from Kurucz *et al*., 1995 [4] was used to recover a correctly refolded protein from inclusion bodies.

A purification procedure comprising three chromatography steps yielded scFv 1696 in the purity necessary for crystallization trials.

The complex was prepared by mixing scFv1696 with an excess of the epitope peptide corresponding to the N-terminus of HIV-2 PR (PQFSLWKR). Monomeric and dimeric forms of the complex were separated by FPLC on a Mono-Q column. In contrast to free scFv 1696 these forms are stable and do not interchange.

In a series of crystallization trials crystals of the complex have been obtained.

For crystallization trials by vapour diffusion method (hanging drop) only monomeric complex of the scFv1696 with epitope peptide was used. Crystals grew spontaneously at 25°C in ammonium sulfate (concentrations: 1.8 - 2.0 M) at pH 4.6. These crystals were very sensitive and flaws on their surface appeared in few days. However, this spontaneous crystallization could not be reproduced with a new batch of the complex, therefore, a streak seeding technique was applied and single crystals of size up to 0.3 x 0.3 x 0.2 mm were obtained.

Solving of 3D structure of the scFv 1696 - epitope peptide complex is expected to lead to antibody- structure-based design of a new class of HIV protease non-active site inhibitors, possibly of different HIV resistance characteristics.

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POSTERY

CRYSTALLIZATION AND PRELIMINARY DIFFRACTION STUDY OF HIV-1 PROTEASE COMPLEXED WITH HYDROXYETHYLAMINE INHIBITOR SI

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The HIV-1 protease is essential for replication of infective virus HIV, and therefore is an attractive target for the design of specific inhibitors. In search for new inhibitors substantial effort is placed on understanding the nature of the inhibitor binding modes in the active site, using X-ray diffraction on crystals as the primary source of structural information. Here we report crystallization of HIV-1 protease complexed with a four amino acid pseudopeptidic inhibitor, where the scissile peptide bond is replaced by hydroxyethylamine isostere. This inhibitor, Boc-Phe-[*(S)*-$CH(OH)CH_2NH$]Phe-Ile-Phe-NH_2 , is assigned here SI.

First crystallization trials were based on crystallization studies performed with complex of HIV-1 PR with inhibitors SE, RE, RQ. These inhibitors differ from SI only in the amino acid at P2' position, carrying Glu or Gln instead of Ile, and in configuration at C4, an hydroxyl bearing carbon of the pseudopeptidic bond. Hanging drop vapor diffusion technique has been used in all experiments. In the case of Glu/Gln containing inhibitors protein - inhibitor mixture of 3 mg/ml HIV PR, 0.544 mM inhibitor (four-fold molar excess over protease) in 50 mM sodium acetate pH 5.6, 1 mM EDTA, 0.05% -mercaptoethanol, 5% DMSO was used. The optimal crystallization conditions found for these crystals are: 1M $NH_4H_2PO_4$, 100 mM sodium citrate, pH 4.5, temperature 6 - 8°C [1].

In contrast to Glu/Gln containing inhibitors, SI inhibitor addition caused protein precipitation even without presence of salt precipitant. Probable reason is higher hydrophobicity of SI inhibitor. Addition of ammonium phosphate at conditions described above produced no crystal growth and no additional precipitation. Crystals of max.

dimensions 0.5x0.05x0.05 mm were grown at pH 6-8, 25°C and low precipitant concentration (0.1 M $NH_4H_2PO_4$, 5 mM sodium citrate, 50 mM sodium acetate), but reproducibility of growing a crystal was very low and crystals often coexisted with precipitate. Good reproducibility has not been achieved until following steps have been undertaken to decrease protease precipitation by inhibitor: 1) decreasing the inhibitor concentration to two-fold molar excess over protease 2) increasing the concentration of inhibitor solvent DMSO to 10% in protease - inhibitor mixture 3) maintaining constant concentration of DMSO in drop after addition of reservoir solution to protease - inhibitor mixture. Also increasing the protein concentration resulted in major improvement of reproducibility. Best crystals have been obtained using NaCl as precipitant, $(NH_4)_2SO_4$ produced no crystals. Most promising conditions in terms of crystal quality and reproducibility of results were obtained with protein sample of 6 mg/ml protease, 0.544 mM SI, 10% DMSO, 1 mM Na_3PO_4 pH 5.6, 1 mM EDTA, 1 mM DTT, 100 mM NaCl equilibrated with precipitant 1.65 M NaCl, 50 mM sodium citrate pH 5.5 at 20°C.

Crystals of dimensions 0.2x0.04x0.06 mm, which were grown from protein sample 3 mg/ml protease, 0.272 mM SI, 5% DMSO, 1 mM Na_3PO_3 pH 5.6, 1 mM EDTA, 1 mM DTT in precipitant 0.77M NaCl, 50 mM sodium citrate pH 5.0, have been tested under X-ray beam at Sincrotrone Trieste and have diffracted to resolution 2.5 Å.

