СРПСКО КРИСТАЛОГРАФСКО ДРУШТВО

SERBIAN CRYSTALLOGRAPHIC SOCIETY

IX КОНФЕРЕНЦИЈА СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА

Изводи радова

IX CONFERENCE OF THE SERBIAN CRYSTALLOGRAPHIC SOCIETY

Abstracts

БЕОГРАД – BELGRADE
2001

ISSN 0354-5741

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Издавач - Publisher
- Српско Кристалографско Друштво,
Ђушина 7, 11000 Београд, Југославија, тел./факс: 635 – 217
- Serbian Crystallographic Society
Đušina 7, 11000 Beograd, Yugoslavia, phone/fax: 381 – 11 – 635 – 217

За издавача – For the publisher
Љиљана Карановић – Ljiljana Karanović

Технички уредник – Technical editor:
Агнеш Капор – Agneš Kapor
Оливера Марковић – Olivera Marković

Издавање ове публикације омогућено је финансијском помоћи Интернационалне уније за кристалографију
This publication is financially supported by International Union of Crystallography

ISSN 0354-5741

Штампа – Printing:
"LINK"
Novi Sad, Futoška 38
"LINK"
Novi Sad, Futoška 38

Тираж – Copies: 100
Нови Сад – Novi Sad
2001

IX КОНФЕРЕНЦИЈА
СРПСКОГ КРИСТАЛОГРАФСКОГ ДРУШТВА
Нови Сад, 20. – 22. 9. 2001

IX CONFERENCE
OF THE SERBIAN CRYSTALLOGRAPHIC SOCIETY
Novi Sad, 20. – 22. 9. 2001

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ПЛЕНАРНА ПРЕДАВАЊА

CRYSTALLOGRAPHY AND STRUCTURAL BIOLOGY: STRUCTURE-ACTIVITY RELATIONSHIPS

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Half of the century after X-rays discovery, a new scientific field - crystallography has been opened. At the beginning crystallography has been applied to the minerals and other inorganic compounds, and much latter to the biological structures. Diffraction of X-rays and computer analysis of experimental data are nowadays the predominant techniques in structural biology and molecular biophysics. One of the most important projects in the world, "Human Genome Project" [1], could not be realized without this technique.

1. X-ray structural analysis of biological molecules

Biologicaly important molecules could be divided in two groups. The first one is made by small molecules (consisting of not more than 100 atoms). They are often activators or inhibitors of some biological processes (steroid hormones, for example). The second group are macromolecules, formed by thousands of atoms. The structure of complex biological systems - proteins [2], consisting of several hundred thousands of atoms, can be obtained today. From 1990 all structures of macromolecules are systematized in "Macromolecular Structures" [3]. About two thousand of structures have been published until now. There are books devoted to the specific group of proteins [4], or specific subjects [5].

Dorothy Hodgkin was the person who obtained the first-ever X-ray diffraction picture from crystalline protein (pepsin in 1934). She was a leader of the group that solved the structure of the first antibiotic - penicillin; a decade later, the structure of vitamin B_{12}; and another decade later, the structure of insulin. She was awarded by Nobel Prize in Chemistry 1964 [6]. The important event in structural biology was a first structural determination of DNA [7], myoglobin [8], and hemoglobin [9], which elucidated the first picture of biological processes at the atomic level. Nobel Prize crowned all of these works.

The structure of hemoglobin was followed by a big number of enzyme structures [10]; the structure of the photoactive yellow protein [11]; the structure of the viruses (bluetongue virus has M ~ 54 x 10^6 and d ~ 700 Å [12]); special attention was paid to flexibility in the free and inhibitor-bound HIV protease and possibility of drug design [13]. Quite a number of papers are devoted to the interaction of proteins with DNA, DNA - RNAs interaction, the role of *t*RNA and *m*RNA and the problems of recognition and transcription [14,15,16]. All this will make possible the struggle against cancer and some other diseases at the atomic level.

2. Structure-activity relationships

Structure-activity relationship can be explained by the interaction between the steroid receptors and hormones. The structure of estrogen receptor, DNA-binding domain/DNA complex, was published in 1993 [17]. The estrogen receptor is an example of steroid hormone receptors. It belongs to a superfamily of nuclear hormone receptors that are ligand-activated DNA-binding transcription factors. They regulate gene expression by binding to DNA response elements associated with their target genes and are involved in

the control of diverse cellular processes. The estrogen receptor binds DNA as a dimmer and the binding activity is localized to a small 70 amino acid domain. This domain contains two zinc-binding sites. Double zinc finger motif is common to other steroid hormone receptors. The structure of each monomer consists of a pair of α-helices packed at right angles and crossing near their midpoints. Each monomer recognizes a six base pair half site.

The steroid hormones are a group of naturally occurring organic compounds and their synthetic derivatives, which are characterized by a strong biological activity. All steroid hormones function via a common pathway: by diffusing into cells and occupying receptors. These receptors then bind hormone response elements on the DNA and interact with the transcriptional machinery to activate or repress transcription of target genes [18]. Some specific steroids play an important role in the cause and cure of cancer. The way in which a given steroid hormone acts in normal, a cancerogenic, or a cancerostatic process is a function of its total structure [19]. Steroids, including 17β-estradiol and androst-5-ene-3β,17β-diol, are potent stimulators of Brest and uterus cancer cell growth. 5α-dihydrotestosterone, a potent male sex hormone (androgen) is implicated in benign prostate hyperplasia and prostate cancer. Steroid receptor/hormone complex is a target for drug design.

Some synthetic estrogen and androgen analogs exibit antiestrogenic and antiandrogenic activity. It has been established that they could act in two ways:

1. competing with natural steroids in biding the specific protein receptor;
2. inhibiting certain enzyms in steroidogenesis in target cells.

Human estrogenic 17β-hydroxysteroid dehydrogenase (17β-HSD) is responsible for the last step of the biosynthesis of 17β-estradiol, the most potent naturally occurring human estrogen and a potent stimulator of breast cancer. It is a member of a superfamily of oxo-reductases, known as short-chain dehydrogenases. The structure of 17β-HSD, as well as of the other similar enzymes [20,21,22], provides a template for design of specific inhibitors as drugs for cancer therapy [23].

More then hundred of potential antiestrogens and antiandrogens have been synthesized by the group of physicists, chemists and biologists from the Faculty of Sciences, University of Novi Sad. For some of them the structure was solved using X-ray structure analysis. Their activity was examined by different biochemical methods. The general idea was the modification of D-ring in estrogens and androgens, which provokes conformational flexibility and, consequently, the change of activity. Most of the compounds belong to 16,17-seco steroids [24,25,26]. One of the compounds exhibits a significant affinity to Cytochrome P450 aromatase [27], the enzyme that catalyzes conversion of androgens into estrogens in the last step of estrogen biosynthesis [28]. Compounds that inhibit aromatase reaction have potential applications in the treatment of advanced estrogen-dependent tumors such as breast cancer, prostatic hyperplasia, and prostate cancer.

3. Prospective

From the beginning of protein crystallography a numerous series of protein structures were solved. There is still a lot of job for the crystallographers. "Human Genome Project" defined the structures of a 100.000 genomes to be solved (it seems that there is "only" 30.000 genomes). Eventually we may see the sequencing of entire genomes and their associations with other macromolecular compounds. The "mistery" of the ribosomes, their functional universality and revolutionary diversity will be the challenge for crystallographers [29]. The questions concerning growing crystals of biomacromolecules will be the task for them too, particularly for the membrane-bound proteins because of their

intransigens to solubilization and crystallization. Further development of the macromolecular synchrotron crystallography will be of great help.

But, understanding biological function requires more than knowing structures and understanding of molecular recognition. It requires knowing why the interaction needs to occur at all. The time will soon come, when the scientists will ask for more detail and precision inferences drown from complete genomes. *This enzyme is very like that one, but how do its catalytic properties differ and why? These genes are controlled by that promoter, but what transcription factor does it need and under what circumstances will they be expressed? Can we foresee the effects of amino acid substitution at the active site? Or, can we predict reaction rates?* A "Nature" editorial in 1999 [31] was: can physics deliver another biological revolution? The answer could be in protein engineering, or the creation of ribosomes. The design of proteins that manifest a specified target backbone structure is becoming possible. Future advances are likely to follow from a tight coupling of experimental and computational work in a protein design cycle, with ever-larger protein sequences designed *de novo* being revealed in the near future.

This is already in progress. So many activities are going on that it is hard to keep up with all developments on so many frontiers. There is no knowledge how far the way physical scientists and molecular biologists interact in research will lead. Or, where it will direct us?

Acknowledgements

The author thanks to Professors Christian Courseille and Gilles Precigoux for the invitation to work at the "Unité de Biophysique Structurele", financially supported by Université Bordeaux 1, and the opportunity to use diffractometer, library and all other facilittes in the Laboratory.

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KRISTALOGRAFIJA U STRUKTURNOJ BIOLOGIJI: VEZA IZMEĐU STRUKTURE I AKTIVNOSTI

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Pola veka posle otkrića x-zraka počela je da se razvija nova naučna oblast - *kristalografija*, koja je, na osnovu analize podataka dobijenih difrakcijom x-zraka na kristalnoj rešeci, omogućila spoznaju strukture tela na atomskom nivou. Primenjivana u početku na odredjivanje struktura minerala i drugih neorganskih materijala, kasnije je omogućila potpuno poznavanje strukture bioloških molekula i time načinila ogroman prodor u strukturnoj biologiji i molekularnoj biofizici. Difrakcija x-zraka i kompjuterska analiza dobijenih eksperimentalnih podataka predstavljaju danas dominantnu tehniku u ispitivanju bioloških struktura na atomskom nivou. Bez ove tehnike ne bi se mogao ni zamisliti niti realizovati jedan od danas najznačajnijih projekata svetske nauke "Human Genome Project" [1], čiji je zadatak određivanje strukture i mapiranje svih humanih gena i njihovih produkata.

1. Rendgenska strukturna analiza bioloških molekula

Biološki značajni molekuli se mogu podeliti u dve osnovne grupe. Prvu grupu čine mali molekuli formirani od oko 100 atoma, koji, izmedju ostalog, mogu imati ulogu aktivatora ili inhibitora bioloških procesa. Primer takvih molekula su steroidni hormoni. Oni su često i farmakološki interesantni. Drugu grupu čine makromolekuli, kod kojih se broj atoma izražava u hiljadama. Danas je moguće dobiti preciznu sliku kompleksnih bioloških sistema - *proteina* [2], čiji molekuli sadrže od više hiljada do više stotina hiljada atoma. Od 1990. godine sve rešene strukture makromolekula sistematizovane su u seriji knjiga, koje se publikuju jednom godišnje pod nazivom "Macromolecular Structures" [3]. Do sada je objavljeno oko 2000 struktura. Poslednjih godina publikovane su knjige koje su posvećene pojedinim grupama proteina [4], ili serije u kojima je jedna knjiga posvećena posebnoj problematici [5].

Slava pionira u istraživanjima strukture bioloških molekula pripada engleskoj naučnici Dorothy Hodgkin, koja je 1945. godine odredila strukturu penicilina, a 1957. godine strukturu vitamina B12 i za to dobila Nobelovu nagradu 1964. godine [6]. 1969. godine odredila je strukturu insulina. Značajan momenat u strukturnoj biologiji je bilo prvo odredjivanje strukture DNK [7], a zatim mioglobina [8] i hemoglobina [9], što je omogućilo dobijanje *prve slike bioloških procesa na nivou atoma*. Svaki od ovih radova krunisan je Nobelovom nagradom.

Od otkrića strukture hemoglobina određene su strukture velikog broja proteina. Tu je, pre svega, velika grupa *enzima*. Poznavanje ovih struktura omogućilo je pogled u mehanizam katalitičkog dejstva enzima [10]. Poznavanje strukture *centra fotosintetske reakcije* bakterija omogućilo je razumevanje mehanizma konverzije svetlosne u hemijsku energiju i rezultiralo još jednom Nobelovom nagradom za 1989. godinu. Zahvaljujući savremenoj tehnici, koja koristi polihromatsko x-zračenje dobijeno pomoću sinhrotrona,

mogla je da se odredi struktura intermedijera u fotosintetskoj reakciji [11] i na taj način prati proces u svim fazama. Sledeća velika grupa proteina su *virusi*, najveći molekuli kojima se do sada bavila kristalografija. Molekul "bluetongue" virusa, na primer, ima molekulsku težinu M ~ 54 x 10^6 i dijametar ~ 700Å [12]. Određivanje strukture HIV-a i njihovih kompleksa sa odgovarajućim enzimima, kao i praćenje konformacionih promena molekula u nanosecundama, predstavljaju solidnu osnovu za razvijanje potencijalnih lekova i vakcina protiv AIDS-a [13].

Od prvog određivanja strukture DNK 1953. godine do danas, objavljen je veliki broj radova posvećen razumevanju načina vezivanja proteina za DNK [14]. Listi treba dodati strukturu *transportne RNK*, molekula koji igra ključnu ulogu u sintezi proteina [15]. Precizno određivanje strukture je pokazalo kako genetski kodoni sadržani u *informacionoj RNK*, koja je direktni replikant transkribovan sa DNK gena, mogu biti pročitani i prevedeni u odgovarajuće amino kiselinske ostatke proteina [16]. Time je borba protiv kancera spuštena na nivo gena.

2. Veza između strukture i aktivnosti

Veza između strukture i aktivnosti može se objasniti na primeru interakcije steroidnog receptora i odgovarajućeg hormona. Struktura estrogenog receptora i njegovog kompleksa sa DNK je publikovana početkom 90-tih godina [17]. Estrogeni receptor je primer receptora steroidnih hormona. Kao i ostali članovi te familije, dolazeći u jedro ćelije vezuje se za odgovarajući domen DNK i stupa u interakciju sa transkripcionom mašinerijom u cilju aktiviranja ili represije transkripcije ciljnih gena [18]. Posledica ove interakcije može biti rast ćelija kancera. Da bi kao transkripcioni faktor stupio u interkciju sa DNK, receptor se mora prethodno aktivirati vezivanjem steroidnog hormona određene strukture i promeniti svoju konformaciju. To znači da su steroidni hormoni posredno stimulatori rasta ćelija kancera, te je od izuzetne važnosti poznavanje strukturnih karakteristika *kompleksa steroidni receptor - hormon*, koji je glavna meta za dizajniranje lekova u cilju sprečavanja njegovog formiranja.

Steroidni hormoni su grupa prirodnih organskih jedinjenja i njihovih sintetičkih derivativa. Svi funkcionišu na jednak način - difuzijom u ćelije i vezivanjem za receptore. Dejstvo steroidnih hormona u normalnim, kancerogenim ili kancerostatičkim biološkim procesima je funkcija njihove totalne strukture [19]. Način vezivanja steroidnih hormona za odgovarajuće receptore može se nedvosmisleno utvrditi samo na osnovu preciznog poznavanja strukture aktivnih mesta receptora i hormona. U kompleksu estrogenog receptora sa DNK, receptor ima formu dimera sastavljenih od dva para α-heliksa, koji stoje pod uglom od 90^0 i ukrštaju se u blizini središnje tačke. Dva kraja dimera se vezuju za DNK. Svaki monomer prepoznaje šest baznih parova polovine mesta vezivanja. Domen vezivanja proteina sastoji se od 70 aminokiselina. Vezivanje se ostvaruje preko dva Zn-prsta i velikog broja vodoničnih veza. Do sada nije određena struktura kompleksa receptor - hormon, pa se može samo pretpostavljati da se hormon vezuje za svaki od dva monomera.

50-tih godina prošlog veka prvi put je uočeno da postoji korelacija između primene estrogena u kontracepciji i prevenciji osteoporoze i učestalosti pojave kancera dojke i uterusa kod žena. Nametao se zaključak da estrogeni hormoni dovode do pojave kancera. Kod muškaraca 5α-dihidrotestosteron, potentni polni androgeni hormon, učestvuje u pojavi benigne hiperplazije i kancera prostate. Ovo su samo dva najčešća slučaja učestvovanja steroidnih hormona u kancerogenezi. S obzirom da se steroidni hormoni sintetišu i u samom organizmu, u borbi protiv njihovog kancerogenog dejstva primenjuju se dve taktike:

1. Kompeticija neaktivnih molekula sa prirodnim steroidnim hormonima u vezivanju za specifične proteinske receptore;

2. Presecanje lanca steroidogeneze inhibicijom određenih enzima.

Kompeticija će se desiti ako se u organizam unose supstrati čiji molekuli imaju veliki afinitet prema određenom receptoru. Vezivanjem za receptor oni blokiraju aktivna mesta i sprečavaju vezivanje steroidnih hormona. Presecanje lanca steroidogeneze ostvaruje se inhibiranjem enzima, čijim se dejstvom u organizmu neaktivni i/ili slabo aktivni steroidni hormoni prevode u veoma aktivne. Primer takvog enzima je humana *17β-dihidroksisteroid dehidrogenaza (17β-HSD)*. Pripada značajnoj klasi enzima uključenih u biogenezu, aktiviranje ili inaktiviranje steroidnih hormona [20,21,22]. Zbog toga predstavljaju, kao i mnogi drugi enzimi i receptori, atraktivnu metu za dizajniranje inhibitora produkcije estrogena i rasta tumora [23].

