neizvodljiva.

Ustanovljeno je da neke Pt-Ru čestice u katalizatorima koji sadrže 20% metalne mase i koji imaju odnos Pt:Ru=3:1, pokazuju izrazito mikrofacetiranje ravnima tipa 111 i 200, stvarajući čestice kub-oktaedarskog oblika, koje su zapažene u česticama platine veličine 10 do 20 nm<sup>[1]</sup>. Pored 111 i 200 faceta (sl.1.a i b), tipičnih za pov-c-k kristale, zapaženo je prisustvo faceta tipa 113 koje nisu tipične (sl. 1.b).



Sl. 1- Elektronske mikrofotografije dvojnikovanih Pt-Ru čestica

Prisustvo ove facete nije praćeno bilo kakvom relaksacijom u medjuravanskom rastojanju blizu površine. U nekim česticama zapaženo je prisustvo dvojnika sa 111 ravnima dvojnikovanja, kao u svim pov-c-k kristalima. Dvojnikovanje, međutim, nije opšta pojava. Internom kalibracijom korišćenjem mrežice od čistog Cu, ustanovljeno je da parametar rešetke ovih čestica iznosi oko 0.3902 nm, što je vrlo blisko čistoj platini, t.j. 0.393 nm. Merenje konstante rešetke sa HREM slikom ili elektronskom difrakcijom nema dovoljnu tačnost<sup>[2]</sup> da bi se odredila količina Ru u Pt, odnosno x vrednost u formuli Pt<sub>x</sub>Ru<sub>y</sub>. To je posebno teško kada je razlika u veličini atoma veoma mala, kao u slučaju Ru i Pt, čiji su poluprečnici 0.189 i 0.183 nm, respektivno.

### Literatura

- [1] J. M. Dominguez, M. J. Yacaman, J. of Catalysis, 64(1980)223-227.
- [2] T. Chojanacki, K. Krause, L. D. Schmidt, J. of Catalysis, 128(1991)161-185.

## STRUCTURAL AND MICROSTRUCTURAL CHANGES OF COLD SINTERED $\alpha$ -COBALT POWDER

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### ABSTRACT

The aim of this work is to point to facts which define differences between various samples of cold sintered cobalt powder. The sample of cobalt powder, which is presented here, is cold sintered at the pressing pressure of 1.2 GPa.

In that sense, this work is focused on structural and microstructural changes of investigated specimen. Special attention is turned on microstructural parameters (mean crystallite size and its distribution, root mean strain and its distribution, paracrystallinity and dislocation), because of theirs significant influence on features of cobalt.

In order to characterize cold sintered cobalt powder on microstructural level, Warren-Averbach method (Klug & Alexander, "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 1974") is used.

The pure diffraction profile is calculated by convolution method which is described by Enzo S., Fagherazzi, G., Benedetti, A., and Polizzi, S., *J. Appl. Cryst.*, 21, 536, 1988.

For extraction of structural parameters Rietveld method is used (Rodriguez-Carvajal, H., computer program Fullprof, Ver. Apr. 95, 1995).

It is well known that crystal cobalt is characterized by stacking faults, as well as with intimate two-phase mixture of face-centered cubic and close-packed hexagonal forms. In addition this fact (Taylor, A., *X-Ray Metalography*, 1961) in addition, cause changes particularly on microstructural parameters.

## STRUKTURNЕ I MIKROSTRUKTURNЕ PROMENE HLADНО SINTEROVANOG PRAHA $\alpha$ -KOBALTA

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### IZVOD

Cilj ovog rada je da ukaže na činjenice koje definišu razlike izmedju različito primenjenih uzoraka hladno sinterovanog kobalta. Uzorak kobaltnog praha, na kome su sprovedena ispitivanja, hladno je sinterovan na pritisku od 1,2 GPa.

U tom smislu, insistira se na definisanju strukturnih i mikrostrukturnih promena ispitivanog uzorka. Posebna pažnja je posvećena izračunavanju mikrostrukturnih parametara (srednja veličina kristalita i njihova distribucija, mikronaprezanja sa distribucijom, parakristalinitet, minimalna gustina dislokacija) zbog njihovog značajnog uticaja na svojstva ovog materijala.

U cilju karakterizacije ispitivanog kobaltnog praha na nivou mikrostrukture, korišćene su različite Fourier-ove metode (Klug & Alexander: "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials, 1974").