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CRYSTAL STRUCTURE AND BIOLOGICAL ACTIVITY OF 1,4-DIHYDROPYRIDINE DERIVATIVES

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A number of 4-aryl-1,4-dihydropyridine derivatives have been prepared and tested for cardiovascular activity. Some of them have been found to possess potent vasodilating activity due to their calcium (Ca)-blocking effect and are now in clinical trials or therapeutic use for the treatment of cardiovascular diseases, such as several kinds of hypertension, angina pectoris and cerebrovascular insufficiency. An illustrative example is dimethyl-1,4-dihydro-2,6-dimethyl-4-(2-nitrophenyl)pyridine-3,5-dicarboxylate(Nifedipine), which is already employed therapeutically. This substance lowers the frequency of attack of angina pectoris and reduces blood pressure. The discovery of the therapeutic activity of this class of substances initiated renewed the synthesis of numerous related compounds. X-ray studies on 1,4-dihydropyridines have shown a great dependence of the geometry of the skeleton on the attached substituents, especially those in the 4 position. We have studied the crystal structure of dimethyl isopropyl 1-ethoxymethyl-6-methyl-4-(3-nitrophenyl)-1,4-dihydropyridine-2,3,5-dicarboxylate prepared by a modified Hantzsch procedure.

Crystal data: monoclinic, $P2_1/c$, a = 9.291(4), b = 9.598(3), c = 27.175(13) Å, β = 99.53(3)°, γ = 0.103 mm^{-1}, Z = 4, D_x = 1.32 $Mg.m^{-3}$, R(F) = 0.039, $wR(F^2)$ = 0.067 for 1420 unique reflections, S = 0.853.

The crystal structure is formed by single molecules linked *via* hydrogen bonds. The substitued 1,4-dihydropyridine ring has a flat boat conformation with the N and C atoms displaced by 0.126(3) and 0.202(3) Å, respectively, from the plane through the other four C atoms which defines the base of the boat. The phenyl ring have an almost planar conformation, with a dihedral angle between the individual planes of the 1,4-dihydropyridine and phenyl rings of 87.1(1)°. The 3-nitro substituent on the phenyl ring is rotated away from the coplanarity with the phenyl ring by only 3.1°.

COMPLEXES OF COPPER AND NICKEL INVOLVING THIODIGLYCOLIC ACID

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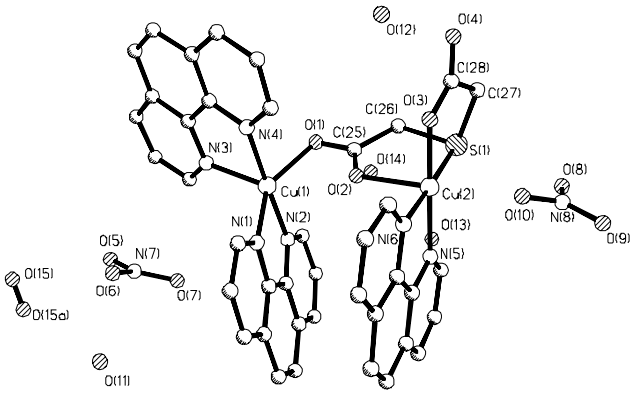
Thiodiglycolic acid as a ligand can be coordinated to metal centres in different modes.[1] In our previous study we have used thiodiglycolate dianion as a bridging ligand between two iron centres and we have found a week antiferromagnetic exchange.[2] We wanted to find if the exchange was intramolecular only. Because we were not successful in preparation of single crystals of iron complexes we have decided for preparation of copper and nickel mono and binuclear complexes.

Complexes of compositions

μ-[(pmdien)(H_2O)Cu(μ-tdga)Cu(pmdien)(H_2O)](ClO_4)$_2$ (1),
[(pmdien)(H_2O)Cu(μ-tdga)Cu(pmdien)(H_2O)](NO_3)$_2$ (2),
[(phen)$_2$Cu(μ-tdga)(phen)](NO_3)$_2$.5H_2O (3),
[(mdpta)Ni((μ-tdga)Ni(mdpta)](ClO_4)$_2$ (4),
[Cu(phen)(tdga)(H_2O)].H_2O (5), [Ni(bpy)(tdga)(H_2O)].H_2O (6),
[Ni(phen)(tdga)(H_2O)] (7),
[Ni(1,8-dan)(tdga)(H_2O)] (8)
and [Ni(nphen)(tdga)(H_2O)].H_2O (9),
where
H_2tdga = thiodiglycolic acid,
pmdien = pentamethyldiethylenetriamine,
phen = 1,10-phenanthroline,
mdpta = 3,3´-diamino-N-methylpropylamine,
bpy = 2,2´-bipyridyl,



1,8-dan = 1,8-diaminonaphthalene,
nphen = 5-nitro-1,10-phenanthroline, have been prepared.

Temperature dependence of magnetic susceptibility was studied for copper binuclear complexes but no exchange between paramagnetic centres was found. Cyclic voltammetry of (1) and (2) proved possibility of reversible reduction of the complexes.

