THE CRYSTAL STRUCTURE OF rac-N-CARBOXYMETHYLASPARTIC ACID

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The cobalt(III) complexes are not only of interest for their stereochemistry, but also for their application in the bioinorganic field because they provide simple structural models of the metalloprotein active sites. Frequently used ligands are: EDTA, NTA, IPDTA etc.

This work is devoted the synthesis and characterization of N-carboxymethylaspartic acid, (H3cmaa, C6H9NO6). The structure was solved as a part of a general study of the chemistry of aspartic acid derivatives as a ligands in coordination compounds. The title compound is a tetradentate chelating agent that is isomer and chemically similar to nitrilotriacetic acid, but it is chiral.

The H3cmaa was prepared by dissolution of maleic anhydride and glycine in aqueous solution of KOH. The solution was refluxed for 48 h. Then the pH was adjusted by HClO4 to 7 and after filtration the pH was adjusted by HClO4 to 2. The crystals of H3cmaa (Fig 1) grew by the slow evaporation of an aqueous solution at 8 °C. After several days obtained colourless crystals were washed by water, ethanol and dried by air.

The crystal data: monoclinic system, P21/n, a = 5.343(5) Å, b = 16.033(2) Å, c = 9.089(12) Å, β = 95.384(12)°, Z = 4, ρc = 1.638 g/cm3 and contains infinite chains of hydrogen bonds. In the crystal it is not possible to define the organic molecule, because the hydrogen atoms are common for neighbouring molecules.

This project was supported by the Ministry of Education of the Slovak Republic (grant VEGA No. 1/7264/20) and by the Comenius University (grant No. 50/2001/UK).

CONFORMATION STUDY OF PROLINE RING G IN STRUCTURES OF ERGOPEPTINES

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Ergopeptines belong to the large ergot alkaloid family [1]. The ergot alkaloids are produced by parasitic fungi of genus Claviceps. Some of their pharmacological effects are known since the Middle Ages. Chemical structure of these substances is close to the structures of natural neurotransmitter [2] (dopamine, adrenaline, serotonin). The ergot alkaloids are used in their natural or chemically modified forms as important drugs. Their most important applications are in the field of treatment of the nerve fibres transport disturbances [3]. They are already used in gynaecology [4], endocrinology, psychiatry, and in treatment of vascular diseases or newly in treatment of obesity [5] as well.

Conformation analysis is relevant for studying interaction between drug and receptor. Not only the chemical structure, but also the conformation of the molecule plays significant role [6]. Molecules of ergopeptines contain four flexible rings C, D, F and G (Fig.1). Flexible central amid bond is fixed by hydrogen bond (O5-H….O1) generally present in all ergopeptines (except ergopeptams).

Figure 1. General demonstration of the molecule of ergopeptines with numbering of the atoms and with labeling of the studied rings.

Four new crystal structures of dihydroergopeptines (dihydro-α-ergokryptine methanesulfonate acetone solvate monohydrate (I), dihydro-α-ergokryptine methanesulfonate nitromethan solvate monohydrate (II), dihydro-ergocornine methanesulfonate methanol solvate
monohydrate (III), dihydro-ergocristin methanesulfonate bis(ethyl-acetate) solvate monohydrate) (IV) were solved. Conformation analysis was done for mentioned structures. Ring C has conformation between an envelope form E3, with C4 atom out of plane of the other five atoms, and half chair 3H2. Ergoline ring D has a stable chair conformation 4C1 with C7 atom above and N2 below the plane of the other four atoms. Stable conformations of ergoline ring D are also fixed by intermolecular hydrogen bonds between hydrogen atoms of protonized N2 and oxygen atoms of methanesulfonate salt. Substituted diketopiperazine ring F adopts an envelope conformation 6E with C25 atom out of plane of the remaining five atoms. Conformations of the rings C, D and F do not differ from already known eleven structures. The proline ring G assumes most often envelope form 4E with C23 atom out of plane of the remaining four atoms or twist 4T5 conformation with C23 atom above and C24 below the plane. Two conformations of the proline ring G in newly solved structures I and II significantly differ from those in known ergopeptines: conformation 1T2 - 1E for I and E2 - 3T2 for II. Thus, this tempted us to study the proline conformations of all already known ergopeptines. Up to now, no such conformation close to I or II was found. The molecular dynamics appears suitable for mapping the conformational space of proline. All the proline ring G conformations found in X-ray structures were proved by molecular dynamics.