Na Prirodno-matematičkom fakultetu u Novom Sadu grupa hemičara, fizičara i biologa, bavi se skoro dvadeset godina ovom problematikom. Sintetizovano je preko sto jedinjenja potencijalnih antiestrogena i antiandrogena od kojih je odabrano nekoliko desetina i podvrgnuto strukturnim i biološkim analizama. Ova grupa se orijentisala na modifikaciju D prstena i njegove supstituente. Najveći broj jedinjenja pripada grupi 16,17-D-seko steroida, kod kojih je raskinuta C16-C17 veza D prstena i time povećana fleksibilnost molekula. Istraživanja su potvrdila neke pretpostavke u vezi sa aktivnošću steroidnih hormona, a dobijeni su i vredni rezultati [24,25,26].

Najnovija ispitivanja serije 17-keto-17metil-16-nitril-16,17-seko androstena pokazala su da jedno od jedinjenja ima značajan afinitet prema enzimu citohrom P450 aromataze (P450arom) [27]. Ovaj enzim je vezan za membranu, kao takav praktično nerastvorljiv i ne može kristalisati, te mu se struktura ne može odrediti kristalografskim metodama. Zbog toga je trodimenzionalna struktura enzima modelirana kompjuterski na bazi poznavanja struktura drugih članova velike familije P450 proteina [28]. P450arom katalizira, u prisustvu NADPH kofaktora, konverziju androgena u estrogen u poslednjem koraku biosinteze.

3. Perspektive

U proteklom periodu od otkrića strukture hemoglobina određene su strukture velikog broja proteina. Međutim, posao kristalografa na ovom polju će trajati godinama, mada se danas u svetu reši bar jedna struktura dnevno. Sam "Human Genome Project" je definisao više desetina hiljada gena, pri čemu većina njihovih produkata ima višestruko funkcionalno stanje i asocijacije sa drugim makromolekularnim komponentama. Ovome treba dodati najnovija ispitivanja strukture ribozoma, koja uvode kristalografiju u samu srž molekularne genetike i evolucije [29]. U zenitu primene kristalografskih metoda u strukturnoj biologiji naučnici počinju da razmatraju i nedostatke. Neki od njih će se otkloniti tehnološkim napretkom u kristalizaciji supstrata, izvorima zračenja ("nanosecond time-resolved crystallography" [30]) i detektorima, daljim razvojem kompjutera i kompjuterskih programa i sl. Postoje, međutim, problemi koji se na ovaj način ne mogu rešiti. Interakcija mernih instrumenata i ispitivanog supstrata je nerešiv problem za sve naučne oblasti, pa i za proteinsku kristalografiju, koja i dimenziono i vremenski duboko zalazi u mikrosvet. A naučnici žele da znaju mnoge detalje i postavljaju mnoga pitanja. Kako i zašto se kod veoma sličnih enzima razlikuju katalitičke osobine? Geni su kontrolisani nekim promoterom, ali pod kojim uslovima će nastati njihova ekspresija? Kako možemo analizirati i predvideti brzinu neke reakcije? U editorijalu časopisa "Nature" pojavilo se pre dve godine pitanje: može li fizika da porodi novu biološku revoluciju [31]?

Jedan od odgovora je u proteinskom inženjeringu, dizajniranju delova ili *de novo* proteina, kreaciji ribozoma koji se uveliko već rade. Ali gde će nas to odvesti?

Zahvalnost

Autor zahvaljuje profesorima Kristijanu Kurseju i Žilu Presigou na pozivu za jednomesečni boravak u Laboratoriji za strukturnu biofiziku, finansiran od strane Univerziteta Bordo 1, kao i za mogućnost korišćenja difraktometra, biblioteke i ostale opreme.

STUDY OF NONCOVALENT INTERACTIONS BY SEARCHING CRYSTAL STRUCTURES IN DATA BANKS

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Two types of noncovalent interactions have been studied: interactions of imidazole axially coordinated to heme in heme-proteins and new type of cation-π interactions - metal ligand aromatic cation-π (MLACπ) interactions.

The factors determining conformations of imidazole axially coordinated to heme in heme-proteins have been found by analyzing crystal structures of heme-proteins and by theoretical modeling of the found interactions [1]. It was shown that there are two main factors that determine the orientations of imidazole ligated to heme. These are the interactions of imidazole with the propionic acid side chains of heme and with the histidine backbone. Generally the NH-group of imidazole is oriented towards the PR groups of the heme. The imidazole adopts also a preferred orientation with respect to its histidine backbone, such that the plane of the imidazole ring is practically never parallel to the Cα-Cβ bond of its histidine backbone. Only in crystal structures of cytochrome c peroxidase the orientation of the imidazole is determined by a strong hydrogen bond of the NH-group with the aspartate.

The interaction of ligands coordinated to a metal with aromatic π-systems, metal ligand aromatic cation-π (MLACπ) interactions, were predicted by quantum chemical calculations and it was proposed that this type of interactions can exist in metalloproteins [2]. MLACπ interactions in metallo-proteins were found out by searching crystal structures of metallo-proteins from the Protein Data Bank [3]. These data reveal that there are quite a number of metallo – proteins, where aromatic rings from phenylalanine, tyrosine, and tryptophan are close to a metal center interacting with coordinated ligands. These interactions play a role in stability and conformation of metallo – proteins, and in some cases may also be directly involved in the mechanism of enzymatic reactions, which occur at the metal center.

Searching crystal structures of transition metal complexes from Cambridge Data Base (CDB) reveals that there are quite a number of metal complexes, where an aromatic ring interacts with a hydrogen atom from a ligand in the same complex [4]. By quantum chemical computations it was evaluated for the model systems of cationic cobalt(III) complexes with charge of +1, that the energy of the intramolecular MLACπ interaction is about 4 kcal/mol.

[1] S. D. Zarić, D. Popović, and E. W. Knapp, Chemistry Eur. J. 6, (2000), 3935-3942.
[2] S. D. Zarić,Chem. Phys. Lett. 311, (1999) 77-80.
[3] S. D. Zarić, D. Popović, and E. W. Knapp, Biochemistry, 40, (2001), 7914-7928.
[4] M. Milčić and S. D. Zarić, Eur. J. Inorg. Chem, (2001), 2143-2150.

PROUČAVANJE NEKOVALENTNIH INTERAKCIJA PRETRAŽIVANJEM KRISTALNIH STRUKTURA U BANKAMA PODATAKA

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Dva različita tipa nekovalntnih interakcija su proučavana: interakcije imidazola aksijalno koordinovanog na hem u hem-proteinima i novi tip katjon-π interakcija - interkcije liganada koordinovanih za metal, sa aromatičnim grupama (MLACπ).

Faktori koji utiču na konformacije imidazola koji je aksijalno koordinovan na hem u hem-proteinima pronadjeni su na osnovu proučavanja kristalnih struktura hem-proteina i pomoću teorijskog modelovanja nađenih interakcija [1]. Pokazano je da postoje dva glavna faktora koja odredjuju orijentaciju imidazola vezanog za hem. To su interakcije imidazola sa bočnim propionatnim grupama (PR) na hemu, i sa ostatkom molekula histidina. Generalno, NH-grupa imidazola je orijentisana ka PR grupama hema. Imidazol takodje zauzima i preferentne orijentacije u odnosu na ostatak molekula histidina, tako da ravan imidazola praktično nikada nije paralelna sa Cα-Cβ vezom histidina. Samo u slučaju kristalne strukture citohrom c peroksidaze, orijentacija imidazola je određena jakom vodoničnom vezom NH-grupe sa aspartatom.

Interakcije liganada koordinovanih za metal sa π-sistemima aromatičnih molekula, MLACπ interakcije, bile su predvidjene kvantno hemijskim proračunima i bilo je pretpostavljeno da ovakav tip interakcija može da se javlja u metaloproteinima [2]. MLACπ interakcije u metaloproteinima su pronađene pretraživanjem kristalnih struktura iz Protein Data Bank (PDB) [3]. Ovi podaci pokazuju da postoji prilično veliki broj metaloporteina gde se aromatični prsten fenilalanina, tirozina i triptofana nalazi blizu metalnog centra i interaguje sa koordinovanim ligandima. Ove interakcije igraju ulogu u stabilizaciji konformacije metaloproteina a nekada mogu direktno biti uključene i u mehanizam enzimatskih reakcija koje se dešavaju na metalnom centru.

Pretraživanje kristalnih struktura kompleksa prelaznih metala iz Cambridge Data Base (CDB), pokazuje da postoji veliki broj kompleksa metala gde aromatični prsten interaguje sa vodonikovim atomima liganada koji se nalaze u istom kompleksu [4]. Na osnovu kvantno hemijskih proračuna, koji su uradjeni na model sistemima katjonskih kobalt(III) kompleksa sa naelektrisanjem +1, procenjeno je da je energija ovih intramolekulskih MLACπ interakcija oko 4 kcal/mol.

[1] S. D. Zarić, D. Popović, and E. W. Knapp, Chemistry Eur. J. 6, (2000), 3935-3942.
[2] S. D. Zarić,Chem. Phys. Lett. 311, (1999) 77-80.
[3] S. D. Zarić, D. Popović, and E. W. Knapp, Biochemistry, 40, (2001), 7914-7928.
[4] M. Milčić and S. D. Zarić, Eur. J. Inorg. Chem, (2001), 2143-2150.

ORAL PRESENTATION

САОПШТЕЊА

SYNTHESIS AND CRYSTAL STRUCTURE OF 3β-HYDROXY-17-PICOLINYLIDENE-5α-ANDROSTANE

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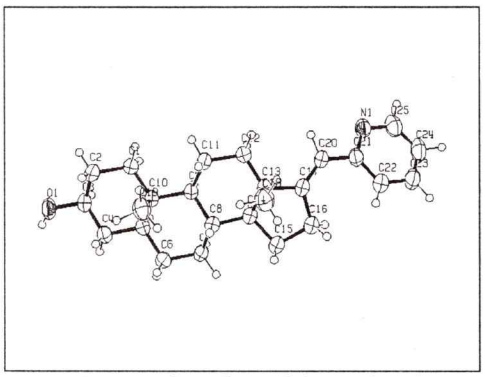
3β-Hydroxy-17-picolinylidene-5α-androstane was obtained in three steps starting from 3β-acetoxy-5α-androstan-17-one. These steps were involved: a) stereospecific addition of α-picolyllithium to the C-17 carbonyl group of starting compound; b) regioselective 17,20-dehidration of the formed diol and c) hydrolysis of formed 3β-acetoxy group.

The compound crystallyzes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters a=11.0264(12), b=11.3096(14), c=17.124(2)Å, Z=4, D_x=1.137 Mgm^{-3}, μ=0.07 mm^{-1}, MoK_α radiation.

The crystal structure was solved by direct methods on the basis of 2402 indipendent reflections using SIR 92 [1], and refined by SHELXL-97 [2]. The final R factor is 0.0315 for 1432 reflections with I>4σ(I).

Hydrogen atoms were generated except two hydrogen atoms in positions 5 and 20. The positions of these two hydrogen atoms were found from ΔF map.

Molecules are conected by O–H.....N hydrogen bond, forming the coils along the x-axis.



Perspective view of the molecule

[1] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori & M. Camalli, SIR92, *J. Appl. Cryst.* **27**, (1994), 435

[2] G.M.Sheldrick, (1997) SHELXL-97, *Program for the refinement of crystal structures*, University of Goettingen, Germany.

SINTEZA I KRISTALNA STRUKTURA 3β-HIDROKSI-17-PIKOLINILIDEN-5α-ANDROSTANA

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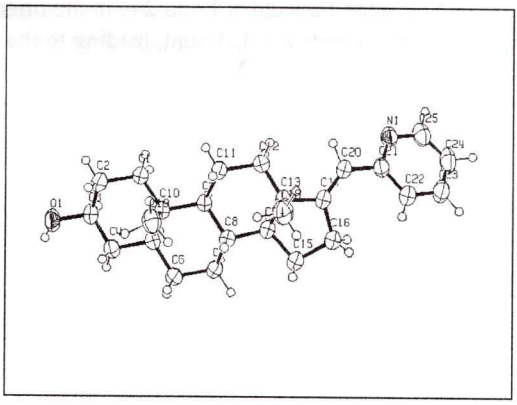
3β-Hidroksi-17-pikoliniliden-5α-androstan je dobijen u tri faze polazeći od jedinjenja 3β-acetoksi-5α-androstan-17-on. Ova tri koraka su: a) stereospecifična adicija α-pikolillitijuma na C-17 karbonilnu grupu polaznog jedinjenja; b) regioselektivna 17,20-dehidratacija dobijenog diola i c) hidroliza dobijene 3β-acetoksi-grupe.

Jedinjenje kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije a=11,0264(12), b=11,3096(14), c=17,124(2)Å, Z=4, D_x=1,137 Mgm^{-3}, μ=0,07 mm^{-1}, MoK_α zračenje.

Kristalna struktura je rešena na bazi 2402 nezavisnih refleksa uz pomoć SIR 92 [1] i utačnjena pomoću SHELXL-97 [2]. Konačna vrednost R faktora je 0,0315 za 1432 refleksa sa I>4σ(I).

Atomi vodonika su generisani, osim dva H-atoma u položajima 5 i 20. Položaji ova dva H-atoma su određeni iz ΔF-mape.

Molekuli su povezani O-H.....N vodoničnom vezom i obrazuju spiralu duž x-ose.



[1] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori & M. Camalli, SIR 92, *J. Appl. Cryst.* **27**, (1994), 435

[2] G.M.Sheldrick, (1997) SHELXL-97, *Program for the refinement of crystal structures*, University of Goettingen, Germany.

SYNTHESIS AND CRYSTAL STRUCTURE INVESTIGATIONS OF TWO ANDROSTENE DERIVATIVES

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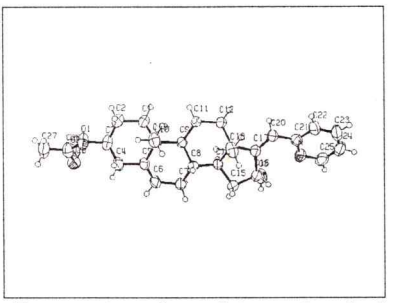
(Z)-3β-Acetoxy-16β-hydroxy-17-picolinylidene-5-androstene (**1**) and (E)-3β-Acetoxy-16β-hydroxy-17-picolinylidene-5-androstene (**2**) were synthesized from two isomeric 3β-acetoxy–17-picolinydene-5-androsten-16-ones whose absolute configurations have been determinated earlier [1].

The compound **1** crystallyzes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters a=7.8949(1), b=10.5960(1), c=28.1774(4)Å, Z=4, D_x=1.174 Mgm^{-3}, μ=0.08 mm^{-1}, MoK_α radiation.

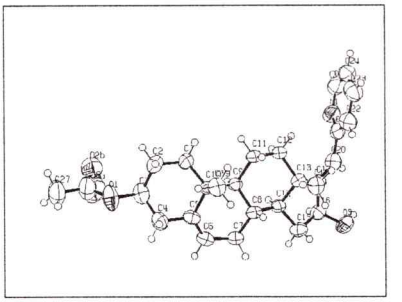
The compound **2** crystallyzes in the monoclinic system, space group $P2_1$, with the unit cell parameters a=12.095(2), b=6.166(2), c=15.887(2)Å, β=103.50(1)°, Z=2, D_x=1.215 Mgm^{-3}, μ=0.614 mm^{-1}, CuK_α radiation.

Both structures were solved by direct methods using SHELXS-97 [2], and refined by SHELXL-97 [2]. The final R factors for compounds **1** and **2** are 0.0571 (for 3587 reflections with $I>4\sigma(I)$) and 0.0475 (for 1417 reflections with $I>2\sigma(I)$), respectively.

The basic difference between molecules **1** and **2** is in the orientation of pyridine ring. Consequently, packing arrangements are different, leading to the existance of the hydrogen bond network only in the compound **2**.



Perspective view of the molecule **1**



Perspective view of the molecule **2**

[1] S. Stanković, B. Ribar, D. Miljković, K. Gaši, C. Courseille, Structures of two isomeric 17-picolinylidene derivatives of 5-androsten-16-ones, *Acta Cryst.* **C45** (1989),491-495

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

SINTEZA, STRUKTURNA I KRISTALOGRAFSKA ISTRAŽIVANJA DVA DERIVATA ANDROSTENA

O. Marković[a], S. Stanković[a], D. Lazar[a], Ch. Courseille[b], E. Đurendić[a], Lj. Medić-Mijačević[a]

[a]Prirodno-matematički fakultet, Univerzitet u Novom Sadu, Trg Dositeja Obradovića 4, 21000 Novi Sad, Jugoslavija, [b]Lab. Université Bordedaux 1, Avenue des Facultés, Bât B8-33405 Talence Cedex, Bordedaux, France
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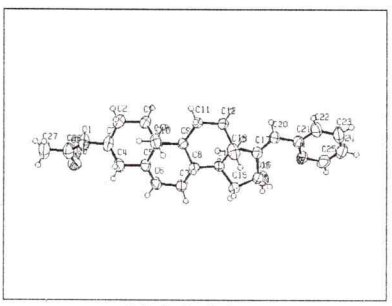
(Z)-3β-Acetoksi-16β-hidroksi-17-pikoliniliden-5-androsten (**1**) i (E)-3β-Acetoksi-16β-hidroksi-17-pikoliniliden-5-androsten (**2**) su sintetizovani iz dva izomerna 3β-acetoksi–17-pikoliniden-5-androsten-16-ona, čije su apsolutne konfiguracije određene ranije [1].