X-ray analysis of (1) proved coordination number five around Cu^{II} centres bridged by thiodiglycolate through one oxygen atom. Coordination is completed by one O atom from water molecule and three N atoms of pmdien. Structure (3) (see Figure) consists also of two pentacoordinated Cu^{II} atoms bridged by thiodiglycolate. One copper atom is coordinated through one O atom of the dianion and four N atoms from two phenanthrolines. The second Cu atom is coordinated by two oxygens of both carboxylate groups, S atom of thiodiglycolate and two N atoms of phenanthroline.

Grant support: IG 31703010 from UP Olomouc.

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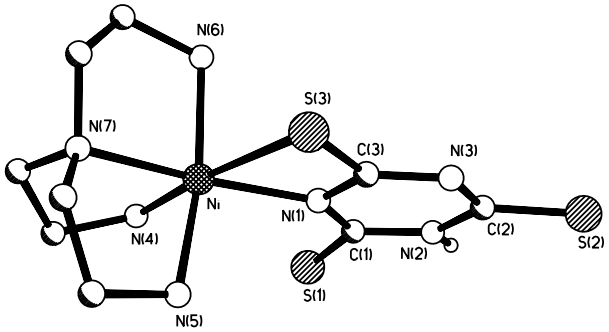

Fig. 1

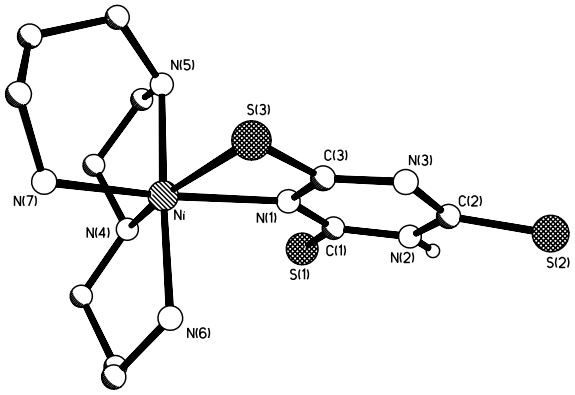

Fig. 2

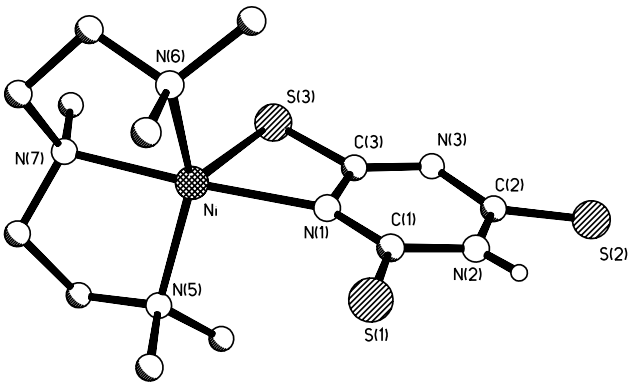

Fig. 3

SEMI-EMPIRICAL ANALYSIS OF NICKEL COMPLEXES WITH TRITHIOCYANURIC ACID

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Recently, we prepared and structurally characterized the following complexes involving dianion of trithiocyanuric acid and nitrogen-donor ligands in the coordination sphere:
[Ni(taa)(ttcH)][(1)] (*Fig. 1*),
[Ni(bapen)(ttcH)].$2H_2O$[(2)] (*Fig. 2*) and
[Ni(pmdien)(ttcH)][(3)] (*Fig. 3*)
(taa = tris(2-aminoethyl)amine,
bapen = N,N'-bis(3-aminopropyl)ethylenediamine,
pmdien = pentamethyldiethylenetriamine,
$ttcH_3$ = trithiocyanuric acid). In addition to the X-ray structures of *1*, *2* and *3* we have performed geometry optimizations of all the complexes. Geometries were optimized by the semi-empirical ZINDO1 method using the HyperChem 5.0 molecular modelling program package[(4)]. As can be seen from the Table (see below) calculated bond lengths and angles are in good agreement with experimentally determined values.

Acknowledgement: *We thank the Grant Agency of the Czech Republic for support (203/98/P220).*

(Å)	*1*		*2*		*3*	
	X-ray	ZINDO1	X-ray	ZINDO1	X-ray	ZINDO1
$Ni\text{-}N(1)_{ttcH}$	2.040(2)	1.882	2.143(3)	1.894	2.096(3)	1.970
$Ni\text{-}N(4)_{amine}$	2.063(3)	2.052	2.080(4)	2.076	-	-
$Ni\text{-}N(5)_{amine}$	2.097(3)	2.097	2.115(4)	2.087	2.081(4)	2.026
$Ni\text{-}N(6)_{amine}$	2.109(3)	2.069	2.077(4)	2.077	2.074(3)	2.026
$Ni\text{-}N(7)_{amine}$	2.086(2)	1.977	2.089(4)	1.954	2.100(4)	2.053
$Ni\text{-}S(3)_{ttcH}$	2.6650(10)	2.534	2.5208(16)	2.464	2.3392(13)	2.359
$S(3)_{ttcH}\text{-}Ni\text{-}N(4)_{amine}$	171.17(8)	162.68	164.93(11)	168.05	108.66(11)	$106.78^{N(6)}$
$N(1)_{ttcH}\text{-}Ni\text{-}N(7)_{amine}$	168.18(9)	175.17	163.44(15)	173.87	174.05(14)	177.31
$N(5)_{amine}\text{-}Ni\text{-}N(6)_{amine}$	163.61(11)	160.40	173.68(15)	177.78	143.55(14)	146.25