Metoda konvolucije korišćena je u cilju izdvajanja čistog difrakcionog profila (Enzo, Fagherazzi, Benedetti, Polzzi: J. Appl. Cryst., **21**, 536, 1988), dok su strukturni parametri dobijeni Ritveldovom metodom uz korišćenje kompjuterskog programa Fullprof (Rodriguez - Carvajal: "Computer program Fullprof, Ver. Apr. 95," 1995).

Veoma defektna struktura kobalta, koja se ogleda u pojavi nepravilnog slaganja slojeva, odnosno mešanja  $\alpha$  i  $\beta$  modifikacije ovog metala, dodatno utiče na izračunate parametre mikrostrukture.

## ADDITIONAL POWDER DIFFRACTION DATA FOR MINERAL STUDENITSITE



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Studenitsite,  $\text{NaCa}_2[\text{B}_9\text{O}_{14}(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ , a new boron mineral was found in Piskanja deposit (Jarando tertiary basen) and was approved by the Commission on New Minerals and Mineral Names International Mineralogical Association in august 1994. The single-crystal structure determination [1], chemical, physical, optical and crystallographic characteristics [2] are recently reported.

In this work the results of X-ray powder diffraction investigation of studenitsite are presented. In the range of  $5-15^\circ 2\theta$  the very high intensity peaks was observed which are not present in the published data [2]. Therefore, the powder sample was investigated in the range  $5-120^\circ 2\theta$  and in the least squares refinement procedure (program LSUCRIPC was used) all reflections were indexed (table 1). The calculated unit cell parameters are in good agreement with those given in previously published data (table 2).

Tabela 2. Vrednosti parametara jedinične celije studenicitata  
Table 2. Unit cell parameters for studenitsite

	<sup>*</sup> a	<sup>**</sup> b
a	11.511(1) Å	11.4994(8) Å
b	12.602(1)	12.5878(9)
c	10.519(1)	10.5297(7)
$\beta$	$98.49 (1)^\circ$	$99.423 (6)^\circ$
V	1509.3 (2) Å <sup>3</sup>	1503.6 (3) Å <sup>3</sup>
S.G.	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> /c

\* podaci iz praha  
\*\* podaci iz monokristala [1]

## REFERENCES

- [1] Yamnova,N.A., Egorov-Tismenko,Yu.K., Puscharovsky,D.Yu., Malinko,S.V., Dorohova,G.I.: Kristallicheskaya struktura novogo prirodnogo Na,Ca-gidroborata  $\text{NaCa}_2[\text{B}_9\text{O}_{14}(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ ; Kristallografiya, T.38, Vyp.6, str.71-76, 1993.
- [2] Malinko,S.V., Anichich,S., Yoksimovich,D., Lisitsyn,A.E., Dorokhova,G.I., Yamnova,M.A., Vlasov,V.V., Ozol,A.A.: Studenitsite  $\text{NaCa}_2[\text{B}_9\text{O}_{14}(\text{OH})_4] \cdot 2\text{H}_2\text{O}$  - the new borate from Serbia, Yugoslavia, Proceedings of the Russian Mineralogical Society, Pt.124, N.3, p.57-64, 1995.

**DOPUNA PODATAKA ZA DIJAGRAM PRAHA BORNOG MINERALA  
STUDENICITA  $\text{NaCa}_2[\text{B}_9\text{O}_{14}(\text{OH})_4] \cdot 2\text{H}_2\text{O}$  IZ LEŽIŠTA PISKANJA**

Aleksandra Rosić

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Studenicit,  $\text{NaCa}_2[\text{B}_9\text{O}_{14}(\text{OH})_4] \cdot 2\text{H}_2\text{O}$  je novi borni mineral otkriven u ležištu Piskanja (Jarandolski terscijarni basen). Priznat je od Komisije za nove minerale i imena minerala Medjunarodne mineraloške asocijacije avgusta 1994. godine. Struktura je rešena na osnovu difrakcionih podataka dobijenih sa monokristala [1], a u okviru objavljenih hemijskih, fizičkih, optičkih i kristalografskih osobina ovog minerala [2], dat je i dijagram praha u intervalu  $15 - 60^{\circ} 2\theta$ .

U ovom radu su prikazani rezultati kristalografskih ispitanja studenicita. Na dijagramu praha ovog minerala se u području  $5 - 15^{\circ} 2\theta$  javljaju difrakcioni maksimumi većeg intenziteta (tabela 1). Zbog toga je uradjeno novo indiciranje u opsegu  $5 - 120^{\circ} 2\theta$  uz pomoć programa LSUCRIPC. Takodje, utaćeni su i parametri jedinične celije, a izračunate vrednosti su u saglasnosti sa vrednostima dobijenim iz podataka za monokristal (tabela 2).