Jedinjenje **1** kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije a=7,8949(1), b=10,5960(1), c=28,1774(4)Å, Z=4, D_x=1,174 Mgm^{-3}, μ=0,08 mm^{-1}, MoK_α zračenje.

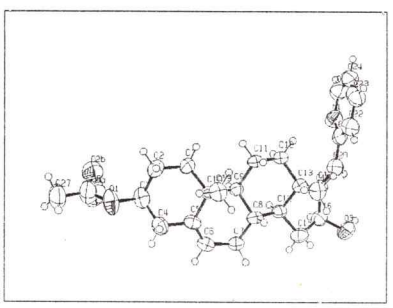
Jedinjenje **2** kristališe u monokliničnom kristalografskom sistemu, prostorna grupa $P2_1$, sa parametrima elementarne ćelije a=12,095(2), b=6,166(2), c=15,887(2)Å, β=103,50(1)°, Z=2, D_x=1,215 Mgm^{-3}, μ=0,614 mm^{-1}, CuK_α zračenje.

Obe strukture su rešene direktnim metodama primenom SHELXS-97 [2] i utačnjene pomoću SHELXL-97 [2]. Konačni R faktori za jedinjenja **1** and **2** su 0,0571 (za 3587 refleksa sa I>4σ(I)) i 0,0475 (za 1417 refleksa sa I>2σ(I)), respektivno.

Osnovna razlika između molekula **1** i **2** je u orijentaciji piridinskog prstena. Sledstveno tome, pakovanje molekula u kristalu je različito, tako da se mreža vodoničnih veza javlja samo u jedinjenju **2**.



Molekul **1**



Molekul **2**

[1] S. Stanković, B. Ribar, D. Miljković, K. Gaši, C. Courseille, Structures of two isomeric 17-picolinylidene derivatives of 5-androsten-16-ones, *Acta Cryst.* C45 (1989),491-495

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

SYNTHESIS AND CRYSTAL STRUCTURE OF S-CIS-(ETHYLENDIAMINE-N, N'-DIACETATO) (N, N-DIMETHYLGLYCINATO)COBALT (III)

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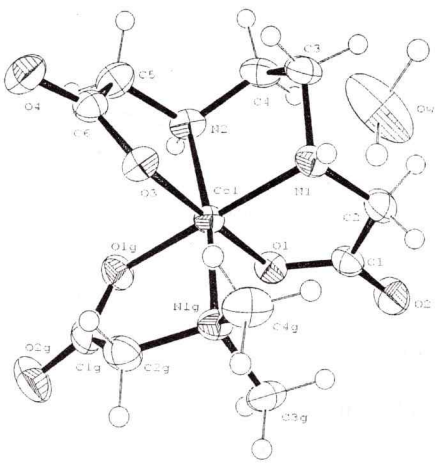
e-mail: snovak@rt270.vin.bg.ac.yu



The *s-cis* geometrical isomer of cobalt(III) complex with *N,N*-dimethylglycine and tetradentate ligand edda (ethylenediamine-*N,N'*-diacetate ion) was prepared by direct synthesis of cobalt(II) chloride hexahydrate with *N,N*-dimethylglycine and edda in the presence of plumbum(IV) oxyde. The complex has been isolated chromatographically and characterized by elemental analysis, electron absorption spectra, infrared spectra and x-ray diffraction analysis.

Crystal data and structure refinement: $C_{10}H_{20}N_3O_7Co$, monoclinic system, space group $P2_1/n$, a = 8.705(2), b = 14.063(4), c = 11.961(5) Å, β = 99.11(3)° V = 1445.8(8) Å^3, Z = 4, Mr = 353.22, D_c = 1.623 Mg/m^3, μ(MoK_α) = 1.224 mm^{-1}, Intensities of 2798 unique reflections are collected on an Enraf-Nonius CAD-4 diffractometer [λ(MoKα) = 0.71073 Å] in range 0 < θ < 26°. The structure was solved using SHELXS97 and refined by SHELXL97 to final R1 = 0.0390 for 2238 (I >2σI) independent reflections and 194 parameters. The largest peak and hole in ΔF map: 0.418 and -0.350 e/Å^3.

SINTEZA I KRISTALNA STRUKTURA S-*CIS*-(ETILENDIAMIN-N,N'-DIACETATO) (N,N-DIMETILGLICINATO) KOBALTA (III)

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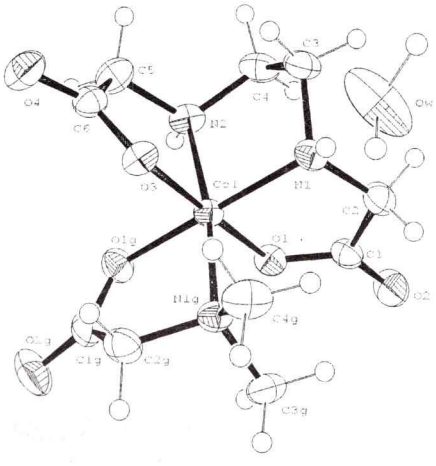
[a]*Institut za nuklearne nauke "VINČA", Laboratorija za teorijsku fiziku i fiziku kondenzovane materije 020/2, P.O. Box 522, 11001 Beograd, Jugoslavija;* [b]*Hemijski fakultet, Univerzitet u Beogradu, p. p. 158, 11001 Beograd, Jugoslavija;*
e-mail: snovak@rt270.vin.bg.ac.yu



S-cis geometrijski izomer kobalt(III) kompleksa sa *N,N*-dimetilglicinom i tetradentatnim ligandom edda (etilendiamin-*N,N'*-diacetat jon) je dobijen direktnom sintezom kobalt(II)-hlorida heksahidrata sa *N,N*-dimetilglicinom i edda u prisustvu olovo(IV)-oksida. Kompleks je izolovan hromatografski i okarakterisan elementarnom analizom, elektronapsorpcionim i infracrvenim spektrima i rendgenskom analizom.

Kristalografski podaci i utačnjavanje: $C_{10}H_{20}N_3O_7Co$, monokliničan sistem, prostorna grupa $P2_1/n$, a = 8,705(2), b = 14,063(4), c = 11,961(5)Å, β = 99,11(3)° V = 1445,8(8) $Å^3$, Z = 4, Mr = 353,22, D_c = 1,623 Mg/m^3, μ(MoK_α) = 1,224 mm^{-1}. Intenziteti 2798 nezavisnih refleksija su izmereni na difraktometru Enraf-Nonius CAD-4 [λ(MoKα) = 0,71073 Å] u rasponu uglova $0 < \theta < 26°$. Struktura je rešena programom SHELXS97 i utačnjena programom SHELXL97 do konačnog R1 = 0,0390 za 2238 ($I > 2\sigma I$) nezavisnih refleksija i 194 utačnjenih parametara. Maksimalni i minimalni pik u konačnoj diferentnoj mapi iznosili su 0,418 and –0,350 e/$Å^3$.

CRYSTAL STRUCTURE OF TRANS-DIBROMO(1,3-PROPYLENEDIAMINE-N,N'-DIACETATO)PLATINUM(IV) MONOHIDRATE

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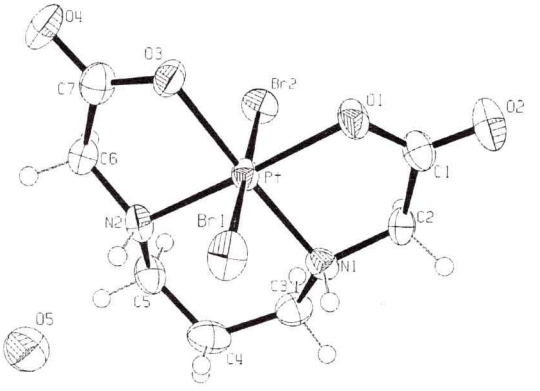

Trans-dibromo(1,3-propylenediamine-*N,N'*-diacetato)platinum(IV) monohydrate was prepared from potassium hexabromoplatinate(IV) and 1,3-propylenediamine-*N,N'*-diacetic acid, in presence of LiOH.

Crystal data and structure refinement: $C_7H_{14}N_2O_5Br_2Pt$, monoclinic system, space group $P2_1/n$, a = 7.304(2), b = 13.839(3), c = 12.769(2) Å, β = 92.71(2)° V = 1289.2(5) Å^3, Z = 4, Mr = 561.11, μ(MoK_α) = 17.092 mm^{-1}, F(000) = 1032. Intensities of 3097 unique reflections were collected on a Enraf-Nonius CAD-4 diffractometer [λ(MoK_α) = 0.71073 Å] in the range of $2 < \theta < 28°$ and they were corrected for absorption. The structure was solved using SHELXS97 and refined by SHELXL97 to the final R1 = 0.0532 for 2260 ($I > 2\sigma I$) independent reflections and 154 parameters.

KRISTALNA STRUKTURA TRANS-(1,3-PROPILENDIAMIN-N,N'-DIACETATO)DIBROMOPLATINA(IV)-MONOHIDRATA

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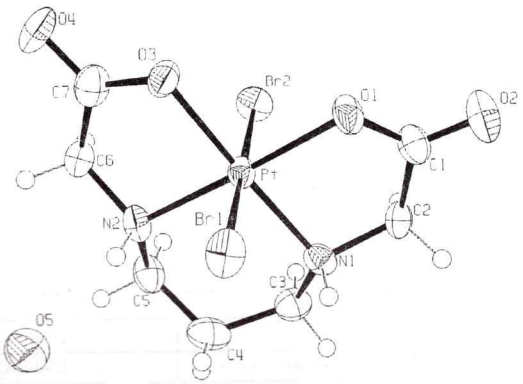

Trans-(1,3-propilendiamin-*N,N'*-diacetato)dibromoplatina(IV)-monohidrat dobijen je u reakciji kalijum-heksabromoplatinata(IV) i 1,3-propilendiamin-*N,N'*-disirćetne kiseline, u prisustvu LiOH.

Kristalografski podaci i utačnjavanje: $C_7H_{14}N_2O_5Br_2Pt$, monokliničan sistem, prostorna grupa $P2_1/n$, a = 7,304(2), b = 13,839(3), c = 12,769(2)Å, β = 92,71(2)° V = 1289,2(5) Å^3, Z = 4, Mr = 561,11, μ(MoK_α) = 17,092 mm^{-1}, F(000) = 1032. Intenziteti 3097 nezavisnih refleksija su izmereni na difraktometru Enraf-Nonius CAD-4 [λ(MoKα) = 0,71073 Å] u rasponu uglova $2 < \theta < 28°$. Izmereni intenziteti refleksija su korigovani na apsorpciju. Struktura je rešena programom SHELXS97 i utačnjena programom SHELXL97 do konačnog R1 = 0,0532 za 2260 ($I > 2\sigma I$) nezavisnih refleksija i 154 utačnjenih parametara.

CRYSTAL STRUCTURE OF A COPPER(I) CYANOGUANIDINE COMPLEX

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Copper (I) cyanoguanidine complex ($[Cu\{(Et_2N)(NH_2)CNCN\}_2(H_2O)_2Cl]Cl$ where Et=ethyl) is biologically active and is used as a medicine against the blood hypertension. From the chemical bonding point of view, this compound exhibits different delocalised C-N bonds, belonging to the $N_\alpha{\equiv}C_\beta{-}N\gamma{=}C_\delta(N_\varepsilon H_2)(N_\varepsilon(C_2H_5)_2)$ moiety. Structures of two different crystals are investigated at 298 and 100 K using two different diffractometers (four-circle Enraf-Nonius CAD4 and Siemens Smart CCD).

Table 1. Selected inter-atomic distances (Å) for cyanoguanidine complex

T (K)	298	100
Crystal	A	B
$Cu\text{-}N_\alpha$	1.946(4) 1.948(4)	1.944(3) 1.948(3)
$N_\alpha\text{-}C_\beta$	1.149(6) 1.147(5)	1.155(5) 1.162(5)
$C_\beta\text{-}N_\gamma$	1.289(5) 1.289(5)	1.289(5) 1.291(5)
$N_\gamma\text{-}C_\delta$	1.349(5) 1.353(5)	1.352(5) 1.366(5)
$C_\delta\text{-}N_\varepsilon$	1.326(5) 1.307(5) 1.324(5) 1.323(5)	1.326(5) 1.332(5) 1.331(5) 1.324(5)
$N_\varepsilon\text{-}C_{Et}$	1.467(5) 1.458(6) 1.466(6) 1.471(6)	1.460(6) 1.473(6) 1.460(6) 1.471(6)

Crystal data: $[Cu\{(Et_2N)(NH_2)CNCN\}_2(H_2O)_2Cl]Cl$, $C_{12}H_{28}Cl_2CuN_8O_2$, $M_r = 450.9$, orthorhombic $P2_12_12_1$, $Z=4$, $F(000) = 939.7$, $\rho_x = 1.39\ g\,cm^{-3}$, $\mu(Mo\ K_\alpha) = 1.285\ mm^{-1}$, dimensions of crystals are 0.28x0.15x0.15 mm (A) and 0.38x0.30x0.30 mm (B).

(Enraf-Nonius, CAD4) at 298 K for crystal A: $a = 9.135(3)$, $b = 12.696(2)$, $c = 18.989(2)$ Å, $\alpha=\beta=\gamma=90°$, $V=2202.4(9)$ Å^3, 5773 independent reflections, $R_1 = 5.68$ % for 3562 observed reflections with $F_o > 4\sigma(F_o)$, $R_{w2} = 12.89$ % (refinement on F^2) for all reflections and 258 refined parameters.

(SIEMENS, SMART CCD) at 100 K for crystal B: $a = 9.1473(4)$, $b = 12.5189(6)$, $c = 18.9396(3)$ Å, $\alpha=\beta=\gamma=90°$, $V=2168.8(1)$ Å^3, 58408 measured reflections, 9396 independent reflections, $R_1 = 6.75$ % for 6842 observed reflections with $F_o > 4\sigma(F_o)$, $R_{w2} = 13.47$ % (refinement on F^2) for all reflections and 310 refined parameters.

KRISTALNA STRUKTURA JEDNOG BAKAR(I) KOMPLEKSA CIJANOGVANIDINA

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Bakar (I) kompleks cijanogvanidina ($[Cu\{(Et_2N)(NH_2)CNCN\}_2(H_2O)_2Cl]Cl$ gde je Et=etil) biološki je aktivan i koristi se kao lek za lečenje povišenog krvnog pritiska. Sa stanovišta prirode hemisjke veze, ovo jedinjenje poseduje različito delokalizovane C-N veze koje pripadaju ligandu $N_\alpha{\equiv}C_\beta{-}N\gamma{=}C_\delta(N_\varepsilon H_2)(N_\varepsilon(C_2H_5)_2)$. Ispitivana je struktura dva različita kristala na 100 i 298 K pomoću dva različita difraktometra (četvorokružni goniometar CAD4 Eraf-Nonius i Siemens Smart CCD).

Tabela 1. Odabrana međuatomska rastojanja (Å) u kompleksu cijanogvanidina

T (K)	298				100			
Kristal	A				B			
$Cu\text{-}N_\alpha$	1,946(4)	1,948(4)			1,944(3)	1,948(3)		
$N_\alpha\text{-}C_\beta$	1,149(6)	1,147(5)			1,155(5)	1,162(5)		
$C_\beta\text{-}N_\gamma$	1,289(5)	1,289(5)			1,289(5)	1,291(5)		
$N_\gamma\text{-}C_\delta$	1,349(5)	1,353(5)			1,352(5)	1,366(5)		
$C_\delta\text{-}N_\varepsilon$	1,326(5)	1,307(5)	1,324(5)	1,323(5)	1,326(5)	1,332(5)	1,331(5)	1,324(5)
$N_\varepsilon\text{-}C_{Et}$	1,467(5)	1,458(6)	1,466(6)	1,471(6)	1,460(6)	1,473(6)	1,460(6)	1,471(6)

Kristalografski podaci: $[Cu\{(Et_2N)(NH_2)CNCN\}_2(H_2O)_2Cl]Cl$, $C_{12}H_{28}Cl_2CuN_8O_2$, $M_r = 450{,}9$, rombičan $P\,2_12_12_1$, $Z=4$, $F(000)=939{,}7$, $\rho_x=1{,}39\ g\,cm^{-3}$, $\mu(Mo\,K_\alpha)=1{,}285\ mm^{-1}$, dimenzije kristala su 0.28x0.15x0.15 mm (A) i 0,38x0,30x0,30 mm (B).

(Enraf-Nonius, CAD4) na 298 K za kristal A: $a=9{,}135(3)$, $b=12{,}696(2)$, $c=18{,}989(2)$ Å, $\alpha=\beta=\gamma=90^\circ$, $V=2202{,}4(9)$ Å^3, 5773 nezavisnih refleksija, $R_1=5{,}68$ % za 3562 opaženih refleksija sa $F_o>4\sigma(F_o)$, $R_{w2}=12{,}89$ % (utačnjavanje pomoću F^2) za sve refleksije i 258 utačnjenih parametara.