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CRYSTAL STRUCTURE OF HALOALKANE DEHALOGENASE LINB FROM *Sphingomonas paucimobilis* UT26 AT 1.6 Å RESOLUTION

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Haloalkane hydrolitic dehalogenase LinB from *Sphingomonas paucimobilis* UT 26 is the enzyme releasing chloride or bromide anion from *n*-halogenated alkanes. The enzyme was crystallized using the hanging-drop vapor-diffusion method at 278 K. The best crystals were obtained by micro-seeding with a PEG 6000 precipitant. They diffract to at least 1.6 Å using synchrotron X-ray under cryogenic (100 K) conditions. The crystal belongs to the orthorhombic space group $P2_12_12$ with unit-cell parameters a=50.29, b=71.70, c=72.73 Å. The crystal structure of LinB has been solved by molecular replacement with known structure of dehalogenase from *Rhodococcus* species and refined at 1.6 Å resolution to crystallographic R/factor of 16.5%. The monomeric enzyme is a spherical molecule and is composed, alike as the other members of the protein superfamily of the a/b-hydrolases, to two domains. Domain I has a/b type structure with central eight-stranded twisted b-sheet, domain II lies like a cap on top of domain I and consists mainly of α-helices.

PREPARATION AND CRYSTAL STRUCTURE OF LEAD TUNGSTEN OXIDE

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Lead tungsten oxide (Pb_2WO_5) was prepared by solid state reaction of powdered WO_3 and PbO at 890°C [1]. Phase transformation take place during cooling of the product at 330°C [2]. Low temperature form of Pb_2WO_5 was created by this way. A good single crystal of the suitable size for X-ray structure measurement was chosen from the polycrystalline sample.

Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer (Cu-Kα λ = 1,54056 Å).

The structure was solved by the direct method using the program SIR92 [3]. The lead and the tungsten atoms were refined anisotropically, the oxygen atoms were refined isotropically only. The minimised function was $w(F_o - F_c)^2$, where *w* is Chebyshev polynom. [4].

Crystal data for lead tungsten oxide stable below 330°C:

Formula	Pb_2WO_5
Mol.wt.	678.245
Crystal system	monoclinic
Space group	*P 21/a*
a, Å	12.679(6)
b, Å	5.856(1)
c, Å	7.273(6)
V, Å^3	476.166

Z	4
D_c, g.cm^{-3}	9.4612
μ, cm^{-1}	1791.1
R, R_w (for observed reflections)	0.0677, 0.0792
Total number of reflections measured	903
No. observed reflections	428
Criterion for observed reflections	$I \geq 1.96(I)$

The tungsten atom is surrounded by four oxygen atoms. The fifth oxygen is connected with two atoms of lead and placed in the tungsten atom co-ordination sphere. Atoms of oxygen form deformed trigonal bipyramid around the tungsten atom.

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CYCLOSPORINS OF SYMMETRY $P2_1$ - GROUP OF PSEUDOISOMORPHOUS CLATHRATES

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Cyclosporins, especially cyklosporin A (Cs A), are fungal metabolites widely used as an immunosupressive drugs in transplantation surgery. The study of different cyclosporin solvates and phase modifications is very important for formulation of new medicinally applicable immunospupresive preparates.

Several solvates of cyclosporin A, which crystallize in $P2_1$, $P2_12_12_1$ and $P4_1$ space groups are known. The $P2_1$ symmetry is suitable not only for cyclosporin A but for the other cyclosporins as well. In addition it is possible to incorporate some solvents to cyclosporin backbone and series of pseudoisomorphous structures crystallize in this way. Till now seven cyclosporin clathrates are known (6 of them were solved in our Laboratory):

The common characteristics of these clathrates are: Conformation of the basic cyclosporin backbone does not change. The solvent is fixed in a backbone cavity (volume about 430 - 560 Å^3) by van der Waals forces only, no hydrogen bond contacts were found. The solvent thermal-motion parameters are very high, sometimes it is impossible to localize the solvent precisely even from low-temperature data.

The authors wish to thank Prof.Z.žák and Dr.I.Císařová for low temperature measurement.