Tabela 1. Deo dijagrama praha studenicita

Table 1. The part of X-ray powder pattern of studenitsite

<i>I/I<sub>o</sub></i>	<i>d<sub>izm</sub></i>	<i>d<sub>izr</sub></i>	<i>h k l</i>	<i>d<sub>izm</sub></i>	<i>d<sub>izr</sub></i>	<i>I/I<sub>o</sub></i>
70	8,02	8,02	0 1 1			
46	6,94	6,94	1 1 1			
15	6,30	6,30	0 2 0			
2	5,52	5,51	1 2 0			
33	5,40	5,39	0 2 1	5,41	5,36	66
65	5,20	5,20	0 0 2	5,20	5,21	57
6	4,80	4,81	0 1 2	4,82	4,80	3
4	4,73	4,73	1 2 1	4,72	4,71	11

#### LITERATURA

- [1] Yamnova, N.A., Egorov-Tismenko, Yu.K., Puscharovsky, D.Yu., Malinko, S.V., Dorohova, G.I.: Kristallicheskaya struktura novogo prirodnogo Na,Ca-gidroborata  $\text{NaCa}_2[\text{B}_9\text{O}_{14}(\text{OH})_4] \cdot 2\text{H}_2\text{O}$ ; Kristallografiya, T.38, Vyp.6, str.71-76, 1993.
- [2] Malinko, S.V., Anichich, S., Yoksimovich, D., Lisitsyn, A.E., Dorokhova, G.I., Yamnova, M.A., Vlasov, V.V., Ozol, A.A.: Studenitsite  $\text{NaCa}_2[\text{B}_9\text{O}_{14}(\text{OH})_4] \cdot 2\text{H}_2\text{O}$  - the new borate from Serbia, Yugoslavia, Proceedings of the Russian Mineralogical Society, Pt.124, N.3, p.57-64, 1995.

## Phase composition and morphology of ZnO powders obtained by ultrasonic spray pyrolysis

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Spray pyrolysis was used for the synthesis and deposition of well-defined submicronic to nanosize particles of ZnO on alumina substrate<sup>1</sup>. The process involves aerosol formation from the precursor solution by ultrasonic mist generator operated at 2.5 MHz and control over aerosol decomposition in the high temperature tubular flow reactor<sup>2</sup>. The droplets underwent evaporation, precipitation, drying and decomposition in dispersed system. The influence of the temperature in the range from 345 to 1165 K, solution concentration of zinc-nitrate as precursor (0.004 and 1.5 mol/dm<sup>3</sup>) and the residence time in the range from about 2 s to 5 h on the phase composition and particle morphology is investigated.

XRPD, DSC and SEM were used in phase and particle characterization. It was shown that spherical and smooth (100-200 nm diameter) particles were obtained at 1165 K from 0.004 mol/dm<sup>3</sup> precursor solution. Spherical particles were also obtained from 1.5 mol/dm<sup>3</sup> precursor solution for the residence time of 1.8 s. They were 0.9 μm in diameter and composed of so called "primary particles". Phase analysis showed that those particles are partly in amorphous and partly in crystalline state. Concentrically layered spherical particles containing pure ZnO phase are observed for the sufficient residence time (5 hours) in the high temperature zone.

The X-ray powder diffraction method was applied to determine phase composition as the function of reaction temperature. The phase Zn(NO<sub>3</sub>)(OH)·H<sub>2</sub>O was identified at 345 K. At 503 K low intensity ZnO-peaks at 0.248, 0.261 and 0.282 nm were observed. Slightly higher crystallinity of ZnO phase was evident at 861 K. At the same temperature a peak at 0.978 nm was appeared indicating the presence of a second intermediate phase Zn<sub>5</sub>(NO<sub>3</sub>)<sub>2</sub>(OH)<sub>8</sub>·2H<sub>2</sub>O. Pure ZnO phase was obtained at 1165 K, for the residence time of 5 h in the high temperature zone.

<sup>1</sup> O. Milošević, V. Gagić, J. Vodnik, A. Mitrović, Lj. Karanović, B. Stojanović, Lj. Živković, E-MRS Spring Meeting, 4-7 jun 1996, Strasbourg, France, Book of Abstracts, B-17.

<sup>2</sup> O. Milošević, M. Mirković, D. Uskoković, J.Am.Ceram.Soc., 1996, accepted for publication.