(SIEMENS, SMART CCD) na 100 K za kristal B: $a=9{,}1473(4)$, $b=12{,}5189(6)$, $c=18{,}9396(3)$ Å, $\alpha=\beta=\gamma=90^\circ$, $V=2168{,}8(1)$ Å^3, 58408 izmerenih refleksija, 9396 nezavisnih refleksija, $R_1=6{,}75$ % za 6842 opaženih refleksija sa $F_o>4\sigma(F_o)$, $R_{w2}=13{,}47$ % (utačnjavanje pomoću F^2) za sve refleksije i 310 utačnjenih parametra.

CRYSTAL AND MOLECULAR STRUCTURE OF E-FORM OF UNSATURATED ESTERS OF C-NUCLEOSIDES

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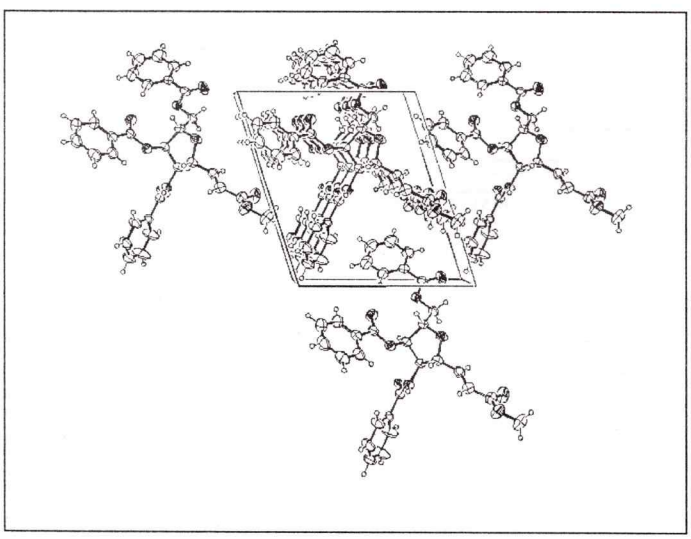
In the search for new and selective anticancer and antiviral agents, the synthesis of novel nucleoside analogues is of immense importance. As the intermediate for preparation of the pyrazole - related C-nucleosides, the mixture of the corresponding Z and E unsaturated esters in 85 % combined yield was prepared. E-isomer crystallized from CH2Cl2 - hexane to afford colorless needles (m.p. 165 C).

The compound C30H27NO8 titled: Methyl E-4,7-anhydro-5-benzamido-6,8-di-O-benzoyl-2,3,5-trideoxy-D-allo-oct-2-enoate crystallize in the acentric triclinic system, space group P1, with the unit cell parameters a=5.319(1), b=10.758(2), c=12.229(2)Å, α=107.62(1)°, β=89.97(2)°, γ=92.93(2)°, V=665.9(3)Å3, Z=1, Mr=529.53, Dx=1.320 Mgm-3, μ=0.799 mm-1. The crystal structure was solved by the direct methods, on the basis of 3257 reflections



collected on a STOE diffractometer (CuKα) using program SHELXS86 and refined by SHELXL98 to final R = 0.0385 for 2356 [I >σ(I)] independent reflections and 356 parameters. The X-ray diffraction analysis, unambiguously confirmed its structure providing a proof that all intermediates generated by the multistep sequences retained the required β - configuration at the anomeric position.

KRISTALNA I MOLEKULSKA STRUKTURA E-FORME NEZASIĆENOG ESTRA C-NUKLEOZIDA

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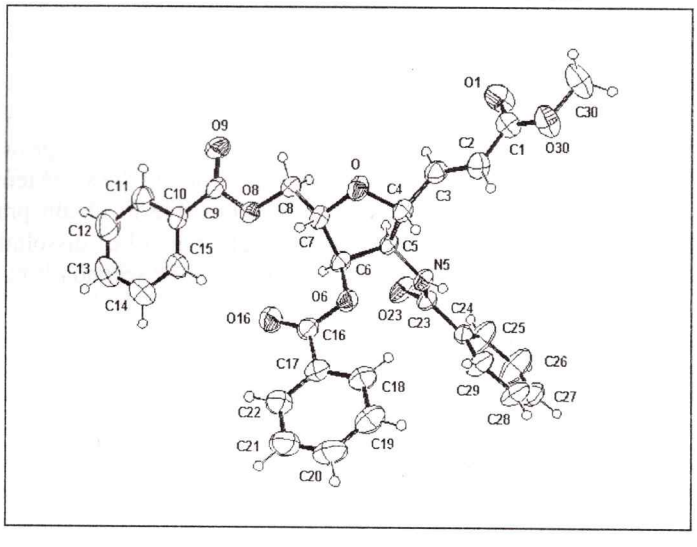
U okviru sistematskih istraživanja novih selektivnih antitumorskih i antivirusnih agenasa, sinteza novih analoga C-nukleozida je od neprocenjivog značaja. Kao međuprodukt pri preparaciji pirazolskih derivata C-nukleozida, dobijena je mešavina Z i E-forme odgovarajućeg nezasićenog estra u prinosu 85 %. E-izomer kristališe iz CH2Cl2 – heksana i daje bezbojne providne igličaste kristale (m.p. 165 C).

Jedinjenje C30H27NO8: Metil E-4,7-anhidro-5-benzamido-6,8-di-O-benzoil-2,3,5-trideoksi-D-alo-okta-2-enoate kristališe u acentričnom triklinskom



sistemu, prostorna grupa P1, sa parametrima jedinične ćelije: a=5,319(1), b=10,758(2), c=12,229(2)Å, α=107,62(1)°, β=89,97(2)°, γ=92,93(2)°, V=665,9(3)Å3, Z=1, Mr=529.53, Dx=1,320 Mgm-3, μ=0,799 mm-1. Kristalna struktura je rešena direktnom metodom na osnovu 3257 refleksa izmerenih na difraktometru STOE (CuKα) korišćenjem programa SHELXS86 i utačnjena programom SHELXL98 do konačnog R faktora R = 0,0385 za 2356 [I >2σ(I)] nezavisnih refleksa i 356 parametara. Analiza geometrije je potvrdila da međuprodukti dobijeni u procesu višefazne sinteze novih derivata zadržavaju β-konfiguraciju na anomernoj poziciji na atomu C4.

IMPROVEMENT OF INITIAL CRYSTAL GROWTH CONDITIONS BY DISSOLUTION AND REFACETING

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For drawing valid conclusions about crystal growth processes, on the basis of statistical analysis, it is necessary to observe the growth of a lot of crystals under the same conditions. Because of the dependence of the crystal growth on initial growth conditions, these conditions must be the same for all crystals under observation. Initial conditions, especially the seed nucleation, are very difficult to control. The influence of significant dissolution and refaceting of KDP and Rochelle salt crystals on their further growth is studied in this paper.

It is shown in Ref. [1] that growth rates of Rochelle salt crystals before and after only a small partial dissolution, do not differ significantly. It is presumed that the crystal "memorizes" something not considerably affected by a small dissolution and refaceting. In our experiments, significant dissolution (more than 20%) of KDP and Rochelle salt crystals, essentially changed the growth rates of a lot of crystals. Higher values of the linear coefficients off correlation between the growth rate and the initial crystal size after the dissolution (0.75-0.79) than before it, indicate that new initial growth conditions for restored growth are better defined in these case. By applying the same temperature changes, during dissolution and refaceting processes, it is possible to obtain practically the same initial conditions for growth of a lot of crystals. The control of dissolution and refaceting processes is much simpler than the control of primary or secondary nucleation, which is very important.

Beside that our investigations show that the range of measured crystal growth rates is wider, and the number of distribution maxima is higher after the dissolution, than before it. A lot of crystals stopped their growth after refaceting.

These results are not in accordance to BCF crystal growth theory [2]. Namely, the dissolution and refaceting processes unified the crystal growth rates, because of unification of the crystal defectiveness (dislocation structure) by well defined initial growth conditions, according to this theory. It cannot be expected dislocation free crystals and crystals with compensated dislocations of oposite signs after refaceting. Only these crystals can stopped their growth, according to this theory.

[1] M.M. Mitrović, *J. Phys. Chem.* **99** (1995) 5438.
[2] W.K. Burton, N. Cabrera and F.C. Frank, Philos. Trans. R. Soc. (London) A243 (1951) 299.

UJEDNAČAVANJE POČETNIH USLOVA RASTA KRISTALA RASTVARANJEM I REFACETIRANJEM

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Za donošenje bitnih zaključaka o procesima rasta, statističkom analizom ovih procesa, neophodno je posmatrati rast velikog broja kristala pod istim uslovima. Zbog zavisnosti brzine rasta kristala od početnih uslova rasta, pomenuti uslovi moraju biti isti za sve posmatrane kristale. Te uslove je veoma teško kontrolisati, posebno nukleaciju. U ovom radu je proučavan uticaj značajnog rastvaranja i refacetiranja rastućih kristala KDP i Rošelske soli na njihov dalji rast.

Ranije je pokazano [1] da se brzine rasta kristala Rošelske soli ne razlikuju mnogo pre i posle malog, delimičnog, rastvaranja. Pretpostavljeno je da kristali "pamte" nešto što značajno ne zavisi od ovih procesa. U našim eksperimentima značajno rastvaranje (veće od 20%) kristala KDP i Rošelske soli bitno menja brzine rasta većine kristala. Velike vrednosti koeficijenata korelacije između brzine rasta i početne veličine kristala posle rastvaranja (0,75-0,79) pokazuju da su novi početni uslovi rasta za ponovni rast bolje definisani nego pre rastvaranja. Istim promenama temperature, u toku procesa rastvaranja i refacetiranja, moguće je dobiti praktično iste početne uslove rasta za veliki broj kristala. Kontrola ovih procesa je znatno jednostavnija od kontrole primarne ili sekundarne nukleacije, što je veoma značajno.

Pored toga, naši eksperimenti pokazuju da su opseg brzina rasta kristala i broj maksimuma u distribucijama brzina veći za rast kristala posle refacetiranja. Veliki broj kristala posle refacetiranja prestaje da raste.

Ovi rezultati nisu u skladu sa klasičnom BCF teorijom [2], prema kojoj se može očekivati da posle rastvaranja i refacetiranja, zbog dobro definisanih uslova rasta, defektnost kristala (dislokaciona) bude ujednačenija, a samim tim i brzine njihovog rasta. Nije očekivano da kristali posle refacetiranja nemaju dislokacije, a prema ovoj teoriji samo takvi kristali i kristali kod kojih se poništavaju dislokacije suprotnog znaka, ne rastu uopšte.

[1] M.M. Mitrović, *J. Phys. Chem.* **99** (1995) 5438.
[2] W.K. Burton, N. Cabrera and F.C. Frank, Philos. Trans. R. Soc. (London) A243 (1951) 299.

CRYSTAL AND MOLECULAR STRUCTURE OF THE DICHLORO-TRIS(3-AMINO-5-PHENYLPYRAZOLE)ZINC(II) COMPLEX

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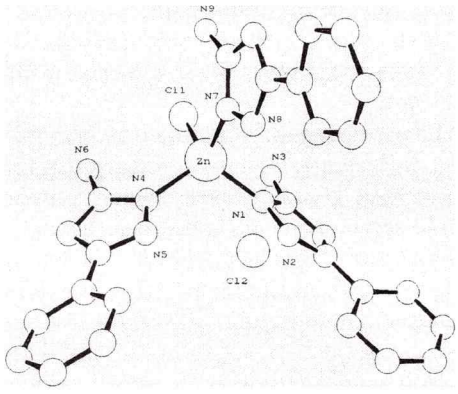

Zinc is tetrahedrally coordinated by the three 'pyridine' nitrogen's from the pyrazole rings, and chlorine atom. The Zn-N distances are experimentally equal, with the angles slightly deviated from the 'ideal' tetrahedral value. The coordinated chlorine atom forms intramolecular hydrogen bonds with the amino nitrogen's from the three pyrazole rings (H···Cl distances range from 2.36 Å to 2.49 Å, with N-H···Cl angles ranging from 151° to 159 °).

Unit cell contains the complex cations $[Zn(C_9H_9N_3)_3Cl]^+$ and Cl^- anions mutually connected by the N9-H···Cl2 hydrogen bonds (H···Cl=2.56 Å, the angle N-H···Cl =172 °), and the π-stacking interactions. The distance between the centers of the aromatic rings involved in π-stacking interaction is 3.620 Å and the corresponding dihedral angle is 4.58 °.

KRISTALNA I MOLEKULSKA STRUKTURA DIHLORO-TRIS(3-AMINO-5-FENILPIRAZOL)CINK(II) KOMPLEKSA

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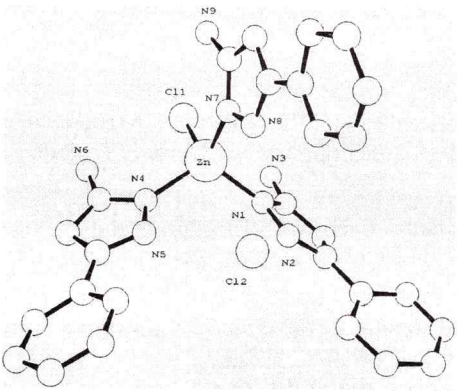

Atom cinka se nalazi u tetraedarskom okruženju koje formiraju tri 'piridinska' azotova atoma iz pirazolnih prstenova i atom hlora. Zn-N rastojanja su jednaka dok uglovi blago odstupaju od idealne vrednosti za tetraedarsku geometriju. Koordinovani atom hlora formira intramolekularne vodonične veze sa amino atomima azota iz tri pirazolna prstena (H···Cl rastojanja se kreću od 2,36 Å do 2,49 Å dok su N-H···Cl uglovi u rasponu od 151° do 159°).

Jedinična ćelija sadrži kompleksne katjone $[Zn(C_9H_9N_3)_3Cl]^+$ i Cl^- anjone povezane N9-H···Cl2 vodoničnim vezama (H···Cl=2,56 Å, ugao N-H···Cl =172°), i "π-stacking" interakcijama. Rastojanje između centara aromatičnih prstenova koji učestvuju u "π-stacking" interakcijama iznosi 3,620 Å dok je odgovarajući diedarski ugao 4,58 °.

CRYSTAL STRUCTURE OF AQUA(PYRIDOXALTHIOSEMICARBAZONATO) COPPER(II)BROMIDE, [Cu(L-H)H_2O]Br

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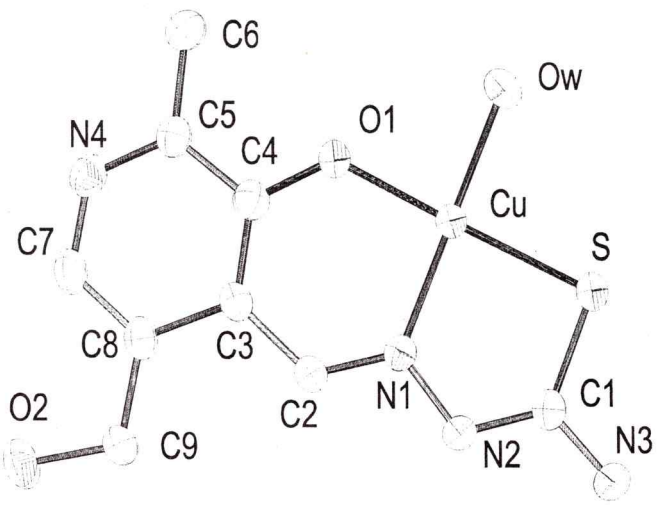
Green monocrystals of the titled complex were obtained by the reactions of aqueous solutions of the stoichiometric amounts of $CuBr_2 \cdot 2H_2O$ and pyridoxale thiosemicarbazone.

Crystallographic data: $C_9H_{12}N_4O_2SBr_2Cu$, triclinic system, space group $P\bar{1}$, a=7.740(4), b=9.517(3), c=9.961(4) Å; α=85.17(3), β=78.74(4), γ=89.98(4)^0, V=721.6(5) Å^3, Z=2, λ=0.71073Å F(000)=428.

Intensitet of 3461 unique reflections are collected on a Enraf-Nonius CAD-4 diffractometer in the range of $2.09<\theta<27.98$ and they were corrected for absorbation. The structure was solved using program SHELXS-97 and refined by SHELXL-97 to final R factor R=0.0528 for 2528 [$I>2\sigma(I)$] indipendennt reflections and 191 parameters.

The crystal structure consists of the complex cation $[Cu(L\text{-}H)H_2O]^+$ and Br^- anion. The geometry of the complex cation correspond to the distorted square-planar coordination, realized by coordination of O, N, S monoanionic form of the organic ligand and atom O of the molecule H_2O.