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APPLICATION OF MODERN COMPUTER GRAPHIC METHODS FOR ELECTRON DENSITY VISUALIZATION

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Several methods of modern computer graphics were used for developing a program for fast 3D electron densities visualization. Following tools and methods were applied:

a) OpenGL graphic language[1] - a computer API designed originally by SGI company for communication between software and graphic hardware. Today, very fast graphic cards which accept this API are available not only for expensive SGI machines but for inexpensive PC as well.

b) Marching cube algorithm [2] - a mathematical algorithm for visualization voxelized information like results of X-ray tomography in medicine. Application of this algorithm to ELD map leads to very fast construction of 3D objects which can represent those ELD map.

Type of cyklosporin	Solvent	Temperature of data collection	A (Å)	B (Å)	C (Å)	β (deg)
ThioCsA.DEE [1]	diethylether	room temp.	15.632(2)	21.030(5)	12.857(2)	101.09(1)
CsA.DMI [2]	dimethyl-isosorbideroom	room temp.	15.521(2)	20.833(3)	12.949(3)	100.21(1)
CsA.THF	tetrahydro-furane	room temp.	15.551(2)	21.216(7)	12.862(2)	98.23(1)
CsA.DBE	di-n-butylether	room temp.	15.47(1)	21.115(5)	12.843(7)	98.96(4)
CsA.DBE	di-n-butylether	150 K	15.37(1)	20.910(4)	12.496(6)	99.44(4)
CsE [3]	acetone . water	room temp.	15.698(2)	21.333(3)	13.224(2)	103.74(1)
CsE2	2-butanol	150 K	15.575(6)	20.584(9)	13.280(5)	105.97(3)
CsA	butylhexyl ether	150 K	15.396(2)	20.840(3)	12.800(2)	99.40(1)

c) Stereographic visualization [3]. Stereographic visualization is an method for computation of two images for left and right human eye. This two images could then be delivered separately (usually by help of LCD glasses) to correct eye. The brain can see the object like real 3D one.

All these methods were combined in Marching Cube ELD program. This program is able to read output from CRYSTALS [4] crystallographic package. The program is capable to visualize ELD in several ways, manipulate with the map and add new atoms to the map. The solvatation of several cyclosporin A crystal forms was determined by this way. New functions of this program, especially input from other systems then CRYSTALS , are under development.

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Ag, Au AND Pd COMPLEXES WITH N-BASES: STRUCTURES AND VIBRATIONAL SPECTRA

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Vibrational spectral studies of interaction between adsorbates and surfaces of SERS (Surface-enhanced Raman Scattering) active metals are the subject of interest. To facilitate elucidation of the structure of the surface species on Ag, Au and Pd colloids by comparison of SERS spectra of studied molecules adsorbed on colloids with vibrational (Raman and infrared) spectra of analogous synthetic complexes of molecules with SERS active metals, it is very useful to know the structure of this complexes.

During the work, five new complexes were prepared. The central atoms were SERS active metals: Ag, Au and Pd. Ligands were studied bases, i.e. acridine (acr), bipyridine (bpy) and phtalazine (pht). Charge compensating ions are chlorides or nitrates. Silver coordination sphere is pseudotetrahedric in all cases, gold and palladium coordination spheres are tetragonal. It corresponds to d^{10} electron configuration on Ag^{I} and d^{8} configuration on Au^{III} and Pd^{II}.

The structures of the two complexes prepared recently, $[Ag(acr)_2NO_3]$ and $[Au(pht)Cl_3]$, are given in Fig.1 and 2. Complexes $[Ag(bpy)_2]NO_3$, and polymeric $([Ag_2(H_2O)(NO_3)(pht)_2].NO_3.H_2O)_x$ are an example how the combination of vibrational and structural information was used for determination of the surface species structure[1]. The structure of the last complex - $[Pd(bpy)Cl_2].1/2C_4H_4O_2$ – helped to decide between chemisorption and physisorption of bipyridine on the surface of Pd colloid[2]. All complexes were characterized by X-ray analysis, infrared spectroscopy and Raman scattering. Some of them were characterized by DSC measurements.

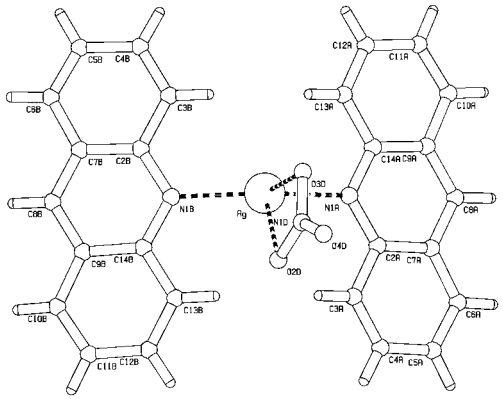

Figure 1: Structure of $[Ag(acr)_2NO_3]$

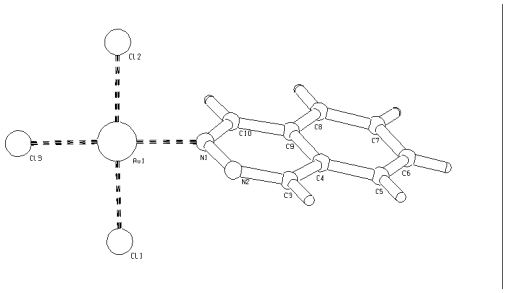

Figure 2: Structure of $[Au(pht)Cl_3]$

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[2] I. Srnová, B.Vlčková, V. Baumruk, *J.Mol.Struct.,* 410-411, **1997**, 201-203

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PROGRAM FOR STRUCTURE DETERMINATION OF 1D CRYSTALS

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The description of a simple demonstration program for structure determination of (hypothetical) one-dimensional crystals will be given. The program, called mc.xls, is a MS Excel 5.0 application, i.e. it uses Excel sheets to provide input and output and Excel modules with Visual Basic code to run.