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6-Benzylaminopurine derivatives are plant growth hormones and belong to the subgroup of aromatic cytokinins. It was found that some of them have anticancer activity on some animal and human tumours. From this reason, cytokinins and their transition metal complexes are intensively studied. We have found that biological activity of cytokinins can be improved by the complex formation with selected transition metals, mainly Fe3+, Cu2+ and Pt2+. To date, we have synthesized, characterized and tested some
transition metal complexes with anti-tumor activity [1-2]. In the present time, we focused our research activities on structural characterization of selected chloro-substituted 6-benzylaminopurine derivatives, namely: 6-(2-chlorobenzylamino)purine, 6-(3-chlorobenzylamino)purine or 6-(4-chlorobenzylamino)purine. The organic compounds have been prepared as depicted in Scheme 1. In dependence on pH medium used during the recrystallization, we have obtained the compounds in both an electroneutral (Fig. 1) and protonated (Figs. 2 and 3) form. Changes in protonation of purine rings have significant influence on differences in some bond lengths and angles.

Authors thank the Grant Agency of the Czech Republic for financial support, a grant No. 203/00/0152.

References

X-RAY STRUCTURE OF [Cu(N,N-dimeen)(ox)(H2O)]2[Cu(N,N-dimeen)2](ClO4)2

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The crystal and molecular structure of the title complex compound (dimeen = N,N-dimethylethylenediammine, ox = oxalate) has been solved by heavy atom methods [1, 2] and basic physico-chemical measurements have been made. It was found that the structure contains two non-equivalent copper atoms in the slightly distorted square-planer (Cu2) and square-pyramidal (Cu1) coordination (see Fig. 1) with deviations of atom positions from square plane smaller then 0.28 Å.

The basic crystallographic data are summarized in Table 1, important bond lengths and angles in Table 2, possible hydrogen bonds according [3] in Table 3.

The results of magnetochemical measurements (\(\mu_{eff} = 1.82 \text{ BM/294 K} \)) correspond with assumption of copper in the oxidation state II. The value of molar conductivity (10 \(^{-3}\) mol/l, in water) \(\chi_M = 307 \text{ Scm}^2\text{mol}^{-1}\) confirms an electrolyte 1:2 with ClO\(_4\) group out from coordination sphere of the central atoms; the characteristic absorption for this group at 1068 and 620 cm\(^{-1}\) were also found in the IR-spectrum.

References
Table 1. Basic crystallographic data of \([\text{Cu(N,N-dimeen)(ox)(H}_2\text{O)}]\textsubscript{2} [\text{Cu(N,N-dimeen)}\textsubscript{2}(\text{ClO}_4)\textsubscript{2}]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
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<tr>
<td>Empirical formula</td>
<td>(\text{C}<em>{10}\text{H}</em>{26}\text{ClCu}_{1.5}\text{N}_4\text{O}_9)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>477.11</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic; PT</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 6.4920(10) , \text{Å} , \alpha = 94.38(3)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(b = 8.501(2) , \text{Å} , \beta = 100.68(3)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(c = 17.079(3) , \text{Å} , \gamma = 103.80(3)^\circ)</td>
</tr>
<tr>
<td>Volume</td>
<td>892.3(3) , \text{Å}^3</td>
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<tr>
<td>Z, Calculated density</td>
<td>2; 1.776 Mg/m\textsuperscript{3}</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>2.006 mm\textsuperscript{-1}</td>
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<tr>
<td>(F(000))</td>
<td>493</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.35 x 0.30 x 0.25 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
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</tr>
<tr>
<td>Reflections collected / unique</td>
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</tr>
<tr>
<td>Completeness to 20 = 29.21°</td>
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</tr>
<tr>
<td>Max. and min. transmission</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
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<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on (F^2)</td>
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<tr>
<td>Final R indices [I&gt;2\sigma(I)]</td>
<td>R1 = 0.0431, wR2 = 0.1440</td>
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<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0461, wR2 = 0.1454</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.972 and -0.780 e.Å</td>
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</table>