KRISTALNA STRUKTURA AKVA(PIRIDOKSALTIOSEMIKARBAZONATO)BAKAR(II) BROMIDA, [Cu(L-H)H_2O]Br

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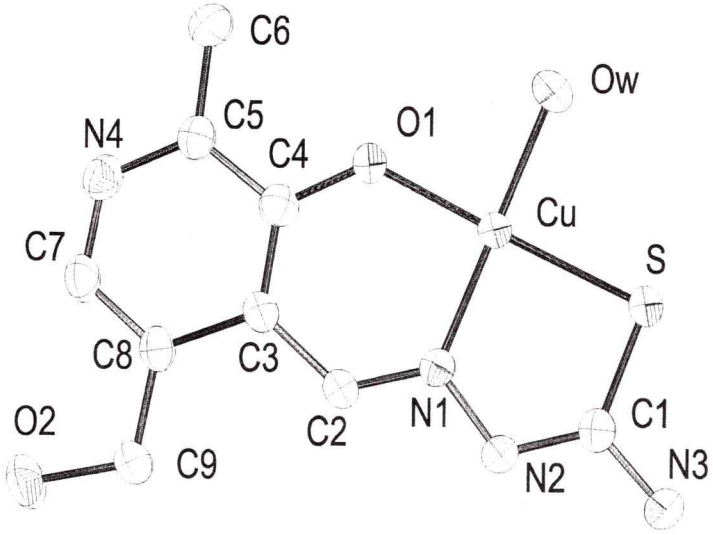
Zeleni monokristali naslovljenog kompleksa dobijeni su reakcijom vodenih rastvora $CuBr_2 \cdot 2H_2O$ i tiosemikarbazona piridoksala u stehiometrijskom odnosu.

Kristalografski podaci: $C_9H_{12}N_4O_2SBr_2Cu$, triklinični sisitem, prostorna grupa $P\bar{1}$, a=7,740(4), b=9,517(3), c=9,961(4) Å; α=85,17(3); β=78,74(4); γ=89,98(4)^0, V=721,6(5) Å^3, Z=2, λ=0,71073Å, F(000)=428.

Intenziteti 3461 nezavisne refleksije izmereni su na difraktometru Enraf-Nonius CAD-4 u rasponu uglova $2{,}09<\theta<27{,}98$ i korigovani su za apsorpciju. Struktura je rešena korišćenjem programa SHELXS-97 a utačnjena je programom SHELXL-97 do konačnog R=0,0528 za 2528 [$I>2\sigma(I)$] nezavisnih refleksija i 191 utačnjavani parametar.

Kristalnu strukturu čine kompleksni katjon [Cu(L-H)H_2O]$^+$ i Br^- anjon. Geometrija kompleksnog katjona odgovara deformisanoj kvadratno-planarnoj koordinaciji, realizovanoj O, N, S koordinacijom monoanjonske forme organskog liganda i atoma O molekula H_2O.



ALUNITE AND NATROALUNITE FROM VELIKI BUKOVIK

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With the X-ray qualitative, semiquantitative powder diffraction analysis it was determined that in investigated sample from Veliki Bukovik there are following mineral species acording to their quantity: alunite (≈47%), natroalunite (≈47%), and insignificant jarosite (≈4%), quartz (≈1,5%) and feldspars (≈0,5%). Throughout LSUCRIPC [1] it were calculated in the space group $R\bar{3}m$ unit cell dimensions of alunite, natroalunite and jarosite (Table 1). The chemical analysis first was recalculated into oxides theoretically may to come into the composition of alunite mineral group, and then was the crystallochemical formula calculated at 28 O basis. These results are represented at the Table 2. From the literature [2], [3], [4] and [5], a_0-axis changes with Al^{3+}-Fe^{3+} contents, while c_0-axis changes with Na^{+}-K^{+} contents. From the diagram dependence a_0 and c_0-axis from relative at.% K and Na [3], it can be seen following: 1. investigated alunite at c_0-axis belongs to the type with 82%K : 18%Na; and 2. investigated natroalunite at c_0-axis belongs to the type with 62%Na : 38%K. From crystallochemical formulas of alunite and natroalunite (Table 3) it can be seen that some of the alkalies are replaced with hydronium ion. In consideration of this and to datas [2], [3], [4], [6], and [7], our opinion is that investigated alunite and natroalunite (and jarosite) from Veliki Bukovik are most probably diagenetic or low-temperature origin in acid conditions with high sulphate activity.

Table 1: Calculated unit cell dimensions of alunite, natroalunite and jarosite.

	a_0(Å)	c_0(Å)	V_0(Å^3)	c_0/a_0
alunite	6.976(1)	17.295(6)	729.0(3)	2.479
natroalunite	6.981(1)	16.884(6)	712.6(3)	2.419
jarosite	7.291(4)	17.23(2)	793(1)	2.363

Table 2: Recalculated chemical analisis (in %) and number of atoms on 28 O basis.

	K_2O	Na_2O	Al_2O_3	Fe_2O_3	SO_3	H_2O
calculated chemical analysis	7.00	1.91	37.27	1.27	38.96	13.60
number of atoms on 28 O basis	1.21 K	0.50 Na	5.95 Al	0.13 Fe	3.96 S	12.29 H

Table: 3. Calculated crystallochemical formulas of alunite and natroalunite.

	crystallochemical formula
alunite	$(K_{0.83}(H_3O)^{+}_{0.17})_{1.00}Al_{3.00}(S_{0.99}O_4)_2(OH)_6$
natroalunite	$(Na_{0.50}K_{0.38}(H_3O)^{+}_{0.12})_{1.00}(Al_{2.95}Fe_{0.13})_{3.08}(S_{0.99}O_4)_2(OH)_6$

[1] R. Garvey, Least-square unit cell refinement, Version 86,2, Dept. of Chemistry, North Dakota State University (1987).
[2] G. P. Brophy, E. S. Scott & R. A. Snellgrove, Am. Min., 47 (1962), p. 112-126.
[3] R. L. Parker, Am. Min., 47 (1962), p. 127-136.
[4] G. P. Brophy & M. F. Sheridan, Am. Min., 50 (1965), p. 1595-1607.
[5] S. Menchetti & C. Sabelli, N. Jb. Miner. Mh., 9 (1976), p. 406-417.
[6] M. F. Sheridan & C. F. Jr. Royse, Am. Min., 55 (1970), p. 2016-2022.
[7] J. E. Knight, Econ. Geol., 72 (1977), p. 1321-1336.

ALUNIT I NATROALUNIT SA VELIKOG BUKOVIKA

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Rendgenskom kvalitativnom, semikvantitativnom difrakcionom analizom praha odre|eno je da se u ispitivanom uzorku sa Velikog Bukovika nalaze sledeće mineralne vrste prema stepenu zastupljenosti: alunit (oko 47%), natroalunit (oko 47%), i neznatno jarozit (oko 4%), kvarc (oko 1,5%) i feldspati (oko 0,5%). Preko programa LSUCRIPC [1] izračunate su u prostornoj grupi $R\bar{3}m$ dimenzije jediničnih ćelija (Tabela 1). Hemijska analiza je prvo preračunata na one okside koji teoretski mogu da uđu u sastav minerala alunitske grupe, a zatim je kristalohemijska formula preračunata na 28 O, jer su alunit i natroalunit podjednako zastupljeni. Ovi rezultati su prikazani u tabeli 2. Iz literature [2], [3], [4] i [5] vidi se promena a_0-ose sa sadržajem Al^{3+}-Fe^{3+} i promena c_0-ose sa sadržajem Na^+-K^+. Iz dijagrama zavisnosti a_0 i c_0-ose od relativnog atomskog sadržaja K i Na [3], vidi se sledeće: 1. alunit po c_0-osi pripada tipu sa 82%K : 18%Na; i 2. natroalunit po c_0-osi pripada tipu sa 62%Na : 38%K. Iz kristalohemijskih formula alunita i natroalunita (Tabela 3), vidi se da je deo alkalija zamenjen sa hidronijum jonom. S obzirom na to i na podatke [2], [3], [4] i [6], i [7], mišljenja smo da su ispitivani alunit i natroalunit (i jarozit) sa Velikog Bukovika najverovatnije postali dijagenetski ili nisko-temperaturno pri kiselim uslovima i sa visokom sulfatnom aktivnošću.

Tabela 1: Izračunate dimenzije jediničnih ćelija alunita, natroalunita i jarozita.

	a_0(Å)	c_0(Å)	V_0(Å^3)	c_0/a_0
alunit	6,976(1)	17,295(6)	729,0(3)	2,479
natroalunit	6,981(1)	16,884(6)	712,6(3)	2,419
jarozit	7,291(4)	17,23(2)	793(1)	2,363

Tabela 2: Preračunata hemijska analiza (u %) i broj atoma na osnovu 28 O.

	K_2O	Na_2O	Al_2O_3	Fe_2O_3	SO_3	H_2O
preračunata hemijska analiza	7,00	1,91	37,27	1,27	38,96	13,60
broj atoma na osnovu 28 O	1,21 K	0,50 Na	5,95 Al	0,13 Fe	3,96 S	12,29 H

Tabela 3. Izračunate kristalohemijske formule alunita i natroalunita.

	kristalohemijska formula
alunit	$(K_{0,83}(H_3O)^+_{0,17})_{1,00}Al_{3,00}(S_{0,99}O_4)_2(OH)_6$
natroalunit	$(Na_{0,50}K_{0,38}(H_3O)^+_{0,12})_{1,00}(Al_{2,95}Fe_{0,13})_{3,08}(S_{0,99}O_4)_2(OH)_6$

[1] R. Garvey, Least-square unit cell refinement, Version 86,2, Dept. of Chemistry, North Dakota State University (1987).
[2] G. P. Brophy, E. S. Scott & R. A. Snellgrove, Am. Min., 47 (1962), str. 112-126.
[3] R. L. Parker, Am. Min., 47 (1962), str. 127-136.
[4] G. P. Brophy & M. F. Sheridan, Am. Min., 50 (1965), str. 1595-1607.
[5] S. Menchetti & C. Sabelli, N. Jb. Miner. Mh., 9 (1976), str. 406-417.
[6] M. F. Sheridan & C. F. Jr. Royse, Am. Min., 55 (1970), str. 2016-2022.
[7] J. E. Knight, Econ. Geol., 72 (1977), str. 1321-1336.

ARSENOPYRITES FROM SOME ORE DEPOSITS OF SERBIA

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Arsenopyrites from five Serbia's ore deposites: Crveni Breg, Rudnik, Sastavci, Belo Brdo and Trepča, were investigated by X-ray method. By the programme's help TREOR 90 [1] it was tested their symmetry and by this occasion for all samples were obtained monoclinic solutions. Afterwards throughout LSUCRIPC programme [2] it were calculated in the space group $P2_1/c$ unit cell dimensions, and those are together with characteristic interplanar spacings d_{131} (sensitive to As/S relation [3]) represented at the Table 1. From these datas which were obtained by X-ray diffraction, and after calculations in regresion expressions [4] and [5], there were obtained average values of As and S (in at. %), and then were calculated relation As : S. Then there were calculated crystallochemical formulas on the basis of [4] and [6]. These results are represented at the Table 2. Mutually, differences and characteristics with regard to their chemistry and crystallographic parameters, and also to formation of arsenopyrites are obviously, which is in accordance with different origin of their main ore deposits [7].

Table 1. Calculated unit cell dimensions and observed d_{131} values.

	Crveni Breg	Rudnik	Sastavci	Belo Brdo	Trepča
a_o (Å)	5.7534(8)	5.7443(9)	5.745(2)	5.737(2)	5.754(1)
b_o (Å)	5.690(1)	5.683(1)	5.676(2)	5.652(2)	5.654(2)
c_o (Å)	5.7927(9)	5.781(1)	5.767(2)	5.771(2)	5.776(2)
β_o (°)	112.34(1)	112.23(1)	112.10(2)	111.84(2)	111.95(2)
V_o (Å^3)	175.21(8)	174.62(8)	174.3(2)	174.1(1)	174.6(1)
d_{131}obs (Å)	1.6325(4)	1.6317(4)	1.6313(1)	1.6292(4)	1.6285(7)

Table 2. Calculated average values As and S (in at.%) from equations [4] i [5], relation As:S and estimated crystallisation temperature [4] and [6].

	Crveni Breg	Rudnik	Sastavci	Belo Brdo	Trepča
av.vel. As/S	36.2 / 29.8	33.2 / 33.7	31.3 / 36.1	29.0 / 38.7	31.7 / 35.1
As : S	1.21	0.98	0.87	0.75	0.90
cris. formula	$FeAs_{1.09}S_{0.91}$	$FeAs_{0.99}S_{1.01}$	$FeAs_{0.94}S_{1.06}$	$FeAs_{0.87}S_{1.13}$	$FeAs_{0.95}S_{1.05}$
[6] / [4] (°C)	≈430/≈510	≈380/≈490	≈360/≈475	≈250/≈350	≈210/≈355

[1] P. E. Werner, L. Eriksson and M. Westdahl, J. Appl. Cryst, 18 (1985), p. 367 – 370.
[2] R. Garvey, Least-square unit cell refinement. Version 86,2, Dept. of Chemistry, North Dakota State University, (1987).
[3] N. Morimoto and L. A. Clark, Am. Min., 46 (1961), p. 1448 – 1469.
[4] U. Kretschmar and S. D. Scott, , Canad. Min., 14 (1976), p. 364 – 386.
[5] E. Tjukova i T. Mahorkina, Zapiski Vsenoznogo Mineralogičeskogo Obšestva, Vipusk 1, 119 (1990), p. 93-97.
[6] L. A. Clark, Econ. Geol., 55 (1960a,b), p. 1345-1381 i 1631-1652.
[7] R. S. Janković, Rudna ležišta Srbije: Regionalni metalogenetski položaj, sredine stvaranja i tipovi ležišta, Beograd (1990).

ARSENOPIRITI IZ NEKIH RUDNIH LEŽIŠTA SRBIJE

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Rendgenski su ispitivani arsenopiriti iz pet rudnih ležišta Srbije: Crveni Breg (Avala), Rudnik (Rudnik), Sastavci, Belo Brdo i Trepča (Kopaonik). Pomoću programa TREOR 90 [1] testirana je njihova simetrija i tom prilikom su za sve uzorke dobijena monoklinična rešenja. Zatim su pomoću programa LSUCRIPC [2] izračunate u prostornoj grupi $P2_1/c$ dimenzije jediničnih ćelija, koje su zajedno sa karakterističnim međupljosnim rastojanjima refleksija d_{131} osetljivim na odnos As/S [3], prikazane u Tabeli 1. Iz ovih podataka dobijenih rendgenskom difrakcijom, a posle preračunavanja u regresionim izrazima [4] i [5], dobijene su srednje vrednosti As i S (u at.%) i izračunat je odnos As : S, a zatim su preračunate i kristalohemijske formule na osnovu radova [4] i [6]. Ovi rezultati su prikazani u Tabeli 2. Međusobne razlike i karakteristike, kako u pogledu hemizma, kristalografskih parametara, tako i u pogledu geneze arsenopirita, su očigledne, što je u skladu sa različitim nastankom matičnih ležišta [7].

Tabela 1. Izračunate dimenzije jediničnih ćelija i izmerene d_{131} vrednosti.

	Crveni Breg	Rudnik	Sastavci	Belo Brdo	Trepča
a_o (Å)	5,7534(8)	5,7443(9)	5,745(2)	5,737(2)	5,754(1)
b_o (Å)	5,690(1)	5,683(1)	5,676(2)	5,652(2)	5,654(2)
c_o (Å)	5,7927(9)	5,781(1)	5,767(2)	5,771(2)	5,776(2)
β_o (°)	112,34(1)	112,23(1)	112,10(2)	111,84(2)	111,95(2)
V_o (Å^3)	175,21(8)	174,62(8)	174,3(2)	174,1(1)	174,6(1)
d_{131}obs (Å)	1,6325(4)	1,6317(4)	1,6313(1)	1,6292(4)	1,6285(7)

Tabela 2. Izračunate srednje vrednosti As i S (u at.%) iz jednačina [4] i [5], odnos As:S, preračunate kristalohemijske formule i procenjene temparature kristalizacije [4] i [6].

	Crveni Breg	Rudnik	Sastavci	Belo Brdo	Trepča
sr.vr. As/S	36,2 / 29,8	33,2 / 33,7	31,3 / 36,1	29,0 / 38,7	31,7 / 35,1
As : S	1,21	0,98	0,87	0,75	0,90
kr. formula	$FeAs_{1,09}S_{0,91}$	$FeAs_{0,99}S_{1,01}$	$FeAs_{0,94}S_{1,06}$	$FeAs_{0,87}S_{1,13}$	$FeAs_{0,95}S_{1,05}$
[6] / [4] (°C)	≈430/≈510	≈380/≈490	≈360≈/475	≈250/≈350	≈210/≈355

[1] P. E. Werner, L. Eriksson and M. Westdahl, J. Appl. Cryst, 18 (1985), str. 367 – 370.
[2] R. Garvey, Least-square unit cell refinement. Version 86,2, Dept. of Chemistry, North Dakota State University, (1987).
[3] N. Morimoto and L. A. Clark, Am. Min., 46 (1961), str. 1448 – 1469.
[4] U. Kretschmar and S. D. Scott, , Canad. Min., 14 (1976), str. 364 – 386.
[5] E. Tjukova i T. Mahorkina, Zapiski Vsenoznogo Mineralogičeskogo Obšestva, Vipusk 1, 119 (1990), str. 93-97.
[6] L. A. Clark, Econ. Geol., 55 (1960a,b), str. 1345-1381 i 1631-1652.
[7] R. S. Janković, Rudna ležišta Srbije: Regionalni metalogenetski položaj, sredine stvaranja i tipovi ležišta, Beograd (1990).