The program gives the opportunity to try the single crystal structure determination on simple examples. Working within one dimension, the Fourier transforms can be drawn as simple charts that can be understood intu-

itively. Moreover, the user can see (or even modify) source code just clicking the mouse. Typical usage of the program is a step-by-step process like the real X-ray structure determination.

In the first step, as no 1D crystal exist, you have to create one. You can create it either yourself or by means of the computer, which has the advantage you do not know the crystal structure in advance like in the real world. In any case, the main part of the input is a table similar to table 1.

The second step is a simulation of the diffraction experiment. As you cannot collect data of a crystal that exist only in the memory of your computer, it is necessary to calculate the diffraction intensities using the Fourier transform.

The third step involves data reduction and space group determination, which is, in the case of 1D crystals, very simple.

Now that you have all the data: diffraction intensities, symmetry an unit cell contents, it comes the main part of the program. In the fourth step you have to solve the phase problem by means of Patterson synthesis. The output has two parts: graphical (see Chart 1) and numerical in the form of peaks table.

In the fifth step you refine the structure in the direct space using repeated Fourier synthesis. You can choose any of five standard types of Fourier synthesis: Patterson synthesis based on $|F_{obs}|^2$, checking Patterson on $|F_{calc}|^2$, Fourier on F_{obs}, checking Fourier on F_{calc}, and difference Fourier on (F_{obs}-F_{calc}). Each type of synthesis gives the graphical output similar to that in Chart 1.

The sixth step consists in refinement in the reciprocal space by means of Least Squares method. The last two steps are usually combined and repeated several times to get the final structure model. At the end, when you think the structure is complete, you can calculate distances and draw a simple picture.

The program provides graphical user interface and contains a help system including small demo. To use it, just a basic knowledge of computers and single crystal X-ray structure determination should be enough. The latest version, which runs under MS Windows 3.1 or higher and MS Excel 5.0 or higher, is freely available at request to mirek@natur.cuni.cz.

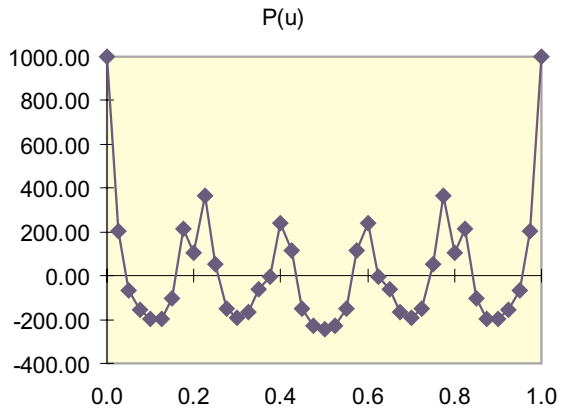

Chart : Patterson map corresponding to the structure of table 1, space group P-1

Struktura krystalu					
Atom	X=x/a	Bizo	upX	upB	pos
Li	0	0.032	0	1	0
Cs	0.09	0.028	1	1	1
Rb	0.32	0.052	1	1	1

Table: Sample input of mc.xls

QUANTITATIVE XRD PHASE ANALYSIS OF FLY ASH COMPOSITES

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The work summarises the results of the research of fly ashes, their mixtures and composites, aimed at their quantitative phase analysis. The percentages of individual components were determined using several methods of X-ray powder diffraction. A procedure of the preparation and application was developed for each of them.

The RIR values were obtained for each phase by evaluation of diffraction patterns of 1 : 1 analyte - corundum mixtures, of non-binary mixtures, and by modelling diffraction patterns of binary 1 : 1 mixtures; based on known crystal structure of the phases involved.

The application of the internal standard method required preparation of several artificial mixtures for each phase. These were used to measure the diffraction peak intensity and derive the linear regression parameters of the dependence of diffraction intensities on the weight percentage of the analyte.

The external standard method proved to be ineligible for the available diffractometer arrangement.

To apply the XQPA method (Weiss et al., 1983), two databases were composed. The first one contains d-values and corresponding intensities of modelled pure phases, the second one was formed from real values obtained by measurement of reference samples of pure phases.

All methods were applied on the 30 artificial test mixtures, whose composition was close to real fly ashes and materials derived of them. The acquired results indicate that the RIR method is very well applicable both with that the factors derived from reference 1:1 phase - corundum mixtures, and factors derived from modelled mixtures. The XQPA method is also applicable to the quantitative analysis of fly ash mixtures, yielding better results when the database of modelled reference materials is used. Both above methods can determine only the relative proportions of individual crystalline components, as there are always some amorphous components in the real mixtures.