## Fazni sastav i morfologija praha ZnO dobijenog metodom ultrazvučnog reakcionog raspršivanja

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Metoda reakcionog raspršivanja korišćena je za sintezu i deponovanje submikronskih i nanostruktturnih prahova ZnO<sup>1</sup>. Proces je baziran na formiraju aerosola polaznog rastvora, primenom ultrazvučnog generatora rezonantne frekvencije 2,5 MHz i kontroli termičkog razlaganja aerosola u visokotemperaturnom protočnom cevnom reaktoru<sup>2</sup>. Pri tome se odigravaju sukcesivni procesi isparavanja, precipitacije, sušenja i razlaganja prekursora u disperznom sistemu gas-tečnost na nivou kapi srednje veličine oko 2 μm. Kao polazni rastvor korišćen je cink-nitrat-heksahidrat, rastvoren u destilovanoj vodi, koncentracije 0,004 i 1,5 mol/dm<sup>3</sup>. Aerosol ovog rastvora je strujom nosećeg gasa (vazduh) uvođen u reaktor u opsegu temperatura od 345 do 1165 K, deponovan na substratu od alumine ili taložen na izlazu iz reaktora. Pri tome je vreme zadržavanja u visokotemperaturnoj zoni bilo u opsegu od približno 2 s do 5 h.

Morfologija praha ispitivana je metodom SEM, fazni sastav rendgenskom analizom polikristalnih uzoraka i termijske karakteristike DSC metodom. Pokazano je da su čestice praha deponovanog na 1165 K iz rastvora koncentracije 0,004 mol/dm<sup>3</sup> sferične sa srednjom veličinom u opsegu 100-200 nm. Pri koncentraciji rastvora od 1,5 mol/dm<sup>3</sup> dobijene su čestice ZnO srednje veličine oko 0,9 μm. Na površini čestica, pri vremenu zadržavanja 1,8 s uočavaju se tzv. primarne čestice. Pri ovim uslovima sinteze prah je delom slabo iskristalisao u ZnO, a delom je u amorfnom stanju. Kompletna kristalizacija praha u ZnO odvija se tek nakon dodatnog termičkog tretmana. Čestice deponovane u dužem vremenskom periodu (5 h) imaju sfroidnu morfologiju sa koncentrično slojevitom pločastom strukturom, koja je nastala kao rezultat kristalizacije primarnih čestica u visokotemperaturnoj zoni.

Promene faznog sastava u funkciji temperature praćene su rendgenskom analizom. Na 345 K prisutna je samo faza Zn(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O. Pikovi ZnO pojavljuju se tek na 503 K, o čemu svedoče slabe refleksije na 0,248, 0,261 i 0,282 nm. Pojava pika na 0,978 nm ukazuje na moguće prisustvo druge intermedijarne faze, Zn<sub>5</sub>(NO<sub>3</sub>)<sub>2</sub>·(OH)<sub>8</sub>·2H<sub>2</sub>O, na temperaturi 861 K, pored slabo iskristalisalog ZnO. Daljim porastom temperature raste udio ZnO u odnosu na intermedijarne faze, tako da je na 1165 K, pri vremenu zadržavanja 5 časova, ZnO jedina prisutna faza u uzorku.

<sup>1</sup> O. Milošević, V. Gagić, J. Vodnik, A. Mitrović, Lj. Karanović, B. Stojanović, Lj. Živković, E-MRS Spring Meeting, 4-7 jun 1996, Strasbourg, France, Book of Abstracts, B-17.

<sup>2</sup> O. Milošević, M. Mirković, D. Uskoković, J. Am. Ceram. Soc, 1996, prihvaćeno za objavljivanje.

