07-Crystallography of Organometallic and Coordination Compounds

This kind of coordination has been observed for coordination compounds of EDTA with different transition metals obtained in presence of water (Solans, X., Font-Altaba, M. & Garcia-Orcin, J. (1984). *Afnidad* 41, 572-578).

PS-07.04.35 INVESTIGATION OF CRYSTAL STRUCTURE REGULARITIES OF $\text{H}_2[\text{Ru(NO)}_2\text{Cl}] \cdot \text{nH}_2\text{O}$ (Bottomley, F. J. Chem. Soc., Dalton, 1972, 19, 2148-2150) and $\text{H}_2[\text{Ru(NO)}_2\text{Cl}] \cdot \text{OH}$, where $\text{M}$ is $\text{Na}$ (Simonov, S. U. et al., J. Inorg. Chem., 1965, 27, 309-329), or $\text{K}$ (Bokil G. B. et al., J. Struct. Chem., 1962, 3, 163-172) are known elsewhere. A procedure of synthesis of hexanitrocubanes (II) of $\text{Li}$ (A), $\text{Na}$ (B) and $\text{K}$ (C) has been developed by us. $\text{A} = \text{Li}_4[\text{Ru(NO)}_2\text{Cl}] \cdot 12\text{H}_2\text{O}$, $\text{B} = \text{Na}_4[\text{Ru(NO)}_2\text{Cl}] \cdot 12\text{H}_2\text{O}$, and $\text{C} = \text{K}_4[\text{Ru(NO)}_2\text{Cl}] \cdot 12\text{H}_2\text{O}$.

X-ray investigation of single and polycrystals has been carried out.

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</thead>
<tbody>
<tr>
<td>A</td>
<td>11,749</td>
<td>11,749</td>
<td>16,807</td>
<td>2320.0</td>
<td>Tetr.</td>
<td>3.8</td>
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<tr>
<td>B</td>
<td>8,105</td>
<td>8,723</td>
<td>8,891</td>
<td>631,1</td>
<td>Monocl.</td>
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<tr>
<td>C</td>
<td>8,595</td>
<td>8,595</td>
<td>8,595</td>
<td>367,0</td>
<td>R3m</td>
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<td>52,23</td>
<td>52,23</td>
<td>52,23</td>
<td>1</td>
<td>R3</td>
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Crystal structures of the compounds investigated are based on the complex anions $\text{Ru(NO)}_2\text{Cl}^-$. Forming a distorted rhombohedral sub-cell, the key metal cations and molecules of crystallized water. The Ru atom has an octahedral environment formed by the N atoms of the nitrate groups. The mean Ru-N distance is 2.06Å. In the crystal structures, all 0 atoms of the nitrate groups and water molecules form polyhedra around the cations to link them with each other and with the complex anions. In A these are octahedra and tetrahedra with mean 0-0 distances of 2.02 and 1.95Å, respectively. In B and C the Na and K atoms are coordinated to light 0 atoms with mean bond distances: Na-0=2.31-2.71, K-0=2.65-3.24Å. A comparative analysis of the orientation of complex anions and nitrate groups about the probable axis of the 1-D order has been performed.

The work was supported by financial help of the Soros Fund.


One of the most interesting classes of volatile coordination compounds of practical use are diethyldithiocarbamates of metals (Larkinov, S.V. Zh. Neorg. Chem., 1993, 24, 293-316). The mixed-ligand complexes of Cu(II) and Cd(II) were obtained, namely four compounds of CuL and three compounds of ZnL (Zn(OH)2(30%), Zn(OH)2(30%), Zn(OH)2(30%), Zn(OH)2(30%)) with nitrogen heterocycles (Phen, Bipy,-im) and Enl:Cd. Phen:II-CdL2(2,2′-Bipy), III-CdL2; IV- (ZnL2)CdL2; V-CdL2(2,2′-Bipy), VI-CdL2(4,4′-Bipy). The crystal data are given in the Table.

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<tbody>
<tr>
<td>I</td>
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<td>15.172</td>
<td>16.967</td>
<td>2320.0</td>
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<td>III</td>
<td>10.597</td>
<td>11.576</td>
<td>11.530</td>
<td>4(6+4N)</td>
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<tr>
<td>IV</td>
<td>10.597</td>
<td>11.576</td>
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<td>V</td>
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<td>VI</td>
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The crystal structures I-V are built of discrete mononuclear and Y-aminocarbonic molecules linked by Van-der-Waals contacts. The central atom environments in the complex IV form different coordination polyhedra: an octahedron and a trigonal prism. The crystal chemical characteristics of complexes studied have been treated following determinations of new mixed-ligand complexes and literature data.