The percentage of the amorphous component in the mixture can be determined using the internal standard method, as proved by the results obtained. A disadvantage of this method is the very time-consuming preparation all calibration mixtures. Therefore, a combination of a direct method (RIR or XQPA) with the internal standard method is recommended. The results from direct methods must be recalculated to the absolute values of phase percentages,

using the determination of the major components by the internal standard method.

All procedures were tested with four real fly ash mixtures. The absolute error values achieved with artificial test mixtures varied in most cases between 5 and 10%.

As a conclusion, the work presents an optimum analytical scheme of XRD quantitative phase analysis of fly ashes, including also the time requirements of each method involved.

MORFOLOGICKÉ TYPY MONAZITU Z VEPORIKA (ZÁPADNÉ KARPATY)

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Monazit je hlavný nositeľ prvkov ľahkých vzácnych zemín (La, Ce, Pr, Nd, Sm, Eu) v kryštaliniku Západných Karpát. Patrí k frekventovaným akcesorickým minerálom v niektorých typoch magmatitov a metamorfitov. V juhozápadnom veporiku (oblasť severne od Lučenca) vytvára kontrastné anomálne koncentrácie vo zvetralinách, v ktorých obsahy niekoľkonásobne prevyšujú bežné obsahy akcesorického monazitu v horninách. Možno opodstatnene predpokladať, že pôvod monazitov je spojený s minerogenetickými (pravdepodobne hydrotermálnymi) procesmi, ktoré umožnili migráciu a koncentrovanie prvkov vzácnych zemín

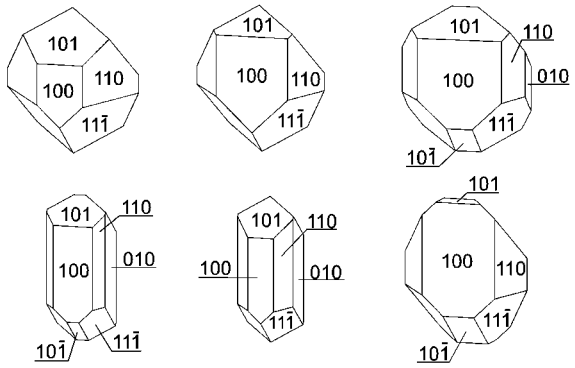
Idealizovaný chemický vzorec monazitu je (Ca, Ce, La, Pr, Nd, Sm)PO_4. Minerál monazit je izomorfná zmes, ktorá sa skladá spravidla z troch zložiek: monazitu ($CePO_4$), huttonitu ($ThSiO_4$) a brabantitu ($CaTh(PO_4)_2$) [1]. Je monoklinický (bodová grupa 2/*m*), súmernosž kryštálovej štruktúry je $P2_1/m$. V štruktúre sa nachádzajú PO_4 tetraédre a $REEO_9$ polyédre ktoré vytvárajú tzv. polyédricko - tetraédrické režazce. Režazce sú rovnobežné s [001], základná bunka obsahuje 4 vzorcové jednotky [2].

Pre výskum monazitu sme získali koncentráty ža žkých minerálov z ktorých sme vyseparovali monominerálne frakcie monazitu. Morfologické štúdium sme robili na súboroch minimálne 200 monokryštálov resp. zrastov. Priemerná veľkosž monazitu v koncentrátoch sa pohybuje v rozmedzí 0,1 - 2 mm ale nie sú zriedkavé ani 3 - 4 mm kryštály, zrasty dvoch jedincov a polykryštálové zrastové agregáty.

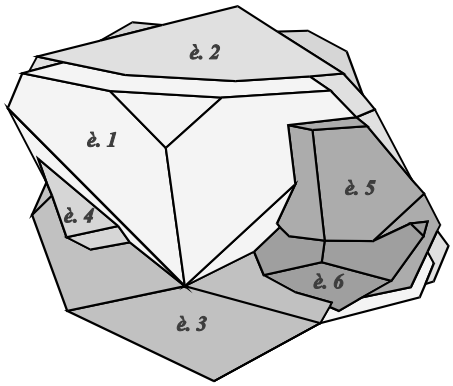
Kryštály sme zaradili do šiestich morfologických skupín (izometrické, izometricko - tabuľkovité, tabuľkovité, tabuľkovito - prizmatické, prizmatické, prizmaticko - izometrické; obr. 1). Prevládajúcim morfologickým typom sú izometrické a izometricko - tabuľkovité kryštály (60 - 90 %).

Zrasty monazitov sú najčastejšie podľa (100) a (001) a sú pomerne hojné. V študovaných vzorkách sme našli penetračné zrasty viacerých (obr. 2) rôzne veľkých jedincov, ktoré však vždy tvorili rovnaké farebné variety.