Table 2. Selected bond lengths [Å] and angles [°] for \([\text{Cu(N,N-dimeen)(ox)(H}_2\text{O)}]\textsubscript{2} [\text{Cu(N,N-dimeen)}\textsubscript{2}(\text{ClO}_4)\textsubscript{2}]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
<th>Angle [°]</th>
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</thead>
<tbody>
<tr>
<td>Cu(1)-O(4)</td>
<td>1.940(3)</td>
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</tr>
<tr>
<td>Cu(1)-O(3)</td>
<td>1.957(3)</td>
<td></td>
</tr>
<tr>
<td>Cu(1)-N(2)</td>
<td>2.015(3)</td>
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<tr>
<td>Cu(1)-N(1)</td>
<td>2.022(3)</td>
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<tr>
<td>Cu(1)-O(9)</td>
<td>2.345(3)</td>
<td></td>
</tr>
<tr>
<td>Cu(2)-N(4)</td>
<td>1.994(3)</td>
<td></td>
</tr>
<tr>
<td>Cu(2)-N(4)#1</td>
<td>1.994(3)</td>
<td></td>
</tr>
<tr>
<td>Cu(2)-N(3)#1</td>
<td>2.095(3)</td>
<td></td>
</tr>
<tr>
<td>Cu(2)-N(3)</td>
<td>2.095(3)</td>
<td></td>
</tr>
<tr>
<td>O(4)-Cu(1)-O(3)</td>
<td>84.50(11)</td>
<td></td>
</tr>
<tr>
<td>O(4)-Cu(1)-N(2)</td>
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</tr>
<tr>
<td>O(3)-Cu(1)-N(2)</td>
<td>164.41(13)</td>
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<td>O(4)-Cu(1)-N(1)</td>
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<tr>
<td>O(3)-Cu(1)-N(1)</td>
<td>92.57(11)</td>
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<tr>
<td>N(2)-Cu(1)-N(1)</td>
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<td>N(4)-Cu(2)-N(3)#1</td>
<td>94.70(12)</td>
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<td>N(4)#1-Cu(2)-N(3)#1</td>
<td>85.30(12)</td>
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</table>

Table 3. Possible hydrogen bonds for \([\text{Cu(N,N-dimeen)(ox)(H}_2\text{O)}]\textsubscript{2} [\text{Cu(N,N-dimeen)}\textsubscript{2}(\text{ClO}_4)\textsubscript{2}]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length [Å]</th>
<th>Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3 -H3A C3 ...O5 (2) H3A ...O5 (2)</td>
<td>1.048(057)</td>
<td>3.517(032)</td>
</tr>
<tr>
<td>C3 -H3A ...O5 (2)</td>
<td>2.507(072)</td>
<td>161.56(36)</td>
</tr>
<tr>
<td>O9 -H9D O9 ...O5 (2) H9D ...O5 (2)</td>
<td>0.849(066)</td>
<td>2.957(028)</td>
</tr>
<tr>
<td>O9 -H9D ...O5 (2)</td>
<td>2.136(060)</td>
<td>162.34(37)</td>
</tr>
<tr>
<td>N4 -H4C N4 ...O4 (6) O4 ...O4 (6)</td>
<td>0.924(125)</td>
<td>2.893(034)</td>
</tr>
<tr>
<td>N4 -H4C ...O4 (6)</td>
<td>2.032(105)</td>
<td>154.31(38)</td>
</tr>
<tr>
<td>C7 -H7A C7 ...O8 (5) H7A ...O8 (5)</td>
<td>0.930(022)</td>
<td>3.226(051)</td>
</tr>
<tr>
<td>C7 -H7A ...O8 (5)</td>
<td>2.484(041)</td>
<td>136.84(62)</td>
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<tr>
<td>N4 -H4C N4 ...O4 (6) H4C ...O4 (6)</td>
<td>0.924(125)</td>
<td>2.893(034)</td>
</tr>
<tr>
<td>N4 -H4C ...O4 (6)</td>
<td>2.032(105)</td>
<td>154.31(38)</td>
</tr>
</tbody>
</table>