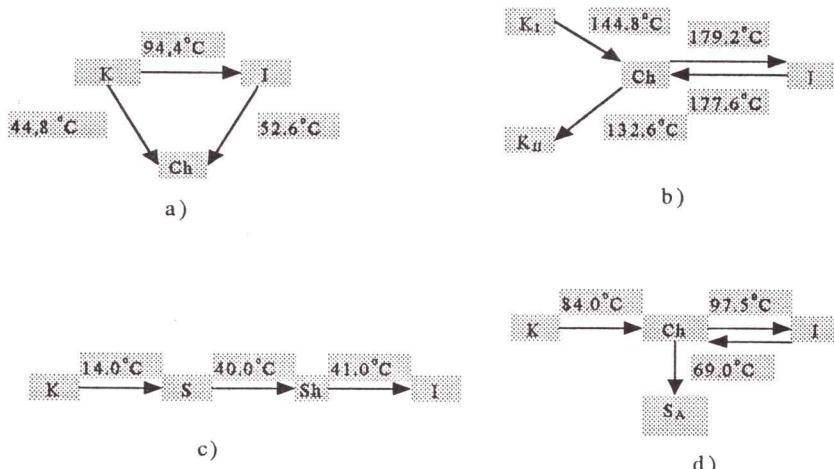
## STRUCTURAL INVESTIGATION OF MULTICOMPONENT MIXTURES OF SOME LIQUID CRYSTALS

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In order to determine the structural characteristics of cholesteric mesophase, we have performed the study using the methods of optical microscopy and X-Ray diffraction on the crystal powder of unoriented samples of the following liquid crystals: Cholesteryl chloride, Cholesteryl nonanoate, Cholesteryl oleyl carbonate and their multicomponent mixtures. The following schemes of the phase transitions based on optical studies can be constructed:



Scheme of the phase transitions:

- a) Cholesteryl chloride, b) Cholesteryl benzoate,
- c) Cholesteryl oleyl carbonate, d) Cholesteryl nonanoate

The mixtures were formed in the following mass percents:

Mixture I: 55% Cholesteryl nonanoate, 35% Cholesteryl oleyl carbonate and 10% Cholesteryl benzoate,

Mixture II: 70% Cholesteryl oleyl carbonate, 20% Cholesteryl chloride and 10% Cholesteryl nonanoate.

New mixtures of liquid crystals were chosen in such a way to form mesophases at room temperature. These mixtures were subjected to the radiation of the continual X-Ray spectrum in order to study the shift of the mesophase temperature. It was concluded that, if the mixtures are subject to the radiation in the period of 30 and 60 minutes, the temperature of mesophase formation shifts towards lower temperatures in the range from 3° to 7°C. The mixtures react also by the change of colour.

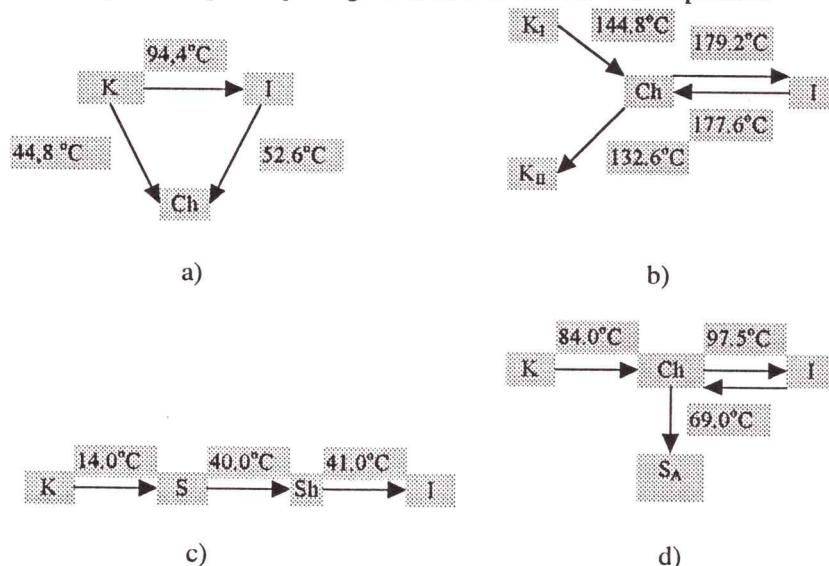
## STRUKTURNA ISPITIVANJA VIŠEKOMPONENTNIH SMEŠA NEKIH HOLESTERIČNIH TEČNIIH KRISTALA

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U cilju određivanja strukturnih karakteristika holesterične mezofaze izvršena su ispitivanja metodom optičke mikroskopije i difrakcije x-raka na kristalnom prahu neorjentisanih uzoraka sledećih tečnih kristala: holesteril hlorida, holesteril benzoata, holesteril nonanoata, holesteril oleil karbonata i njihovih višekomponentnih smeša. Na osnovu optičkih ispitivanja mogu se konstruisati šeme faznih prelaza.



Šeme faznih prelaza: a) holesteril hlorid, b) holesteril benzoat,  
c) holesteril oleil carbonat, d) holesteril nonanoat

Formirane su sledeće smeše u masenim procentima:

I smeša: 55% holesteril nonanoata, 35% holesteril oleil karbonata,  
10% holesteril benzoata

II smeša: 70% holesteril oleil karbonata, 20% holesteril hlorida,  
10% holesteril nonanoata

Novoformirane smeše tečnih kristala odabrane su tako da formiraju mezofaze na sobnoj temperaturi. Ovako formirane smeše tečnih kristala izložene su zračenju kontinualnog spektra x-zraka u cilju ispitivanja pomeranja temperature formiranja mezofaze. Utvrđeno je da, ako se smeša izlože dejstvu x-zraka u vremenskom periodu od 30 i 60 minuta, dolazi do pomeranja temperature formiranja mezofaze ka nižim temperaturama u opsegu od 3°C do 7°C. Pri tome smeše reaguju promenom boje.