Monazit na študovanom území vystupuje v pomerne širokej škále farieb, pričom jednotlivé farebné variety sú kvantitatívne nerovnako zastúpené. Vo všetkých vzorkách prevládajú kryštály žltohnedej farby (v priemere od 53 - 73 %). Zostatok sú tmavé, zelenkasté a červenkasté monazity.



Obr. 1: Kryštálové tvary monazitu podľa [3]: izometrický, izometricko - tabuľkovitý, tabuľkovitý, tabuľkovito - prizmatický, prizmatický, prizmaticko - izometrický.



Obr. 2: Penetračný zrast monazitu.

Podľa výsledkov elektrónových mikroanalýz sú študované monazity blízke zloženiu ($Ce_{0.38}$, $La_{0.17}$, $Nd_{0.16}$, $Th_{0.06}$, $Pr_{0.06}$, $Sm_{0.04}$, $Ca_{0.04}$, $Gd_{0.02}$) (P, $Si_{0.02}$) O_4.

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STRUKTURA VYBRANÝCH KOMPLEXŮ HIV PROTEASYSE SUB-NANOMOLÁRNÍMI INHIBITORY

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Byly studovány krystalové struktury komplexů HIV-1 proteasy (bru izolát) /1/ se dvěma tetrapeptidovými 2-hydroxyethylaminovými inhibitory:

Boc-Phe-[(R/S)CH(OH)CH_2NH]-Phe-Glu-Phe-NH_2 /2/,/3/.

Difrakční data byla získána měřením monokrystalů látek na zdroji synchrotronového záření - MAR image plate detektor – v Terstu při teplotě kapalného dusíku. Struktury obou komplexů jsou řešeny do rozlišení 2.0 Ĺ v prostorové

grupě $P6_1$. Ačkoli chemicky se tyto struktury liší jen R/2S absolutní konfigurací tetrahedrálního uhlíku skupiny –CHOH-, jsou prostorové struktury odlišné v řadě dalších míst. Jde o rozdílné konformace mnoha postranních řetězců a rozdíl ve výskytu jejich vícenásobných konformací. Dále je možné ve strukturách pozorovat různý počet navázaných molekul vody a molekul dimethylsulfoxidu a ani jejich poloha vůči protease není vždy shodná.

Pozornost byla věnována zejména aktivnímu centru HIV-1 proteasy a v něm vázánému inhibitoru, který je v obou komplexech vázán asymetricky uvnitř aktivního tunelu proteasy a je v obou případech modelován do dvou poloh (1:1) podle nekrystalografické dvojčetné osy. Vazba hydroxylové skupiny tetrahedrálního uhlíku inhibitoru v aktivním centru je odlišná od modelu předpokládaného podle analogie se strukturou komplexu HIV-1 se saquinavirem /4/. Molekula inhibitoru je vůči předpokladu posunuta tak, že OH skupina směřuje mezi Gly127 a Asp25 a NH hlavního řetězce inhibitoru patřící k P1´ se váže mezi Asp25 a Asp125. Tento fakt v podstatě vyvrací dosavadní teorie, které považovaly za klíčové, že do centra aktivního místa je navázána hydroxylová skupina.

Projekt je podporován GAČR 203/98/PO31, 203/98/KO23 a GAAV A4050811.

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COMBINATION OF MÖSSBAUER SPECTROSCOPY AND X-RAY POWDER DIFFRACTION - A POWERFUL TOOL FOR THE CHARACTERIZATION OF IRON OXIDES QUA PRODUCTS OF THERMAL TRANSFORMATIONS

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FeO, Fe_3O_4 (magnetite), α-Fe_2O_3 (hematite), β-Fe_2O_3, γ-Fe_2O_3 (maghemite) and ε-Fe_2O_3 can be formed as products of the thermally induced processes (oxidation, the thermal decomposition of iron salts and minerals or solid-state reactions of iron compounds [1-5]). Majority of these processes is accompanied by the mutual structural transformations of the individual oxide forms. Thus the miscellaneous mixture of iron oxides can be present in the thermally treated samples. The combination of Mössbauer spectroscopy and x-ray powder diffraction is a very effective technique for the identification of the individual phases and determination of the reaction mechanism.

The quantitative results accessible by both methods yield important information for the study of reaction kinetics. The different well crystalline forms as well as the amorphous or superparamagnetic nanoparticles of iron oxides can be isolated by the appropriate choice of the heat treatment conditions and the following chemical separation. Their magnetic characterization, the relation between the structure and magnetic properties, particles size, structure defects, temperatures of magnetic transitions can be successfully investigated using Mössbauer measurements in a wide range of temperatures (4.2-1200K) and x-ray powder diffraction analysis.

In this work, our previous published and literary data respecting the structural and magnetic properties of iron oxides, their hyperfine Mössbauer parameters, processes of their formation and the mechanism of thermal transformation will be reviewed and summarized. The possibility to discern the individual oxide phases using Mössbauer spectroscopy and x-ray powder diffraction, advantages and disadvantages of both methods will be discussed.

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