Figure 1

[\text{Cu(N,N-dimeen)(ox)(H}_2\text{O)}]\textsubscript{2} [\text{Cu(N,N-dimeen)}\textsubscript{2}(\text{ClO}_4)\textsubscript{2}]

(Cu2 atom is situated in the center of symmetry)
IRON(II) AND MAGNESIUM(II) COMPLEXES WITH NON-COORDINATED TRITHIOCYANURIC ACID

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Trithiocyanuric acid is well known to form both mononuclear and polynuclear complexes with many metal ions. A manner of its coordination depends not only on the central atom but also on the number and dentacity of the next entering ligands. Some of the structures have been determined by X-ray structure analysis [1-3]. In our previous works we were interested in preparation and study of nickel(II) complexes with trithiocyanuric acid. To date, we have determined five structures of these compounds by a single crystal X-ray analysis [4-6]. The complexes are mononuclear and contain coordinated trithiocyanurate dianion. The coordination number is five or six and the dianion is bonded by N atom or both N and S atoms. We have also prepared nickel complexes with three coordinated bidentate N-donor ligands of the type [Ni(N-N)_3](ttcH). However, we were not able to obtain suitable single crystals. In the present work we have focused our attention on preparation and structural characterization of complexes with trithiocyanuric acid situated outside of the coordination sphere of the central atom. We have synthesized and structurally characterized the following complexes:

- [Fe(bpy)_3](ttcH_2)_{2.0,5bpy.EtOH.2H_2O} (1)
- [Fe(phen)_3](ttcH_2)(ClO_4) (2)
- [Mg(phen)_3](ttcH_2)_{2} (3)

where ttcH_3 = trithiocyanuric acid, phen = 1,10-phenanthroline, bpy = 2,2’-bipyridyl.


DESCRIPTION AND CRYSTAL STRUCTURE OF VAJDAKITE, [(MO6+O2)2(H2O)2 As+3 2O5] · H2O – A NEW MINERAL FROM JÁCHYMOV, CZECH REPUBLIC

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Vajdakite, a new mineral from Jáchymov, NW Bohemia, Czech Republic, forms minute acicular gray-green crystals associated with arsenolite, scorodite, parascorodite, kaňkite, annabergite, köttigite, pyrite, marcasite, nickelskutterudite, and löllingite. Microprobe analysis gave (wt%): As 27.72, Mo 35.39, O 36.66, totaling 99.77. The simplified chemical formula is [(Mo6+O2)2(H2O)2 As3+2O5] · H2O.

The mineral is monoclinic, P21/c, a = 7.0515(6), b = 12.0908(9), c = 12.2190(14) Å, β = 101.268(9)°, V = 1021.7(2) Å3, Z = 4, D meas = 3.50(2) g/cm3, and D calc = 3.509 g/cm3. The strongest lines in the X-ray powder diffraction pattern d(I)(hkl) are: 6.046 (100)(020), 3.324 (59)(023), 6.915 (26)(100), 2.264 (19)(310), 3.457 (16)(200), 2.624 (230), 3.819 (10)(031). Optically positive, X || b, Z/c = 12°, elongation positive, birefringence is 0.28, 2V calc = 35.1°, α = 1.757(2)°, β = 1.778(2°), γ = 2.04(1)°, pleochroism in X ~ Y light greenish gray, in Z yellowish gray. Crystal size varies between 0.1 to 0.5 mm. TG curve and IR spectra show that vajdakite contains two distinct types of water molecules. The crystal structure was solved by direct methods (MoKα radiation) and refined using 1787 unique reflections to R = 0.0455, Rw = 0.1143. There are double-chains built up by two individual chains with a sequence -O-As-O-Mo- interconnected by oxygens of two triangles AsO3 and two structurally non-equivalent MoO6(H2O) octahedra. Two vertex-sharing triangles of AsO3 form an (As2O5)6+ diarsenite group. Two distinct types of water molecules occur in the structure, the first is not included in the coordination, the second one is in octahedral coordination around Mo. They are linked by a complicated net of interlayer and intralayer hydrogen bonds.