## THE CHANGE OF THE STRUCTURE OF THE CATALYST FOR HDS UNDER THE CONDITIONS OF ACCELERATED AGING

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The process of hydrodesulphurization (HDS), being the basic process in the refinery oil treatment, is based on the application of NiO(CoO)/MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts. These catalysts are distinguished by their high ability of removing the sulphur, the nitrogen and metals from the complex hydrocarbons. The catalysts activity, however, decreases during their use as the result of its aging i.e. deactivation.

In this paper we have performed a comparative study of the stability of two types of HDS catalysts: NiO(CoO)/MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> in oxide and sulfide form under the conditions of accelerated aging in the static atmosphere of the air, nitrogen and water vapor at critical temperature under laboratory conditions. Structural changes due to deactivation were registered using XRD and DRS methods. Our previous studies of the aging process of the HDS catalyst have shown that oxidation atmosphere is the critical factor for the kinetics of structural and textural changes [1] and that sintering is one of the basic processes causing the decrease of the activity in inappropriate regeneration conditions [2]. On the basis of the distribution of the intensities of diffraction maxima at  $2\theta \approx 46^\circ$  and  $67^\circ$ , which correspond to the contents of sintered alumina and  $2\theta \approx 23^\circ$  corresponding to the formation of aluminium molibdate, it was concluded that the support sintering is more expressed at Ni- catalysts with respect to Co-catalyst. In addition it is most prominent when the deactivation occurs in the vapor atmosphere. Such intensive sintering is presumably responsible for the intermediary occurrence of the peaks at  $2\theta \approx 29^\circ$  corresponding to MoO<sub>3</sub>, indicating the loss of the active component (MoS<sub>2</sub> crystals are sintered at the support). This process is accompanied by the formation of spinel structure of Co(Ni)-catalyst, due to the interaction of metal ions and the support. The results of these studies represent the basis for the determination of the mechanism of deactivation of the HDS catalyst.

[1] R.Marinković-Nedučin, P.Putanov., Ind.J.Eng.& Mat.Sci. 2, 83 (1995)

[2] R.Marinković-Nedučin, E.Kiš, J.Kiurski, R.Mičić., 37 Int.Conf.  
on Petroleum, Bratislava, D43-1, (1995)

## PROMENA STRUKTURE KATALIZATORA ZA HDS U USLOVIMA UBRZANOG STARENJA

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Proces hidrodesulfurizacije (HDS), kao bazni proces u rafinerijskoj preradi nafte, zasnovan je na primeni NiO(CoO)/MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> katalizatora. Ovi katalizatori se odlikuju visokom sposobnošću uklanjanja sumpora, azota i metala iz kompleksnih ugljovodonika. Medjutim, aktivnost katalizatora tokom upotrebe opada kao rezultat njegovog starenja, odn. deaktivacije.

U ovom radu su vršena komparativna ispitivanja stabilnosti dva tipa katalizatora za HDS : NiO(CoO)/MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, u oksidnom i sulfidnom stanju u uslovima ubrzanog starenja u statičkoj atmosferi vazduha, azota i vodene pare na kritičnoj temperaturi u laboratorijskim uslovima. Strukturne promene nastale deaktivacijom registrovane su primenom XRD i DRS metoda. Naša prethodna ispitivanja procesa starenja katalizatora za HDS su pokazala da je oksidaciona atmosfera kritičan faktor u kinetici strukturalnih i teksturalnih promena [1] i da je sinterovanje jedan od glavnih procesa koji uslovljava pad aktivnosti u neodgovarajućim uslovima regeneracije [2]. Na osnovu raspodele intenziteta difrakcionih maksimuma na  $2\theta \approx 46^\circ$  i  $67^\circ$ , koji odgovaraju sinterovanju postojeće alumine i  $2\theta \approx 23^\circ$  koji odgovara obrazovanju aluminijum-molibdata, utvrđeno je da je sinterovanje nosača izraženije kod Ni-katalizatora u odnosu na Co-katalizator, a najizrazitije je ako se deaktivacija vrši u atmosferi vodene pare. Ovako intenzivnom sinterovanju pripisana je i intermedijarna pojava pikova na  $2\theta \approx 29^\circ$  koji odgovaraju MoO<sub>3</sub>, što ukazuje na gubitak aktivne komponente (MoS<sub>2</sub> kristali se sinteruju na nosaču). Ovaj proces praćen je obrazovanjem spinelske strukture Co(Ni)-katalizatora, nastale interakcijom jona metala i nosača. Rezultati ovih ispitivanja predstavljaju osnovu za utvrđivanje mehanizma deaktivacije katalizatora za HDS.