REFINEMENT OF THE CRYSTAL STRUCTURE OF $Li_{1.33-0.665x}Co_xTi_{1.67-0.335x}O_4$ IN TWO SPACE GROUPS AT TWO WAVELENGTHS

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In this paper we present results of structure properties investigation of ternary spinels $Li_{1.33-0.665x}Co_xTi_{1.67-0.335x}O_4$. The samples were prepared by ceramic technology. The starting oxides Li_2CO_3, Co_3O_4 and TiO_2 were mixed in appropriate stoichiometric ratio and fired in air. The spinel phase was obtained in full concentration region ($0 \leq x \leq 2$). The samples with $0.25 \leq x \leq 1.00$ crystalize in space group $P4_332$ and the other in space group Fd-3m.

Diffraction data were collected at Rigaku diffractometer (CuK_α and CuK_β). Crystal structures were refined by the Rietveld method using Fullprof softvare package.

The sample with x=0.50 is nearly full ordered spinel with ordering of Li and Ti in the octahedral crystallographic sites 4b and 12d (1:3 ordering type). Degree of ordering is determined by cationic distribution at all three cationic sites. It was found that degree of ordering is smaller in spinels with x=0.25 and 1.00. Crystal structure of $Li_{0.33}Co_{1.5}Ti_{1.17}O_4$ is refined from X-ray diffraction data colected by two different radiations CuK_α and CuK_β in tha space groups $P4_332$ and Fd-3m. Four refinement were made and compared. Crystal structure of the sample with x=1.25 is refined in two space groups $P4_332$ and Fd-3m.

Lattice parameters dependence of the concentration x is nonlinear function due to the change in crystal structure. In the spinels $Li_{1.33-0.665x}Co_xTi_{1.67-0.335x}O_4$ (x=0.25, 0.50 and 1.00) the changes in crystal structures at high temperature were investigated.

[1] B. Antić, D.Rodić, A. S. Nikolić, Z. Kačarević-Popović and Lj. Karanović, submited to *J. All. Comp.*

UTAČNJAVANJE KRISTALNE STRUKTURE $Li_{1,33-0,665x}Co_xTi_{1,67-0,335x}O_4$ U DVE PROSTORNE GRUPE SA DVE TALASNE DUŽINE

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U radu su prikazani rezultati istraživanja strukturnih osobina ternarnih spinela $Li_{1.33-0.665x}Co_xTi_{1.67-0.335x}O_4$. Uzorci su pripremljeni keramičkom tehnologijom. Polazni oksidi, Li_2CO_3, Co_3O_4 i TiO_2, su mešani u odgovarajućim stehiometrijskim odnosima i žareni na vazduhu. Iz podataka difrakcije X-zraka utvrdjeno je da je dobijena spinelna faza u celom opsegu koncentracija ($0 \leq x \leq 2$). Difraktogrami uzoraka sa $0,25 \leq x \leq 1,00$ indeksovani su u prostornoj grupi $P4_332$, dok za ostale koncentracije u prostornoj grupi Fd-3m.

Uzorci su snimani na difraktometru RIGAKU sa promenljivim korakom u ugaonom opsegu od $10 < 2\vartheta < 120°$. Kristalne strukture su utačnjavane Ritveldovim metodom koristeći programski paket Fullprof.

Uzorak sa x=0,50 skoro je potpuno uredjen spinel, sa uredjenjem Li i Ti u oktaedarskim 4b i 12d mestima (uredjenje tipa 1:3). Stepen uredjenja je odredjen katjonskom raspodelom u oktaedarskim mestima. Stepen uredjenja je niži u spinelima sa x=0,25 i 1,00. Struktura $Li_{0,33}Co_{1,5}Ti_{1,17}O_4$ je utačnjavana u prostornim grupama $P4_332$ i Fd-3m iz podataka dobijenih upotrebom CuK_α i CuK_β zračenja. Struktura uzorka sa x=1,25 je utačnjavana u prostornim grupama $P4_332$ i Fd-3m. Za sva nezavisna utačnjavanja daju se kristalografski podaci.

Usled promene kristalne strukture sa koncentracijom x zavisnost parametra rešetke od koncentracije a(x) je nelinearna funkcija. U uzorcima sa x=0,25, 0,50 i 1,00 praćene su strukturne promene sa temperaturom.

[1] B. Antić, D.Rodić, A. S. Nikolić, Z. Kačarević-Popović and Lj. Karanović , submited to *J. All. Comp.*

CRYSTAL AND MAGNETIC STRUCTURE OF $Fe_{2-x}Cr_xO_3$ SOLID SOLUTIONS

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The $Fe_{2-x}Cr_xO_3$ solid solutions (x = 0.2, 0.4, 0.6, 1, 1.4, 1.8, 2) were synthesized by use of a ceramic technology. The starting compounds were mixed in appropriate stoichiometric ratios, mechanically homogenized and fired at 900° C for 24 hours.

Obtained samples were investigated by use of the neutron diffraction at the Swedish experimental reactor R2 located in Studsvik. Experimental data were collected at 10 K and 295 K within the 2 theta range 4° -139°. The obtained neutron diffraction patterns were refined with the Rietveld full profile method using the Fullprof refinement program.

The results of refinement showed that all the samples crystallize in the space group R-3c, without any visible presents of remaining or odd phases. The magnetic structure was refined in the space group P1. The magnetic reflections were generated through the program HKLGEN.

Concerning the magnetic structure, it was observed that one group of samples (x = 0.2, 0.4, 0.6, 1, 2) have linear antiferomagnetic structure, while in the case of two of them (x = 1.4, 1.8), a number of satellite reflections were observed pointing to the helical magnetic ordering. It was also observed that even 10% amount of chromium presence (x = 0.2) leads to complete stability of the magnetic structure of the Fe_2O_3 high-temperature magnetic phase.

KRISTALNA I MAGNETNA STRUKTURA ČVRSTIH RASTVORA $Fe_{2-x}Cr_xO_3$

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Čvrsti rastvori $Fe_{2-x}Cr_xO_3$ (x = 0,2; 0,4; 0,6; 1; 1,4; 1,8; 2) sintetisani su keramičkom tehnologijom. Polazni prahovi Fe_2O3 i Cr_2O_3 su mešani u odgovarajućim stehiometrijskim odnosima, mehanički homogenizovani i žareni na 900° C tokom 24 h. Dobijeni čvrsti rastvori ispitivani su pomoću neutronske difrakcije na švedskom istraživačkom reaktoru R2 u Studsviku. Podaci su prikupljani u intervalu uglova 4° -139°, na temperaturama od 295 K i 10 K. Dobijeni neutronogrami su analizirani Ritveldovom punom profilnom metodom pomoću programa Fullprof.

Rezultati utačnjavanja su pokazali da se kristalna struktura svih uzoraka može opisati u okvirima prostorne grupe R-3c u kojoj kristališu i polazni prahovi, bez vidljivog prisustva zaostalih ili stranih faza.

Vrednosti magnetnih momenata jona Fe^{3+} i Cr^{3+} odredjene su utačnjavanjem magnetne strukture u prostornoj grupi P1, pri čemu je za generisanje magnetnih refleksija korišćen program HKLGEN.

U pogledu magnetne strukture, uočeno je da jedna grupa uzoraka (x = 0,2; 0,4; 0,6; 1; 2) pokazuje strukturu linearnih antiferomagnetika, dok je kod dva uzorka (x = 1,4; 1,8) otkriveno prisustvo satelitskih refleksija koje ukazuju na postojanje helikoidalne strukture.

Takođe je uočeno da prisustvo hroma već pri koncentraciji od 10% (x = 0,2) u potpunosti stabiliše magnetnu strukturu visokotemperaturske magnetne faze Fe_2O_3.

PAIR DISTRIBUTION FUNCTION AND THE LOCAL STRUCTURE OF DISORDERED MATERIALS

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Many modern functional materials contain defects or are quite disordered, such as glasses, liquids, melts or gels. The local structure of these materials we can discribe using pair distribution function (PDF). PDF is a direct avereged representation of the atomic arragement and gives the probability of finding an atom at a distance r from a reference atom [1]. The PDF we can obtain from normailised powder diffraction data. The structure factor $S(q)$ is the only structure dependent part of the recorded intensities. From the experimental $S(q)$ data we can obtain the PDF via a simple Fourier transformation as follows

$$G(r) = \frac{2}{\pi}\int_0^\infty q[S(q)-1]\sin(qr)dq$$

Where r is the radial distance and q the magnitude of the wave vector.

PDF is an representation of the powder diffraction data in real-space, where the distances of characteristic peaks represent the separation of pairs of atoms and by calculating the PDF from model comparing them to the measured values we can obtain the information about the local structure.

The structure factor for our sample disordered materials has been obtained by x-ray diffraction. We obtained PDF via described standard method, using computer program RAD [2], and via MEM (maximum entropy method) using computer program IFO [3]. Program IFO gives smooth PDF, which is free of termination and other spurious ripples. The results obtained by two different ways were compared.

[1] H. Klug, L. Alexsander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley (1974), New York
[2] V. Petkov, J. Appl. Cryst. 22 (1989) 387-389
[3] V. Petkov, R. Danev, J. Appl. Cryst. 31 (1998) 609-619

FUNKCIJA RASODELE PAROVA I LOKALNA STRUKTURA NEUREĐENIH MATERIJALA

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Mnogi novi materijali sadrže defekte ili su sasvim neuređeni kao što su stakla, tečnosti, rastopi ili gelovi. Lokalnu strukturu ovih materijala možemo opisati pomoću funkcije raspodele parova (pair distribution function, PDF). PDF predstavlja srednju reprezentaciju atomskog uređenja i daje verovatnoću nalaženja određenog atoma na rastojanju r od određenog referentnog atoma [1]. PDF možemo dobiti iz normiranih difrakcionih intenziteta sa praškastih uzoraka. Strukturni faktor $S(q)$ je jedini strukturno zavisni deo snimljenih difrakcionih intenziteta. Iz eksperimentalno dobijenih $S(q)$ dobijamo PDF preko Furije transformacije

$$G(r) = \frac{2}{\pi}\int_0^\infty q[S(q)-1]\sin(qr)dq$$

gde je r radijalno rastojanje, a q intenzitet talasnog vektora.

PDF je prikaz difrakcionih podataka dobijenih sa praškastih uzoraka u realnom prostoru gde rastojanje između karakterističnih pikova prikazuje razmak između parova atoma. Izračunavanjem PDF iz modelne strukture i njenim poređenjem sa merenim vrednostima možemo dobiti informaciju o lokalnoj strukturi.

Eksperimentalni strukturni faktor za naše primere neuređenih materijala je dobijen pomoću difrakcije x-zraka. PDF smo dobili preko opisanog standardnog metoda, koristeći kompjuterski program RAD [2] i preko MEM (maximum entropy method - metod maksimalne entropije), koristeći kompjuterski program IFO [3]. Program IFO daje glatku i neprekidnu PDF koja ne sadrži prividne fluktuacije. Rezultati dobijeni pomoću dve različite metode su upoređeni.

[1] H. Klug, L. Alexsander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley (1974), New York
[2] V. Petkov, J. Appl. Cryst. 22 (1989) 387-389
[3] V. Petkov, R. Danev, J. Appl. Cryst. 31 (1998) 609-619

CRUCIBLE FURNACE FOR OBTAINING CRYSTALS

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During investigation of the possibility for obtaining monocrystals substances with unknown crystallization parameters in laboratory crucible furnace, we have constructed an air cooler (Fig. 1), which enables the simultaneous regulation of several different temperature gradients and crystallization rate intervals in a series of Tamman's test tubes.

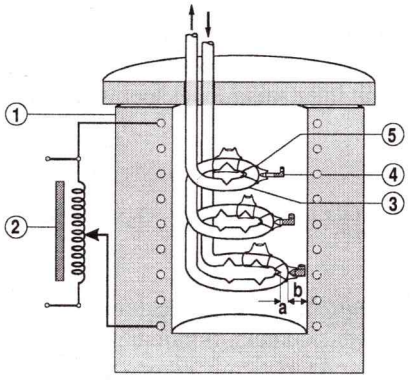

Figure 1. Crystallization apparatus: (1) laboratory crucible furnace, (2) continuously changeable transformer, (3) air cooler model ("crystallization spiral"), (4) curved Tamman's test tubes (family group) and (5) movable rings.

The crystallization rate interval in each test tube is regulated by the air flow rate, i.e. the cross-section of the air flow (**a**), which is regulated by the position of the test tube ring. The temperature gradient along test tube axis is regulated by the distance between the cooler and furnace wall (**b**), i.e. by translatory movement of the cooler and rotation movement of the ring. Tamman's test tubes of various shapes and dimensions (a family group [1]) can be mounted on the rings, i.e. simultaneously tested. The cooler can be modified into a rectilinear shape and installed into a tube furnace in a horizontal position ("crystallization bench") [2].

[1] K.-Th.Wilke, J. Bohm, *Kristallzüchtung,* Deutscher Verlag der Wissenschaften, Berlin (1988), p. 591.
[2] B. Čabrić, T. Pavlović, *J. Appl. Cryst.,* **33** (2000), pp. 387-388.

ТИГЛ ПЕЋ ЗА ДОБИЈАЊЕ КРИСТАЛА

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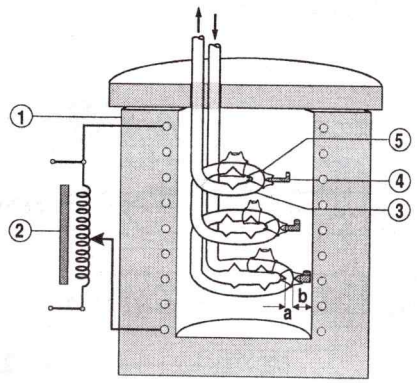
У току истраживања могућности добијања монокристала супстанци са непознатим параметрима кристализације у лабораторијској тигл пећи, конструисали смо ваздушни хладњак (сл. 1), који омогућава симултану регулацију неколико различитих температурских градијената и интервала брзина кристализација у низу Таманових епрувета.



Слика 1. Апаратура за добијање кристала: (1) лабораторијска тигл пећ, (2) континуално променљиви трансформатор, (3) ваздушни хладњак ("кристализациона спирала"), (4) савијене Таманове епрувете (ансамбл фамилије) и (5) помични прстенови.

Интервал брзине кристализације у свакој епрувети се регулише помоћу брзине кретања ваздуха, тј. пресека ваздушне струје (**a**), што се подешава помоћу положаја прстена са епруветом. Температурски градијент дуж осе епрувете се регулише помоћу растојања хладњака од зида пећи (**b**), тј. транслаторним померањем хладњака и ротационим померањем прстена. Таманове епрувете различитих облика и димензија (фамилја епрувета [1]) могу се поставити на прстеновима, тј. симултано тестирати. Хладњак се може модификовати у праволинијски облик и инсталирати у цилиндричној пећи у хоризонталном положају ("кристализациона клупа") [2].

[1] K.-Th.Wilke, J. Bohm, *Kristallzüchtung,* Deutscher Verlag der Wissenschaften, Berlin (1988), стр. 591.

[2] Б. Чабрић, Т. Павловић, *J. Appl. Cryst.*, **33** (2000), стр. 387-388.

A CHAMBER FURNACE FOR OBTAINING CRYSTALS

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In [1] a model of an air cooler ("heat seal") in a laboratory chamber furnace was presented, for regulating the interval of crystallization rate along the test tube, with the purpose of test of obtaining crystals of substances with an unknown crystallizaation rate. In this exposition we will show the development and improvement of the internal geometry of the cooler for the regulation of the air flow rate through the cooler, with the purpose of simultaneous regulation of a series ("scale") of intervals of crystallization rates in a column of Tamman's test tubes (Fig. 1).

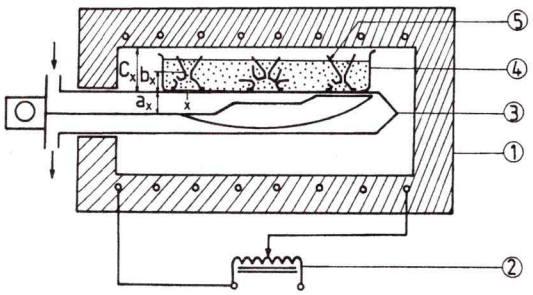

Figure 1. Crystallization apparatus: (1) laboratory chamber furnace, (2) continuously changeable transformer, (3) air cooler ("crystallization finger"), (4) crucible, and (5) a column of Tamman's test tubes.

The crystallization rate in each test tube is regulated by the cross-section of the air flow ($\mathbf{a}_x$), that is the position of Tamman test tube and the distance between the capillary and the cooler ($\mathbf{b}_x$). The temperature gradient is regulated by the distance $\mathbf{c}_x$. Tamman's test tubes with various shapes and dimensions [2] can also be tested simultaneously. If the cooler is rotated around the horizontal axis for 180 °, a different intervals of crystallization rates are obtained in test tubes along the cooler (the second crystallization "channel"). Several coolers can be installed ("family cold fingers", i.e. ensemble of instruments into the chamber), which enable crystallization tests in several columns i.e. a matrix: various test tubes, temperature gradients and intervals of crystallization rates for obtaining crystals. This method can also be applied in a tube furnace.

[1] B. Čabrić, B. Žižić, M. Lj. Napijalo, *Eur. J. Phys.*, **11** (1990), pp. 233-235.
[2] K.-Th.Wilke, J. Bohm, *Kristallzüchtung,* Deutscher Verlag der Wissenschaften, Berlin (1988), p. 591.