CALCULATED X-RAY POWDER DIFFRACTION PATTERNS FOR ZEOLITE-GROUP MINERALS FROM SLOVAKIA

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Calculated X-ray powder diffraction patterns as possible reference data for identification of analcime, garrisonite, gismondine, harmotome, heulandite, chabazite, klinoptilolite, laumontite, mezolite, mordenite, natrolite, phillipsite, skolecite, stilbite and thomsonite. Calculation procedure were those presented by Kraus and Nolze (1997), input data were coming from original crystal structure refinements. Results are presented in tabular (20, interplanar distances d, diffraction indices h, k, l and relative intensities) as well as in pictorial form.

TEXTURES OF ALUMINIUM ALLOY THIN SHEETS FOR HEAT EXCHANGER FINS

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Texture analysis of different sheets from Al1.5FeMnSi (AA 8006) and AlFeSi (AA 8011) alloys was carried out in order to compare textures of materials for heat exchangers fabricated by several producers and by different technologies. The textures were determined by X-ray back reflection goniometric method using SIEMENS diffractometer. A majority of samples exhibit recrystallization R-texture, remaining sheets have a cubic texture or a combination of both texture types. Several samples, fabricated by different technologies, have a texture of the same type. Consequently it is not possible to predict the type of the texture from the technology of casting and downstream processing.
POSITRON-LIFETIME INVESTIGATIONS OF PRECIPITATION EFFECTS IN AL-CU ALLOY

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2Research Institute of Metals, Panenské Břežany 50, 250 70 Odolena Voda, Czech Republic

The development of new workable aluminium-based alloys is one of the topics in current material science of light alloys. Most of wrought aluminium alloys are based on Al-Cu alloy. Also due to these reasons, there was heavy effort to characterize in details precipitation effects in Al-Cu system. The precipitation effects lead to significant hardening, which improves mechanical properties of Al-Cu based alloys. On the base of a number of investigations [1] performed by various techniques, the following decomposition sequence of Al-Cu system was established:

Supersaturated Solid Solution (SSS) ⇒ GP zones ⇒ θ′ ⇒ θ.

Precipitation starts from the formation of GP zones, which may be regarded as fully coherent metastable particles. With increasing temperature GP zones are replaced by more stable semicoherent precipitates of θ′ phase and finally by incoherent precipitates of equilibrium θ phase. Although known for more than 50 years, GP zones in Al-Cu alloys still attract much interest because definitive conclusions on their structure, formation and evolution have not been reached, see [2] and references therein.

Positron lifetime spectroscopy represents well-developed non-destructive and non-local experimental technique for characterisations of microstructure [3]. PL spectroscopy is very sensitive to open volume defects such as vacancies, vacancy clusters, dislocations, grain boundaries, etc. Moreover, under some conditions positrons may be trapped also in precipitates. Lifetime of trapped positrons gets information about kind of defect, while from relative fraction of trapped positrons one can determine concentration of defects. PL spectroscopy is, therefore, ideal tool for investigation of precipitation effects as was proved also in this work on Al-Cu alloy.

The investigated Al-2.0 at.% Cu alloy was firstly homogenized at 525 °C for 30 min to obtain solid solution. Homogenization was finished by rapid quenching and PL measurement at room temperature. After characterisation of microstructure of as-quenched (AQ) state, the specimen was subjected to isochronal annealing with effective heating rate 1 K/min. Each annealing step was finished by rapid quenching and PL measurements at room temperature.

Two exponential components was found in PL spectrum of AQ specimen: contribution of positrons trapped at quenched-in vacancies associated with Cu atoms (204.9 ± 0.4 ps, 97.3 ± 0.2 %) and contribution of positrons trapped in large vacancy clusters (voids) with diameter above 10 nm (570 ± 20 ps, 2.7 ± 0.1 %). It was found that the AQ microstructure is stable at room temperature at least in time scale of 50 hours.