Regular interest in coordination compounds is accounted for by their wide usage in various chemical processes and technical fields. Crystal structure peculiarities have been considered for sufficiently large classes of inorganic compounds, containing such complex ions as (M₈O₆X₆)₄⁺ (MX₄(aq)), where n=0-6; M-transition metal, A-neutral (H₂O or NH₃), and X-oxid (O, Cl, Br, I) ligands (N.V. Podberezskaya, T.S. Yudanova, S.A. Magarill, et al., Probl. Kristallogr. M.Nauka, 1990, 82-98; Zh. Strukt. Khim., 1991, 32, No. 6, 137-156). Complex cations or anions are considered to pack as quasi spheres of radii Rₑ=δ(M-X-A)⁹/₂=δ(X,A), where δ(M-X,A) is the distance between the central atom of a complex ion and X or A atoms, and Rₑ is the van-der-Waals radius of these atoms. Structures of inorganic coordination compounds may be divided into structure types as fluoride CaF₂ anti-
fluorite R$_3$(PtO$_3$)$_2$), and NaCl, giving a rough picture. The successive changes from cubic to trigonal symmetry have been observed while preserving the packing rules of complex centers as the most "hard" scattering fragments. It was shown that polyatomic atoms or linear anions such as NCS$, \text{N}_2$, ONO make the complex ions [MA$_3$X] oriented in the direction of octahedral cavities of closest packing. To estimate lattice parameters of hexagonal (a$_h$=2R$_m$) and cubic (a$_c$=2R$_m$) unit cells, R$_m$ is the radius of the basic sphere in the closest packing arrangement has been used. The estimated and observed lattice parameters have been compared and the efficiency of this geometrical approach demonstrated. Estimation of complex ion size permits prediction of crystalization and possible isomorphous substitution. It may be used to suggest selective synthesis reactions for complex formation and help to index powder diffraction data.

**07-Crystallography of Organometallic and Coordination Compounds**

07.04.38 A STUDY OF REGULARITIES IN LAYER FORMATION OF SOME VOLATILE B-DIKETONATES OF Cu(2+), Y(3+), AND Pb(2+). By S.A. Grumilov, I.A. Baidina*, S.A. Prokhorova, and V.I. Alekseev, Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Novosibirsk, Russia.

Volatility coordination compounds can be used to prepare layers of inorganic substances from the gaseous phase (MO GD). B-Diketonates of metals are often used as the initial components. It is of interest to study layers of formation on different substrates and to predict their breakdown into metals, oxides, or fluorides under outside influences.

Single crystals, the volatile B-diketonates of Cu(2+), Y(3+), and Pb(2+) have been chosen for X-ray analysis. Cu(zinol)$_2$, Cu(zis7)$_2$, Y(dpm)$_2$, C, Y(dph)$_2$, Pb(gla)$_2$, Pb(pta)$_2$. Molecule configurations of these compounds involve a planar (A,B,E,F) and an isotropic (C,D) form. The crystal structures reveal the presence of monomeric (A,B,C,D) and dimeric (E,F) forms.

Powder samples of the compounds and layers prepared by sublimation on substrates of silicon of different orientations and fused quartz have been studied by X-ray diffraction (DRON-3M, R-192 mm, CuKα radiation).

In all cases except A oriented poly-crystal line films have been prepared. The orientation direction is perpendicular to a crystallographic plane with the largest interplane distance regardless of the molecule configurations and crystal structures.

#Heis1 = pivaloyldimethylmethoxycacetone,
#Heis7 = pivaloylpropanoic acid,
#Hdp = pivaloylmethan,
#Hgra = hexafluorocacetone,
#Hpta = pivaloyitrifluoroacetone.

**PS-07.04.39**

A SUBSTRUCTURE-SUPERSTRUCTURE RELATIONSHIP IN LITHIUM HYDROGEN MALEATE DIHYDRATE LiC$_2$H$_4$O$_4$•2H$_2$O

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Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, Venezuela 5101

During the course of our investigations on the crystal chemistry and solid state behavior of metal derivatives of unsaturated mono- and dicarboxylic acids, crystals of lithium, sodium, potassium, magnesium, calcium, strontium, barium, and magnesium, cobalt, nickel, zinc, and cadmium derivatives of maleic acid (cis-2-butenedioic acid) have been prepared. To properly follow any structural changes that might take place in the maleate crystals upon exposure to UV, γ- or X-rays or heat, it has been necessary to carry out single crystal X-ray diffraction experiments in the materials before treatment even though the structures of most of these compounds have been reported in the literature. The photographic study of lithium hydrogen maleate crystals, performed on a Bragg reflection camera, showed a particularly interesting structural aspect in this material. A set of intense reflections defined a monoclinic subcell with space group P2$_1$/m and lattice parameters a = 5.862(1) Å, b = 6.622(1) Å, c = 9.772(2) Å, β = 105.99(2)°. The geometric disposition of the entire diffraction pattern is described by a pseudo-B-centered cell with space group P2$_1$/m and lattice parameters a = 5.862(1) Å, b = 6.622(1) Å, c = 18.838(3) Å, β = 91.34(1)° in good agreement with the results previously reported[1].

The unit cell can be derived from the subcell through the transformation matrix [a,b,c] = [1,0,0] (0,1,0) (0,0,1). The structure refinement of the subcell led to discrepancy factors R(F) = 0.0375, R_w(F) = 0.0470, S = 1.02 for the 643 substructure independent reflections while the refinement of the unit cell led to R(F) = 0.0585, R_w(F) = 0.0528, S = 1.25 for all 1161 independent reflections. In the subcell, the C$_2$H$_4$O$_4$H anion and the water molecules are in special position (mirror plane) while the Li atoms are located in between the sheets, in general positions but with an occupancy factor of 1/2.

In this contribution, we discuss in detail the interesting substructure-superstructure relation present in LiC$_2$H$_4$O$_4$H•2H$_2$O, a structural feature infrequently found in organic and metal-organic materials.

The purchase of the P3/F Nicolet diffractometer was possible thanks to grants F-74 and YC-19 from CONICIT and CDCHT-ULA, respectively. This work was possible thanks to grant C-475-90 from CDCHT-ULA.