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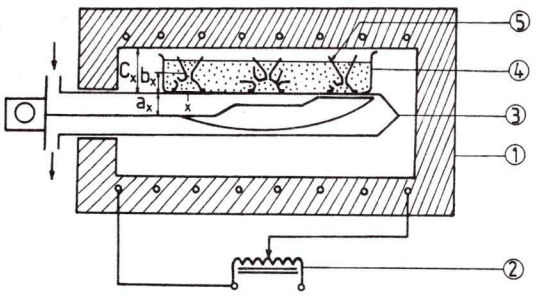

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[2] K.-Th.Wilke, J. Bohm, *Kristallzüchtung,* Deutscher Verlag der Wissenschaften, Berlin (1988), p. 591.

A NEW POLYMERIC COBALT(II) COMPLEX CONTAINING TEREPHTHALATE IONS AND 1,10-PHENATHROLINE

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Described compound presents continuation of our studies on ternary transition metal complexes containing terephthalate ions (tpht) and some aromatic amines, like 1,10-phenathroline (phen). Although some mononuclear tpht complexes are known too [1], binuclear or polymeric complexes, where tpht ions act as bridging ligands, are more frequently encountered [2].

In the title complex, two crystallographically different, but chemically identical tpht ions exist. Both of them behave as bridges with monodentately coordinated COO groups and with a centre of symmetry coinciding to the centre of aromatic ring. In this manner zigzag chains are formed. Similar chains have been already found [3] in one copper-ethylenediamine (en) complex, $[Cu(tpht)(en)(H_2O)_2]$, where tpht is also coordinated as bis-monodentate ligand and in $[Cu(tpht)(dipya)]\cdot H_2O$ (dipya=2,2'-dipyridylamine), with tpht as bis-bidentate ligand [4].

Co(II) environment consists of two N atoms (from phen) and three O atoms (from two COO groups and a water molecule). The coordination polyhedron can be described as very deformed trigonal bipyramid with N, O and Ow atom in the equatorial plane. Bond distances are between 2.012(3) and 2.142(3) Å. Angles in the equatorial plane are in the range 94.23(9) - 140.20(10) °, whereas N(apical)–Co–O(apical) angle is 167.34(8) °.

The coordinated H_2O molecule is a double H bond donor toward free O atoms from COO groups. One of these H bonds is intramolecular, while the other is intermolecular and connects adjacent chains.

Crystal data: $[Co(tpht)(H_2O)(phen)]$, $C_{20}H_{14}CoN_2O_5$, $M_r=421.26$, triclinic, sp. gr. $P\bar{1}$, $a=9.2688(17)$, $b=10.4550(18)$, $c=11.349(2)$ Å, $\alpha=112.462(3)$, $\beta=94.924(2)$, $\gamma=113.908(2)$ °, $V=890.6(3)$ Å^3, $Z=2$, $F(000)=430$, $\rho_x=1.571$ g cm^{-3}, $\mu(\text{Mo K}_\alpha)=0.999$ mm^{-1}, 3179 independent reflections, $R_1=3.67$ % for 2017 observed reflections with $I>2\sigma(I)$, $R_{w2}=6.32$ % (refinement on F^2) for all reflections and 309 refined parameters, with $(\Delta/\sigma)_{max}=0.001$, $\Delta\rho_{max}=0.208$ and $\Delta\rho_{min}=-0.258$ e Å^{-3}.

[1] J.Rogan, D.Poleti, Lj.Karanović, G.Bogdanović, A.Spasojević-de Biré, D.M.Petrović, *Polyhedron*, **19** (2000), 1415

[2] Z. Huaqiang, Y. Min, H. Xiaoyung, C. Xueyuan, *Cryst. Res. Technol.*, **32** (1997), 467

[3] E.G.Bakalbassis, A.P.Bozopoulos, J.Mrozinski, P.J.Rentzeperis, C.A.Tsipis, *Inorg.Chem.*, **27** (1988), 529

[4] D. Poleti, Lj. Karanović, J. Rogan, G. Bogdanović, A. Spasojević-de Biré, *VIII Conference of the Serbian Crystallographic Society, Abstracts*, Kragujevac, 2000, p. 63

NOVI POLIMERNI KOBALT(II) KOMPLEKS SA TEREFTALAT-JONIMA I 1,10-FENANTROLINOM

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Opisano jedinjenje predstavlja nastavak naših istraživanja u oblasti ternernih kompleksa prelaznih metala koji sadrže tereftalat-jon (tpht) i neke aromatične amine, kao što je 1,10-fenantrolin (phen). Mada su poznati i mononuklearni tpht-kompleksi [1], mnogo su češći binuklearni ili polimerni kompleksi gde se tpht-jon ponaša kao mostovni ligand [2].

U ovom jedinjenju postoje dva kristalografski nezavisna, ali hemijski identična tpht-jona. Oba jona se ponašaju kao mostovi sa monodentatno koordiniranim COO-grupama i centrom simetrije koji se poklapa sa centrom aromatičnog prstena. Tako nastaju cik-cak lanci. Slični lanci već su opisani [3] kod jednog bakar(II)-etilendiaminskog (en) kompleksa, $[Cu(tpht)(en)(H_2O)_2]$, gde je tpht takođe koordiniran kao bis-monodentat i kod kompleksa $[Cu(tpht)(dipya)]\cdot H_2O$ (dipya=2,2'-dipiridilamin) sa tpht kao bis-bidentatnim ligandom [4].

Okruženje oko Co(II) sastoji se od dva atoma N (iz phen) i tri atoma O (iz dve COO-grupe i molekula vode). Koordinacioni poliedar može se opisati kao jako deformisana trigonalna bipiramida sa atomima N, O i Ow u ekvatorijalnoj ravni. Dužine veza su između 2,012(3) i 2,142(3) Å. Uglovi u ekvatorijalnoj ravni su u opsegu između 94,23(9) i 140,20(10) °, dok ugao N(vrh)–Co–O(vrh) iznosi 167,34(8) °.

Koordinirani molekul vode je dvostruki H-donor i to prema slobodnim atomima O iz COO-grupa. Jedna vodonična veza je intramolekulska, dok je druga intermolekulska i povezuje susedne lance.

Kristalografski podaci: $[Co(tpht)(H_2O)(phen)]$, $C_{20}H_{14}CoN_2O_5$, M_r=421,26, triklinični, prostorna grupa $P\bar{1}$, a= 9,2688(17), b= 10,4550(18), c= 11,349(2) Å, α= =112,462(3), β=94,924(2), γ= 113,908(2) °, V= 890,6(3)Å^3, Z=2, $F(000)$=430, ρ_x= 1,571 g cm^{-3}, μ(Mo K$_\alpha$)= 0,999 mm^{-1}, 3179 nezavisnih refleksija, R_1= 3,67 % za 2017 opaženih refleksija sa $I>2\sigma(I)$, R_{w2}= 6,32 % (utačnjavanje pomoću F^2) za sve refleksije i 309 utačnjavanih parametara, sa $(\Delta/\sigma)_{max}$ = 0,001, $\Delta\rho_{max}$= 0,208 i $\Delta\rho_{min}$= –0,258 e Å^{-3}.

[1] J.Rogan, D.Poleti, Lj.Karanović, G.Bogdanović, A.Spasojević-de Biré, D.M.Petrović, *Polyhedron*, **19** (2000), 1415

[2] Z. Huaqiang, Y. Min, H. Xiaoyung, C. Xueyuan, *Cryst. Res. Technol.*, **32** (1997), 467 i citirana literatura

[3] E.G.Bakalbassis, A.P.Bozopoulos, J.Mrozinski, P.J.Rentzeperis, C.A.Tsipis, *Inorg.Chem.*, **27** (1988), 529.

[4] D. Poleti, Lj. Karanović, J. Rogan, G. Bogdanović, A. Spasojević-de Biré, *VIII konferencija srpskog kristalografskog društva, Izvodi radova*, Kragujevac, 2000, s. 64

X-RAY DIFFRACTION ANALYSIS IN THE VEGETABLE FAT POLYMORPHISM STUDY - STARTING COMPONENTS

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While continuing the work of characterization of polymorphism of vegetable fats by x-ray diffraction [1,3], the most common starting components such as hard and soft soya, palm oil and palm stone were studied.

All of the samples were treated thermally multiple times to their melting temperature, and then cooled in several different ways (gradually and quickly). The treated samples were examined by x-ray diffraction in the characteristic range $16 < 2\theta < 25^{o}$, and maximum intensities of present crystal and amorphous phases were determined by applying the profile analysis. From these data and the relation

$$\%\beta = I_{4,6} / (I_{4,6} + I_{4,2}) \cdot 100$$

participation of undesireable β-phase was calculated [2].

The results revealed differences in crystal / amorphous ratio between starting components as well as between the thermally treated samples of the same component. Thermal treatment reduces the degree of crystalinity in present phases, but not in relation to the total participation of the crystal matter. Also, the participation of β-phase increases under thermal treatment, depending differently on the type of component. Amount of β-phase and amorphous component is larger in gradually cooled samples comparing to quickly cooled samples.

Beside the examination described here, the samples were examined by polarizing microscope. Microphotographs reveal changes in size of crystal granules and aggregates under thermal influence and different treatment.

[1]. A. Rosic, I. Petrovic-Prelevic i D. Jovanovic, *VIII konferencija SKD, Kragujevac, Izvodi radova*, (2000), 75-76.
[2]. J.M. deMan, *Food Research International*, **25**, (1992), 471-476.
[3]. J.M. deMan and L. deMan, *Malaysian oil science and technology*, **4** (1995), 56-60.

ISPITIVANJE POLIMORFIZMA BILJNIH MASTI RENDGENSKOM DIFRAKCIJOM - POLAZNE KOMPONENTE

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U nastavku rada na karakterizaciji polimorfizma biljnih masti primenom metode rendgenske difrakcije [1,3], ispitane su najzastupljenije polazne komponente: tvrda soja, meka soja, palmino ulje i palmina koštica.

Svi uzorci su više puta termički tretirani do temperatura topljenja, a zatim hlađeni u različitim režimima (postepeno i naglo). Ovako obrađeni uzorci ispitani su metodom rendgenske difrakcije u karakterističnom opsegu $16 < 2\theta < 25^{\circ}$. Primenom profilne analize difraktograma određeni su intenziteti maksimuma prisutnih kristalnih i amorfnih faza. Iz dobijenih podataka i relacije

$$\%\beta = I_{4,6} / (I_{4,6} + I_{4,2}) \cdot 100$$

izračunato je učešće nepoželjne β-faze [2].

Dobijeni rezultati pokazali su da postoje razlike u odnosu kristalnog i amorfnog dela kako između polaznih komponenti, tako i kod tretiranih uzoraka iste komponente. Termički tretman utiče na opadanje stepena kristaliniteta prisutnih faza, ali to nije u vezi sa ukupnim učešćem kristalne materije. Takođe, učešće β-faze povećava se prilikom termičkog tretmana različito kod različitih komponenti. Količine β-faze i amorfne komponente veće su kod postepeno hlađenih uzoraka u odnosu na naglo hlađene.

Osim navedenih ispitivanja, karakteristični uzorci proučeni su pomoću polarizacionog mikroskopa. Na mikrofotografijama zapažaju se promene veličine kristalnih zrna i agregata pod uticajem temperature i različitog tretmana.

[1]. A. Rosic, I. Petrovic-Prelevic i D. Jovanovic, *VIII konferencija SKD, Kragujevac, Izvodi radova*, (2000), 75-76.
[2]. J.M. deMan, *Food Research International*, **25**, (1992), 471-476.
[3]. J.M. deMan and L. deMan, *Malaysian oil science and technology*, **4** (1995), 56-60.

STRUCTURAL CHARACTERIZATION OF THE ALICINE COMPLEX WITH β-CYCLODEXTRINE AND UREA

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Starting from known baktericide and fungicide properties of the extract from garlic bulb, the synthesis was performed of alicine $C_6H_{10}S_2O$, on active component of extract. Taking into account alicine instability, the complexation of alicine was performed with β-cyclodextrine ($C_{42}H_{70}O_{35}$) and urea (CH_4N_2O) in various molar ratios in order to implant alicine into the host crystal lattice and obtain stable inclusion complex which would retain the microbiological activity.

The first group of complexes made from **β-cyclodextrine + alicine**, was obtained in the form of white powder. Powder diffractograms were recorded with CuK_α radiation within the range 2θ=8-35°, for the samples with molar ratios BCD:A=1:1, 1:3, 1:6, as well as the sample BCD:A-D_2O=1:6, prepared from the solution with deuterated water. Diffractograms correspond to data from JCPDS-tables for β-cyclodextrine (32-1626;27;28). The comparison of diffractograms shows only a change of intensities of certain peaks, indicating that alicine implanting does not change the crystal lattice of the host.

Second group of complexes is made of **urea+alicine**. The obtained samples are of expressed crystalline character. Powder diffractogram was recorded with CuK_α radiation within the range 2θ=5-65° for samples UR:A=4:1, 6:1, 8:1 and UR:A-D_2O=4:1. Peak indexing was performed starting from data for urea (JCPDS 28-2015). Powder diffractograms indicate to the presence of the amorphous peak, change of intensity , as well as a slight displacement of the peaks characteristic for urea. The change of intensities of the indexed peaks can indicate the presence of the alicine in a certain plane of the urea crystal lattice, while from the displacement we can deduce the variation of the unit cell parameters of the inclusion complex.

Since the presence of alicine in the samples is confirmed by IR, NMR and microbiological analyses, the structural analysis can only tell that implantation of the alicine molecule into the crystal lattice of both hosts is possible in the limited molar range and it is completely non-stechiometric and disordered.

[1] G.Torri, A.Naggi, G.B.Fregnan, A.Trebbi: Dipyridamole-β-cyclodextrin complex: preparation and characterization, *Pharmazie*, **45**, (1990), 11.3, 193-195.

[2] S.Shawky Tous, A.M.El-Sayed, S.Ali El-Harras, W.Jun: Availability of phenindione-β-cyclodextrin inclusion complex, *Pharmazie*, **47** (1992), 11.5, 365-367.

STRUKTURNA KARAKTERIZACIJA KOMPLEKSA ALICINA SA β-CIKLODEKSTRINOM I UREOM

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Polazeći od poznatih baktericidnih i fungicidnih svojstava ekstrakta iz lukovice belog luka, izvršena je sinteza alicina $C_6H_{10}S_2O$, aktivne komponente ekstrakta. S obzirom na nestabilnost alicina izvršena je kompleksacija alicina sa β-ciklodekstrinom ($C_{42}H_{70}O_{35}$) i ureom (CH_4N_2O) u različitim molskim odnosima u cilju ugradnje alicina u kristalnu rešetku domaćina i dobijanja stabilnog inkluzionog kompleksa koji zadržava mikrobiološku aktivnost [1], [2].

Prvu grupu kompleksa koju čine **β-ciklodekstrin + alicin**, dobili smo u obliku belog praha. Snimljeni su difraktogrami praha sa CuK_α zračenjem u opsegu 2θ=8-35°, za uzorke sa molskim odnosom BCD:A=1:1, 1:3, 1:6, kao i uzorak BCD:A-D_2O=1:6 koji je pripremljen iz rastvora sa deuterisanom vodom. Difraktogrami odgovaraju podacima iz JCPDS-tablica za β-ciklodekstrin (32-1626;27;28) . Poređenjem difraktograma uočena je samo promena intenziteta pojedinih pikova, što ukazuje da ugrađivanje alicina ne menja kristalnu rešetku domaćina.

Drugu grupu kompleksa čine **urea+alicin**. Dobijeni uzorci su bili izrazito kristalični. Difraktogram praha je snimljen sa CuK_α zračenjem u intervalu 2θ=5-65° za uzorke UR:A=4:1, 6:1, 8:1 i UR:A-D_2O=4:1. Izvršeno je indiciranje pikova polazeći od podataka za ureu (JCPDS 28-2015). Analiza difraktograma pokazuje prisustvo amorfnog pika, promenu intenziteta, kao i neznatno pomeranje položaja pikova karakterističnih za ureu. Promena intenziteta indiciranih pikova može da ukaže na prisustvo alicina u određenoj ravni kristalne rešetke uree, dok iz pomeranja možemo odrediti promenu parametara elementarne ćelije inkluzionog kompleksa

Pošto je prisustvo alicina u uzorcima potvrđeno IC, NMR i mikrobiološkim analizama, strukturno bi se samo moglo reći da je ugrađivanje molekula alicina u kristalnu rešetku oba domaćina moguće u ograničenom molskom odnosu i potpuno je nestehiometrijsko i neuređeno.

[1] G.Torri, A.Naggi, G.B.Fregnan, A.Trebbi: Dipyridamole-β-cyclodextrin complex: preparation and characterization, *Pharmazie*, **45**, (1990), 11.3, 193-195.

[2] S.Shawky Tous, A.M.El-Sayed, S.Ali El-Harras, W.Jun: Availability of phenindione-β-cyclodextrin inclusion complex, *Pharmazie*, **47** (1992), 11.5, 365-367.