PL spectra of the Al-Cu specimen were well fitted by two exponential components (lifetimes τ1, τ2) for all annealing temperatures. The first component with lifetime τ1 comes from free positrons, while the second one with lifetime τ2 represents contribution of positrons trapped at defects. The lifetime τ1 lies between the lifetime 180 ps for Cu monovacancy [4] and 250 ps for Al monovacancy [4]. Thus, the component τ2 is contribution of positrons trapped at vacancies associated with Cu atoms. The decrease of τ2 with increasing temperature up to 240 °C is caused by increase of number of Cu atoms in vicinity of vacancy. At temperature 240 °C the quenched-in vacancies are surrounded exclusively by Cu atoms, which is reflected by τ2 ≈ 180 ps. Concentration of quenched-in vacancies was calculated in the present work as a function of annealing temperature.

Formation of semicoherent θ′ precipitates takes place from 260 °C. Positrons are trapped at misfit defects associated with the θ′ particles or directly inside the θ′ precipitates. Precipitation of θ′ phase causes slight increase of lifetime τ2, as well as noticeable increase of relative intensity I2 in temperature region 240-350 °C. Phase transformation of θ′ to θ starts at temperature 320 °C. In this temperature interval incoherent spherical precipitates of equilibrium θ phase (Al3Cu) are formed. It is reflected by remarkable increase of lifetime τ1 to ≈ 250 ps. As θ precipitates are incoherent with Al matrix, positrons are trapped at precipitate-matrix interface. Above 400 °C dissolution of θ precipitates starts. The dissolution of θ precipitates is reflected by radical decrease of relative intensity I2 in our PL spectra. Clearly, it is due to decreasing number of positron traps at θ precipitate-matrix interfaces. On the other hand, lifetime τ2 of trapped positrons remains unchanged because there is no change of type of traps.

Theoretical calculations of positron lifetimes and affinities for θ′ and θ precipitates were performed in the present work using LMTO technique [5]. It was found that θ precipitates do not represent attractive sites for positrons. Therefore, positrons are trapped at precipitate-matrix interface of incoherent θ precipitates. On the other hand, the θ′ precipitates represent attractive sites for positrons. Lifetime of positrons trapped inside the θ′ phase particles is 174 ps, i.e. close to the experimental lifetime of trapped positrons in temperature region when θ′ phase is present in the specimen. Thus, in the case of θ′ precipitates, positrons are trapped at misfit defects introduced into the specimen due to formation of the θ′ precipitates and/or directly inside the θ′ precipitates.

It was shown in the present work that PL spectroscopy represents powerful tool for investigation of microstructure evolution connected with decomposition of supersaturated solid solution and precipitation effects. Particularly, valuable information about lattice defects and their local chemical surrounding is obtained.
References:

COCRystallization behaviour of low-molecular-weight PEO Fractions in polymer blends

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The aim of this study was to assess the real-time development of poly(ethylene oxide) (PEO) cocrystalline structures in two different kinds of binary blends and thus to contribute to a deeper knowledge of the behaviour of these systems. The time-resolved SAXS/WAXS method on synchrotron and time-modulated DSC were used in this study.

Blends of PEO (3000) and PEO (4000) were studied during isothermal crystallization and during heating. A single cocrystal system or this system with a small amount of another lamellar systems are formed in all types of blends during crystallization. The LP1 lamellae in blends with PEO (3000) consist of extended chains of PEO (3000) and of thicker lamellae in neat PEO. A single lamellar system is developed. The cocrystal systems are formed in all types of blends during crystallization. The LP1 lamellae in blends with PEO (3000) consist of extended chains of PEO (3000) and of extended PEO tails of copolymer. The LP1 cocrystal structures developed in blends with PEO (4000) are probably formed by NIF chains of PEO (4000) and NIF and EC of PEO tails of the copolymer. The LP2 lamellar systems are, in both kinds of blends, cocrystals consisting of 1F and NIF chains of both components. The PPO part of the copolymer predominantly forms amorphous interlayers of lamellae incorporating also chain ends and folds.

X-ray diffraction analysis of ettringite

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Phase composition was determined by X−ray powder diffractometer. In first period of work, distilled water, aluminium sulphate (p. a.) and calcium oxide annealing from CaCO₃ were used as starting materials. In second step, drinking (industrial) water, ammonium aluminium sulphate from the production of chemical exploitation of uranium and technical burnt−lime were used. It was established that staring materials do not play important role in the product composition if their dosage is optimal. Differences were found in crystal morphology only.