[1] R.Marinković-Nedučin, P.Putanov., Ind.J.Eng.& Mat.Sci. 2, 83 (1995)

[2] R.Marinković-Nedučin, E.Kiš, J.Kiurski, R.Mićić., 37 Int.Conf.

on Petroleum, Bratislava, D43-1, (1995)

# STRUCTURAL CHARACTERISTICS OF MIXED CRYSTALS

$(Al_{1-x}Fe_x)(H_2O)_6(NO_3)_3 \cdot 3H_2O$

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Five solid solutions of the type  $(Al_{1-x}Fe_x)(H_2O)_6(NO_3)_3 \cdot 3H_2O$  with a compositional range of  $x = 0, 0.25, 0.5, 0.75, 1$  have been prepared from aqueous solutions of isostructural compounds *Al* and *Fe* nitrate nonahydrates. Yellow monocrystals have been crystallized by slow evaporation at room temperature and under atmospheric pressure.

All samples have been analysed by the *X*-ray powder diffraction method under pressure of  $p = p_a$ . The data collection has been carried out on a *PHILIPS PW1350* diffractometer ( $CuK\alpha$  radiation) equipped with a high - temperature supplement *HTK-10* (Anton Paar). Recorded diffractograms of pure samples and mixed crystals confirm isostructurality of obtained crystals. For all samples temperature dependence has been investigated in a range from 16° C to the melting point. Obtained results reveal a structural phase transition at the temperature up to 17° C. This transition should depend on parameter  $x$ , but that measurement was not possible at low temperatures.

The melting point has been found following the powder diffractogram data by raising temperature around melting point in the  $2\theta$  range from 10° to 32° with temperature step of 2° C, until sample began to melt. The melting point of  $Al(H_2O)_6(NO_3)_3$  is 79°C and of  $Fe(H_2O)_6(NO_3)_3$  is 41°C. For mixed crystals the melting point is between those values. The melting point dependence on parameter  $x$  is approximately linear, which corresponds to the solid solutions of substitution type. It has been perceived that sample transits to amorphous form after cooling to ambient temperature.

# STRUKTURNE KARAKTERISTIKE MEŠANIH KRISTALA

$(Al_{1-x}Fe_x)(H_2O)_6(NO_3)_3 \cdot 3H_2O$

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Polazeći od izostrukturnih jedinjenja  $Al$  i  $Fe$  nitrata nonahidrata dobijeni su čvrsti rastvori tipa  $(Al_{1-x}Fe_x)(H_2O)_6(NO_3)_3 \cdot 3H_2O$  metodom mešanja vodenih rastvora ovih jedinjenja u određenom masenom odnosu ( $x = 0; 0,25; 0,5; 0,75; 1$ ). Na sobnoj temperaturi i atmosferskom pritisku laganim isparavanjem iskristalisali su se žućkasti monokristali.

Uzorci su ispitani metodom difrakcije  $x$ -zraka na praškastom uzorku pri pritisku od  $p = p_a$ , korišćenjem difraktometra PHILIPS PW1350 sa  $CuK\alpha$  zračenjem i visokotemperaturskim dodatkom HTK - 10 (Anton Paar). Snimljeni su difraktogrami za čiste uzorce i mešane kristale koji su potvrdili izostruktturnost dobijenih kristala. Za svaki uzorak je ispitana i temperaturska zavisnost difraktograma uzorka u intervalu od  $16^\circ C$  do tačke topljenja. Dobijeni rezultati ukazuju na strukturni fazni prelaz na temperaturi do  $17^\circ C$ . Ovaj prelaz bi trebalo da zavisi od parametra  $x$  ali zbog nemogućnosti merenja na nižim temperaturama ova zavisnost nije izmerena.