SYNTHESIS AND CRYSTAL STRUCTURE OF 4-SOLANIDENE-3-ONE

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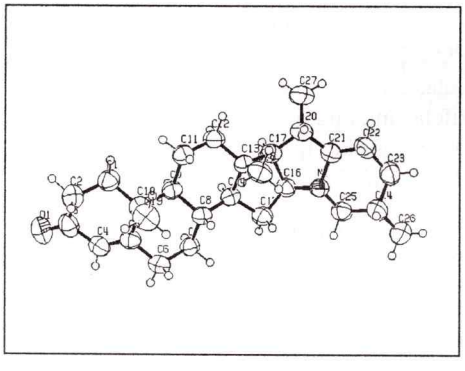
In our previous report [1] some novel chemical transformations of solanidine were performed with the goal of obtaining 16-dehydro-pregnane derivatives, the key intermediates in the industrial synthesis of progesterone and cortisone derivatives. To achive these goals, we have studied some new solanidene degradation proceses as in the case of 4-solanidene-3-one [2].

The compound crystallyzes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters a=10.4728(10), b=14.0101(14), c=15.7409(14)Å, Z=4, D_x=1.138 Mgm^{-3}, μ=0.07 mm^{-1}.

The intensities were collected on Bruker SMART APEX diffractometer, using MoK_α radiation.

The crystal structure was solved by direct methods on the basis of 3001 indipendent reflections using SIR 92 [3] and refined by SHELXL-97 [4]. The final R factor is 0.0295 for 1257 reflections with $I>4\sigma(I)$.



Perspective view of the molecule

[1] K. Gaši, D. Miljković, *J. Serb, Chem Soc.* **53** (1988) 165.

[2] K. Penov-Gaši, D Rackov-Čolić, O. Arcson, Z. Sakač, E. Đurendić, M. Sakač, LJ. Medić-Mijačević, D. Miljković, *Collect. Czech. Chem Commun.* **61** (1996), 1655

[3] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori & M. Camalli, SIR 92, *J. Appl. Cryst.* **27** (1994), 435

[4] G.M.Sheldrick, (1997) SHELX-97, *Program for the solution and refinement of crystal structures*, University of Goettingen, Germany.

SINTEZA I KRISTALNA STRUKTURA 4-SOLANIDEN-3-ONA

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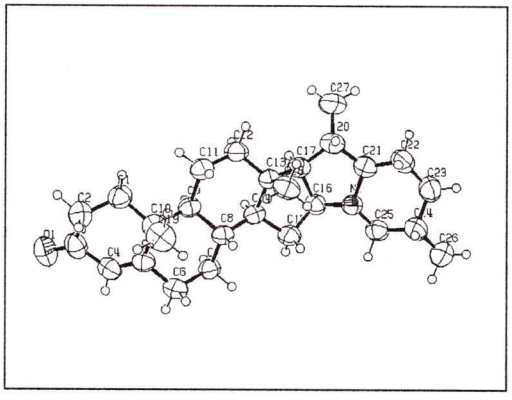
U našem ranijem radu [1] primenjene su nove hemijske transformacije solanidena sa ciljem dobijanja derivata 16-dehidro-pregnana, ključnog intermedijera u sintezi progesteronskih i kortizonskih derivata. U tom cilju, proučavane su nove reakcije degradacije solanidena, kao u slučaju sa jedinjenjem 4-solaniden-3-on [2].

Jedinjenje kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije a=10,4728(10), b=14,0101(14), c=15,7409(14)Å, Z=4, D_x=1,138 Mgm^{-3}, μ=0,07 mm^{-1}.

Intenziteti su sakupljeni na Bruker SMART APEX difraktometru, uz upotrebu MoK_α zračenja.

Struktura kristala rešena je primenom direktnih metoda na bazi 3001 nezavisnih refleksa pomoću SIR 92 [3] i utačnjena pomoću SHELXL-97 [4]. Konačna vrednost R faktora je 0,0295 za 1257 refleksa sa $I>4\sigma(I)$.



[1] K. Gaši, D. Miljković, *J. Serb, Chem Soc.* **53** (1988) 165.
[2] K. Penov-Gaši, D Rackov-Čolić, O. Arcson, Z. Sakač, E. Đurendić, M. Sakač, LJ. Medić-Mijačević, D. Miljković, *Collect. Czech. Chem Commun.* **61** (1996), 1655
[3] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori & M. Camalli, SIR 92, *J. Appl. Cryst.* **27** (1994), 435
[4] G.M.Sheldrick, (1997) SHELX-97, *Program for the solution and trefinement of crystal structures*, University of Goettingen, Germany.

SYNTHESIS AND CRYSTAL STRUCTURE INVESTIGATIONS OF TWO ANDROSTANE DERIVATIVES

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3β,17β-Dihydroxy-17α-picolile-5α-androstane (**1**) and their 5β-isomer (**2**) were synthesized from dehydroepiandrosterone acetate by catalitic hydrogenation of Δ^5-double bond and further stereospecific addition of α-picolyllithium to the C-17 carbonyl group.

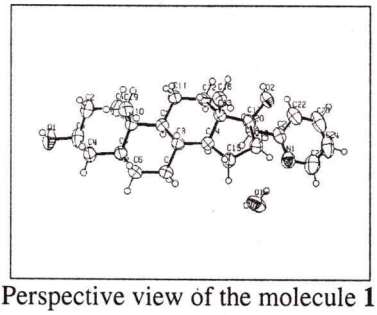
The compound **1** crystallyzes in the orthorhombic system, space group $P2_12_12_1$, with the unit cell parameters a=7.234(5), b=13.678(5), c=23.028(5)Å, Z=4, D_x=1.171 Mgm^{-3}, μ=0.075 mm^{-1}. There is one water molecule in the asymmetric unit.

The compound **2** crystallyzes in the monoclinic system, space group $P2_1$, with the unit cell parameters a=7.280(1), b=12.535(5), c=12.092(1)Å, β=95.354(4)°, Z=2, D_x=1.159 Mgm^{-3}, μ=0.07 mm^{-1}.

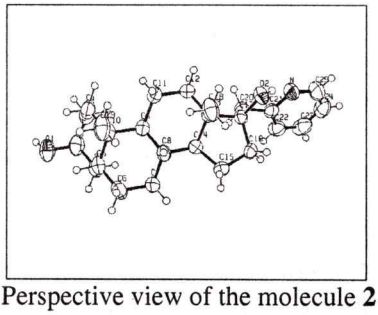
The intensites, for both compounds were collected on Bruker SMART APEX diffractometer, using MoK_α radiation.

Both structures were solved by direct methods using SIR 92 [1], and refined by SHELXL-97 [2]. The final R factors for compounds **1** and **2** are 0.0324 (for 1940 indipendent reflections with $I>2\sigma(I)$) and 0.0416 (for 1800 indipendent reflections with $I>4\sigma(I)$), respectively.

The different orientation of hydrogen atom in position 5 in two molecules is due to the trans and cis fusion between the A and B rings in compound **1** and **2**, respectively. Consequently, packing arrangements and hydrogen bond-networks are also different.



Perspective view of the molecule **1**



Perspective view of the molecule **2**

[1] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori & M. Camalli, SIR 92, *J. Appl. Cryst.* **27**, (1994), 435

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

SINTEZA, KRISTALOGRAFSKA I STRUKTURNA ISTRAŽIVANJA DVA DERIVATA ANDROSTANA

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3β,17β-Dihidroksi-17α-pikolil-5α-androstan (**1**) i njegov 5β-izomer (**2**) su sintetizovani iz dehidroepiandrosteron acetata katalitičkom hidrogenizacijom Δ^5 - dvostruke veze i daljom stereospecifičnom adicijom α-pikolillitijuma na C-17 karbonilnu grupu.

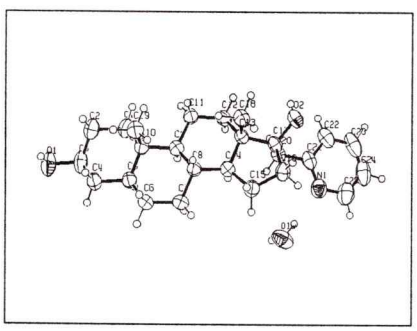
Jedinjenje **1** kristališe u ortorombičnom kristalografskom sistemu, prostorna grupa $P2_12_12_1$, sa parametrima elementarne ćelije a=7,234(5), b=13,678(5), c=23,028(5)Å, Z=4, D_x=1,171 Mgm^{-3}, μ=0,075 mm^{-1}. U asimetričnoj jedinici postoji jedan molekul vode.

Jedinjenje **2** kristališe u monokliničnom kristalografskom sistemu, prostorna grupa $P2_1$, sa parametrima elementarne ćelije a=7,280(1), b=12,535(5), c=12,092(1)Å, β=95,354(4)°, Z=2, D_x=1,159 Mgm^{-3}, μ=0,07 mm^{-1}.

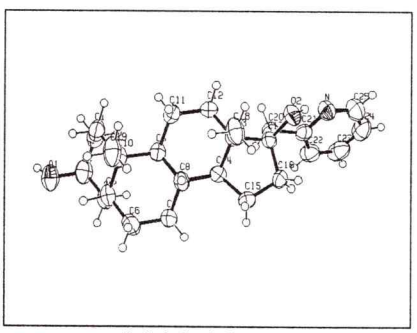
Intenziteti za oba jedinjenja su sakupljeni na Bruker SMART APEX difraktometru, uz upotrebu MoK_α zračenja.

Obe strukture su rešene direktnim metodama pomoću SIR 92 [1] i utačnjene sa SHELXL-97 [2]. Konačni R faktori za jedinjenja **1** i **2** su 0,0324 (za 1940 nezavisnih refleksa sa I>2σ(I)) i 0,0416 (za 1800 nezavisnih refleksa sa I>4σ(I)), respektivno.

Različita orijentacija vodonikovog atoma u položaju 5 u ovim molekulima posledica je trans i cis vezivanja A i B prstenova u jedinjenjima **1** i **2**, respektivno. Sledstveno tome, pakovanja molekula u kristalu i mreže vodoničnih veza, za ova dva jedinjenja, su takođe različiti.



Molekul **1**



Molekul **2**

[1] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori & M. Camalli, SIR 92, *J. Appl. Cryst.* **27**, (1994), 435

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

IN MEMORIAM

Др ДУБРАВКО РОДИЋ

13. 6. 1955 - 12. 6. 2001.

Дана 12. 6. 2001. године изненада је преминуо наш драги пријатељ и колега др Дубравко Родић, научни саветник Института "Винча". Сахрањен је на Новом гробљу у Београду, 14. 6. 2001. године.

Др Дубравко Родић рођен је у Дрвару 13. 6. 1955. године. На природно-математичи факултет у Београду, одсек Физика, уписан је 1974. године, где је и дипломирао 1979. године. Од 1979. године радио је у Институту за нуклеарне науке "Винча". Магистрирао је 1987. године на Природно-математичом факултету у Београду, одсек Физика. Докторску дисертацију под насловом "Структурне карактеристике и физиче особине простих и мешовитих граната ретких земаља" одбранио је на Природно-математичком факултету у Београду, одсек Физика, 1992. године.

Др Дубравко Родић је радио у области физике чврстог стања и бавио се кристалним и магнетним структурама магнетних материјала као и њиховим магнетним особинама. Научно-истраживачка активност др Дубравка Родића била је усмерена на подобласт магнетизма и физике магнетних материјала, са израженим интересом за везу структурних и магнетних особина. Користио је више експерименталних и теоријских метода у истраживањима интерметала, метал-хидрида, магнетних и попумагнетних полупроводника.

Био је предавач на последипломским студијама на Хемијском и Физичком факултету у Београду и Природно-математичком факултету у Новом Саду. Објавио је неколико десетина радова у водећим међународним часописима и мноштво радова у зборницима са међународних и домаћих

конференција. У међународним часописима цитиран је више од 40 пута, неколико десетина пута у Инорганиц Црйстал Струцтуре Датабасе. Његови научни резултати из материјала са структуром граната су значајно истакнути у монографији Елецтрониц анд Магнетиц Пропертиес оф Металс анд Церамицс серије Материалс Сциенце анд Тецхнологй (волуме 3Б, едитор К. Х. Ј. Бусцхоњ). Био је руководилац више пројектних задатака.

Волео је свој посао. Поседовао је огромну енергију, ентузијазам и способност да у свему пронађе оно што други не могу. Због тога је и било могуће да наша Лабораторија која је у време оснивања од физичара имала Дубравка као јединог магистра, за протеклих дест година израсте у значајну истраживачку лабораторију, где су сви тадашњи почетници постали доктори наука. И то за време десет кошмарних година испуњених ратовима, свеколиком несрећом и немаштином. Нема ниједне наше тезе, било магистарске или докторске, где Дубравко није био или ментор или прво име у захвалници. Била нам је част и понос да радимо с њим и да учимо од њега. Његову смрт осећамо као лични губитак и као дуг који незнамо како да одужимо.

Нашем пријатељу Дубравку је наш успех био важнији од његовог, наше потребе нужније од његових, његова изгарања ситница, а он сам и његови прохтеви нешто што не постоји. Тако је било и за најближе пријатеље и за случајне познанике, јер се он давао свима несебично и искрено и увек до краја, а при томе није тражио ништа за узврат. Само је давао и давао... Вероватно да је такву личну скромност и једноставност тешко и замислити некоме ко га није познавао.

С једне стране скромност, а са друге нескромна ширина, знање, ерудиција, култура и емоције без задршке нешто што носе само визионари и посвећеници. Дубравко је био и једно и друго. И зато је могао с једне стране да буде загледан у атоме, а са друге стране у судбине.

На жалост све има цену, а овога пута цена је била његово здравље. Он је и преко тога прелазио као преко нужних препрека које се једноставно морају прескочити, а онда идемо даље ... Али несрећа његовог родног Дрвара се није могла прескочити. ... ни колоне, ни збегови. То су били ножеви које му нико из срца није могао ишчупати. Само би понекад пред пријатељима уздахнуо и објаснио како је његово срце увек тамо. Волео је дружења и забаве и увек би запевао песму из родног краја о "маги и вуку", о бојама Динаре и мирисима Крајине. Само би скромно испричао понеки детаљ о својој породици.

Више пута је боравио у Пољској и Шведској као гостујући истраживач у Институту за физику Јагелонског Универзитета у Кракову, Ангстрем Лабораторији у Упсали и Лабораторији за неутронска истраживања у Штуцвику. Његова смрт болно је одјекнула и у тим институцијама.

Био је члан Југословенског друштва физичара. Био је један од оснивача Српског кристалографског друштва и члан Европског кристалографског друштва.

Због свега нека му је вечна слава и хвала.

Сарадници Лабораторије за теоријску физику и физику кондензоване материје Института "Винча"

IN MEMORIAM

Dr. DUBRAVKO RODIC

13 June 1955 – 12 June 2001

On 12 June 2001 suddenly deceased our dear colleague and friend Dr. Dubravko Rodic, Senior Researcher of the Condensed Matter Physics Laboratory, Vinca Institute in Belgrade. The funeral took place on 13 June 2001 at the New Cemetery in Belgrade.

Dr. Dubravko Rodic was born on 13 June 1955 in Drvar, former Yugoslavia. On 1974 he started his study of Physics at the Faculty of Natural Sciences in Belgrade, Department of Physics, where he obtained his BSc. degree on 1979. The same year he obtained permanent position with the Vinca Institute of Nuclear Sciences in Belgrade where he spent his whole scientific career. On 1987 he obtained his MSc. degree at the Faculty for Natural Sciences, Department of Physics, Belgrade. On 1992 he defended his PhD. Thesis entitled "Structural Characteristics and Physical Properties of Pure and Mixed Rare-Earths Garnets" at the Department of Physics, Faculty of Natural Sciences, Belgrade.

Dr. Dubravko Rodic worked in the field of Condensed Matter Physics with the focus on magnetism and magnetic materials. He studied crystal and magnetic structures of various magnetics with the emphasis on the interplay between these properties. He used several experimental techniques as well as different theoretical approaches in his investigations on intermetalics, metal-hydrides, spinels, garnets, semimagnetic semiconductors and other diluted magnetics. He had published a few dozens of papers in leading international journals and numerous works in proceedings of international and domestic conferences. He had more than 40 citations in international journals especially in the Inorganic Crystal Structure Database. His most significant results on garnet materials have been sharply propound in the "Electronic and Magnetic Properties of Metals and Ceramics" monograph of the Materials Sciences and Technology series (Vol. 3B, ed. K.H.J. Buschow). He was a leader of several Research Projects.

Dr. Dubravko Rodic held a lecturer position on the post-graduated studies at the Faculty of Physics and Faculty of Chemistry in Belgrade as well as at the Faculty of Natural Sciences in Novi Sad. In addition he was a mentor for many BSc, MSc and PhD thesis which have been successfully completed at these faculties.

Dr. Rodic had established a fruitful collaboration with several scientific institutions abroad. He was a guest-scientist in numerous occasions at the Institute of Physics of the Jagelonian University at Krakow (Poland), Angstrom Laboratory at Uppsala and Neutron Research Laboratory at Studsvik (Sweden). He was a member of the Yugoslav Physical Society, one of the founders of the Serbian Crystallographic Society and the member of the European Crystallographic Society.

Our gratitude and the warm memory of Dr. Dubravko Rodic shall remain in our research community.

Members of the Condensed Matter Physics Laboratory,
The Vinca Institute, Belgrade.

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