Introduction

Ettringite 3 CaO . Al₂O₃ . 3 CaSO₄ . 32 H₂O is the prototype of the AFt phases of hydrated cement which have the general formula (tricalcium)−Aluminate Ferrite . tri (sulphate, hydroxide, etc.) . 32 (hydrate). Smoleczyk first suggested the AFt designation in 1961 publication in order to distinguish the high sulphate hydrate phases from the low sulphate phases, which are collectively termed AFm (Aluminate Ferrite . mono) [1]. Ettringite occurs as a natural mineral along with others of similar structure and com-
positions fitting into the ettringite group of minerals. The crystal structure of ettringite was described by Moore and Taylor [2].

The aim of the presented work is:

- preparation of ettringite from pure chemicals (distilled water, CaO or Ca(OH)₂ and Al₂(SO₄)₃ with an analytical purity)
- preparation of ettringite from secondary raw materials like ammonium aluminium sulphate from the production of chemical exploitation of uranium and commercially produced lime
- determination of dependence of sample structure on starting materials and used water by X-ray analysis method
- characterisation of morphology of prepared samples

**Experimental**

Primarily the ettringite from suspension of Ca(OH)₂ and solutions of aluminium sulphate (p.a. Lachema, Brno) with mass concentration 40 g/l, then 80 and 160 g/l was prepared.

In the second step, the formation of ettringite was realised from solutions of technical ammonium aluminium sulphate (alum, produced by DIAMO enterprise, Stráž pod Ralskem). Mass concentrations of the alum in water were 40, 80 and 130 g/l, where the last concentration represents saturated solution. In the table 4 result of ICP–OES analysis of alum solution is shown.

The apparatus has consisted of automatic burette with a solution of aluminium sulphate or ammonium aluminium sulphate, beaker with Ca(OH)₂ suspension, magnetic stirrer and pH meter – Precision Digital pH meter OP–208/1 Radelkis with two electrodes (glass and reference saturated calomel). At last period of ettringite preparation, an aluminium sulphate or ammonium aluminium sulphate solution was dropped from an automatic burette. During experiment, pH value was measured. Titration of solution was finished at pH = 10,7.

Finally an ettringite suspension was by low-pressure filtration processed and placed into a desiccator.

Phase analysis of samples was made by automated X-ray diffractometer X’Pert with central focusing configuration (Bragg–Brentano) in 0/0 implementation produced by firm PHILIPS (in 1999 Almelo, Netherlands). The diffractometer X’Pert had a Cu target X-ray tube operated by firm PHILIPS (in 1999 Almelo, Netherlands). The control PC for evaluation of results contained a powder database PDF3 (ICDD–JCPDS) and a structure database ICSD. Morphology of samples was by scanning electron microscope PHILIPS XL30 detected.

**Results and discussion**

Presented work shows that ettringite formation is possible without sucrose improving transport of ions through solution by increasing of Ca²⁺ ions concentration as was reviewed in [3]. It was demonstrated, the ettringite crystals preparation is significantly influenced by proportionality of adding of individual compounds into reaction water system. Pure ettringite phase can be prepared from large scale of water purity (distilled, drinking, industrial).

Generally ettringite formation can be described by the scheme:

$$6 \text{CaO} + \text{Al}_2(\text{SO}_4)_3 + 32 \text{H}_2\text{O} \rightarrow \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26 \text{H}_2\text{O}$$

Besides this reaction, four types of local simultaneous reactions may play role in kinetics of crystallisation process, morphology and properties of products:

1. Ca²⁺ + SO₄²⁻ → CaSO₄
   CaSO₄ + Al(OH)₆⁻ → ettr.

The both reactions run, when stoichiometric ratio of starting materials (lime and aluminium sulphate or ammonium aluminium sulphate) is retained. In this only pure ettringite is present as is shown in Fig. 1 and 2. Fig. 1 represents sample prepared from solution of aluminium sulphate and Fig. 2 ammonium sulphate respectively. Comparison both results documents no difference in reaction mechanism.