Tačka topljenja je nađena praćenjem difraktograma uzorka na povišenoj temperaturi oko tačke topljenja u odabranom intervalu  $2\theta = 10 - 32^\circ$  sa porastom temperature u koracima od  $2^\circ C$ , sve dok nije došlo do topljenja uzorka. Tačka topljenja  $Al(H_2O)_6(NO_3)_3 \cdot 3H_2O$  je  $79^\circ C$ , a  $Fe(H_2O)_6(NO_3)_3 \cdot 3H_2O$   $41^\circ C$ , dok se za mešane kristale nalazi između ovih vrednosti. Zavisnost tačke topljenja od parametra  $x$  je približno linearна što odgovara čvrstim rastvorima tipa zamene. Uočeno je da posle topljenja kristala laganim hlađenjem istog, uzorak prelazi u amorfnu formu.

THE EFFECT OF THE CRYSTALLINE FIELD ON THE TRIGONAL  
DEFORMATIONS IN TRIS(1,2-ETHANEDIOATO)METALLATE(III) IONS\*

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Tris(1,2-ethanedioato) complexes of trivalent transition metal ions are well known three-bladed propeller-like structures which belong to the  $D_3$  point group. The characteristic mode of deformation of these structures is the trigonal twist which may result in the compression or the elongation of the coordination polyhedron with respect to the  $C_3$  axis of symmetry. A quantitative measure of this deformation is provided by the value of the twist angle,  $\omega$  ( $60^\circ$  for the octahedron, or  $0^\circ$  for the trigonal prism).

Among the known crystal structures of tris(1,2-ethanedioato) complexes variations of the twist angle are observed, not only with respect to the ionic radius of the  $M^{III}$  atom, but also within the structures of the same transition metal ion. In order to elucidate the nature of the latter deformations, we have performed molecular mechanics (MM) analysis of the  $[M(C_2O_4)_3]^{3-}$  ion in a fixed environment of the neighbouring ions and/or molecules of the crystal lattice.

Using this approach, we concluded that the crystalline field influences the  $[M(C_2O_4)_3]^{3-}$  structure in a way which is too complex to allow reliable predictions or simple generalizations. However, we were able to pinpoint specific intermolecular interactions (hydrogen bonds and nonbonded contacts) which are responsible for the trigonal twist of the  $[M(C_2O_4)_3]^{3-}$  moiety in each of the 20 crystal structures included in this study.

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\* Dedicated to the memory of Professor Bogdan Prelesnik — a fine teacher and a dear colleague.

UTICAJ KRISTALNOG POLJA NA TRIGONNALNE DEFORMACIJE  
TRIS(OKSALATO)-METALAT(III) JONA\*

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Tris(oksalato) kompleksi trovalentnih jona prelaznih metala predstavnici su poznate klase struktura trolistih propeleri koji pripadaju  $D_3$  grupi simetrije. Karakteristična deformacija ovih struktura je tzv. **trigonali uvrt** koji dovodi ili do kompresije ili do elongacije koordinacionog poliedra u odnosu na njegovu  $C_3$  osu simetrije. Kvantitativno merilo ove deformacije predstavlja uvrtni ugao  $\omega$  ( $60^\circ$  za pravilan oktaedar, odnosno  $0^\circ$  za trigonalnu prizmu).

Medju poznatim kristalnim strukturama tris(oksalato) kompleksa primećene su varijacije uvrtnog ugla, i to ne samo u odnosu na jonski poluprečnik  $M^{III}$  atoma, već i u okviru različitih struktura istog jona prelaznog metala. U cilju da proučimo prirodu ovih potonjih deformacija, mi smo uradili konformacionu analizu  $[M(C_2O_4)_3]^{3-}$  jona u fiksnom okruženju susednih jona i/ili molekula u kristalnoj rešetki metodom molekulske mehanike (MM).

Iz rezultata MM proračuna zaključili smo da je uticaj kristalnog polja na  $[M(C_2O_4)_3]^{3-}$  strukture suviše složen da bi se pomenute deformacije mogle s dovoljno pouzdanosti predvideti, odnosno, da bi se mogle formulisati jednostavne i opšte veze izmedju smera i stepena trigonalnog uvrta i okruženja  $[M(C_2O_4)_3]^{3-}$  jona. S druge strane, MM proračun nam je omogućio da, u svakoj od 20 ispitivanih kristalnih struktura, identifikujemo upravo one intermolekulske interakcije (vodonične veze i/ili nevezivne kontakte) za koje se očekuje da imaju dominantan uticaj na trigonalni uvrt  $[M(C_2O_4)_3]^{3-}$  jedinke.

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**ОРГАНИЗАЦИЈУ ОВЕ КОНФЕРЕНЦИЈЕ ПОМОГЛИ СУ:  
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