Ettringite creates good developed needle and pillar crystals with length about 1 μm and width 0,1 μm. Samples prepared from aluminium sulphate and ammonium aluminium sulphate are characterised by different morphology. Distribution of particle size in last said figures is more regular. It is probably caused by:

- different ratio of Al(OH)₆⁻ and SO₄²⁻ ions in initial materials
- pH value controlled by presence of Ca²⁺/NH₄⁺ ions
- NH₄⁺ volume influenced nucleation and crystallisation of ettringite

2. Al(OH)₆⁻ → Al(OH)₃ + OH⁻

This reaction manifests the non-stationary reaction condition. Local deficit of SO₄²⁻ ions in concentration gradient causes nucleation of metastable amorphous gibbsite Al(OH)₃. Precipitated alumina gel can block temporarily ettringite nucleation by reducing of Al(OH)₆⁻ ions in solution. Alumina gel formation is manifested by higher background in X–ray pattern in Fig. 3.

Presence of portlandite Ca(OH)₂ is interesting with respect to deficit of Ca²⁺ ions. This fact can be explained by fast formation of alumina gel and by high activation energy of gibbsite dissolution. Beside these phases may crystallise gypsum CaSO₄.2H₂O too. It is caused by no stoichiometric ratio of input compounds.

In the first period of reaction, ettringite cannot form because all negligible compounds for building of crystal structure are not present in surround of possible nucleus. Only Al(OH)₃ and CaSO₄.2H₂O create.

In the second period, a part of soluble CaSO₄.2H₂O reacts with sulphates to ettringite. Insoluble alumina gel or gibbsite does not take part crystallisation. In final account, the deficit of aluminate ions causes presence of Ca(OH)₂ in phase composition of product. It can be concluded that low solubility of aluminate gel is a kinetic barrier for ettringite crystallisation.

3. Ca²⁺ + 2 OH⁻ → Ca(OH)₂

The reaction describes the situation with excess of Ca²⁺ ions in solution. Resultant solid phase composition is shown in Fig. 4. In the solid products are portlandite Ca(OH)₂ and ettringite. Last disposes all SO₄²⁻ and Al(OH)₆⁻ ions. Higher content of Ca²⁺ ions increases pH
value and contributes to better transport of Al(OH)₄⁻ ions in liquid phase. This fact leads to increasing of ettringite formation rate and reduction of gypsum precipitation probability. X-ray pattern in Fig. 4 is characterised by relative high ratio of amorphous phase.

4. Ca²⁺ + SO₄²⁻ \rightarrow CaSO₄
   
Local excess of SO₄²⁻ ions in solution causes gypsum crystallisation (Fig. 5). These conditions may be expected in technological plants with high rate of flow and that is why part of Al³⁺ is not effectively exploited for ettringite production. Fig. 18: System with precipitated gypsum beside ettringite

**Conclusions**

- The preparation of ettringite was realised from solutions of pure aluminium sulphate and technical ammonium aluminium sulphate.
- The apparatus for sample preparation was developed.
- On the basis of big number of samples, ettringite preparation was optimised.
- The ettringite crystals preparation is significantly influenced by proportionality of adding of individual compounds into reaction water system.
- Pure ettringite phase can be prepared from large scale of water purity (distilled, drinking, industrial).
- Beside main general reaction, four types of local simultaneous reactions may play role in kinetics of crystallisation process, morphology and properties of products.
\[
\begin{align*}
\text{Ca}^{2+} + \text{SO}_4^{2-} & \rightarrow \text{CaSO}_4 \\
\text{CaSO}_4 + \text{Al(OH)}_3^- & \rightarrow \text{etr.} \\
\text{Al(OH)}_3^- & \rightarrow \text{Al(OH)}_3 + \text{OH}^- \\
\text{Ca}^{2+} + 2 \text{OH}^- & \rightarrow \text{Ca(OH)}_2 \\
\text{Ca}^{2+} + \text{SO}_4^{2-} & \rightarrow \text{CaSO}_4
\end{align*}
\]

References:


Figure 3. X-ray pattern with higher background caused by alumina gel formation

Figure 4. X-ray pattern representing phase composition with \( \text{Ca}^{2+} \) ions in solution

Figure 5. System with precipitated gypsum beside ettringite