

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-Orcaín, J. (1984). *Afinidad* **41**, 572-578).

PS-07.04.35 INVESTIGATION OF CRYSTAL STRUCTURE REGULARITIES OF $M_4[Ru(NO_2)_6] \cdot nH_2O$ (M=Li, Na, K;

$n=12, 2, 0$). By S.A. Gromilov*, V.A. Emelyanov, V.I. Alekseev, I.A. Baidina, A.V. Belyaev. Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Novosibirsk, Russia.

Data on crystal structures of nitrocompounds of Ru(II) - $[Ru(NH_3)_5NO_2] \cdot Cl \cdot H_2O$ (Bottomley F., J.Chem.Soc., Dalton, 1972, 19, 2148-2152) and $M_2[RuNO(NO_2)_4OH]$, where M is Na (Simonsen S.H. et al., J. Inorg. Chem., 1965, 27, 309-320), or K (Bokij G.B. et al., J.Struct.Chem., 1962, 3, 2, 163-172) are known elsewhere. A procedure of synthesis of hexanitroruthenates(II) of Li (A), Na (B) and K (C) has been developed by us.

A - $Li_4[Ru(NO_2)_6] \cdot 12H_2O$
 B - $Na_4[Ru(NO_2)_6] \cdot 2H_2O$
 C - $K_4[Ru(NO_2)_6]$

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

	a, Å	b	c	V, Å ³	Simm.	R, %
	α , deg	β	γ	Z	Sp.gr.	
A	11,749	11,749	16,807	2320,0	Tetr.	3,8
	90	90	90	4	I4	
B	8,105	8,723	8,931	631,1	Monocl.	2,9
	90	91,87	90	2	P2 ₁ /n	
C	8,595	8,595	8,595	367,0	Rmbhdr.	3,2
	52,23	52,23	52,23	1	R3	

Crystal structures of the compounds investigated are based on the complex anions

$Ru(NO_2)_6^{4-}$ forming a distorted rhombohedral sub-cell, alkaline metal cations and molecules of crystallized water. The Ru atom has an octahedral environment formed by the N atoms of the nitrite groups. The mean Ru-N distance is 2.065Å. In the crystal structures all O atoms of the nitrite 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 Li-O distances of 2.02 and 1.95Å, respectively. In B and C the Na and K atoms are coordinated to light O atoms with mean bond distances: Na-O=2.31-2.71, K-O=2.85-3.24Å.

A comparative analysis of the orientations of complex anions and nitrite groups about the probable axe of the 3-D order has been performed.

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PS-07.04.36 MIXED-LIGAND DIETHYLDITHIOCARBAMATES OF Zn(II) AND Cd(II): PREPARATION AND CRYSTAL STRUCTURES. By L.A. Glinskaya*, R.F. Klevtsova, S.M. Zemskova, S.V. Larionov. Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Russia.

One of the most interesting classes of volatile coordination compounds of practical use are diethyldithiocarbamates of metals (Larionov S.V. Zh.Neorg.Chim., 1979, 24, 6, 1446). The mixed-ligand complexes of Zn(II) and Cd(II) were obtained, namely four compounds of CdL₂ and three compounds of ZnL₂ (L=(C₂H₅)₂NCS₂⁻) with nitrogen heterocycles (Phen, Bipy, Im) and En: I-CdL₂Phen; II-CdL₂(2,2'-Bipy); III-CdL₂Im; IV-[ZnEn₃][CdL₃]₂; V-ZnL₂(2,2'-Bipy); VI-[ZnL₂]₂(4,4'-Bipy). The crystal data are given in the Table.

	Sp.gr.	a, Å	b, Å	c, Å	Z	CN
I	P1	11.044	15.172	16.967	4	6(4S+2N)
		100.38	99.79	101.40		
II	C2/c	18.103	8.381	16.965	4	6(4S+2N)
			105.97			
III	P2 ₁ /a	20.820	8.576	11.520	4	5(4S+1N)
IV	I4 ₁ cd	20.348	-	28.744	4	6N, 6S
V	Pnaa	17.246	-	6.792	4	6(4S+2N)
VI	Pnca	17.411	-	22.161	8	5(4S+1N)

The crystal structures I-V are built of discrete mononuclear and VI - binuclear molecules linked by Van-der-Waals contacts. The central atom environments in the complexes 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.

PS-07.04.37 'CLOSEST PACKING' IN INORGANIC COORDINATION CRYSTALS. By N.V. Podberezskaya*, T.S. Yudanov, S.A. Magarill, E.N. Ipatova, G.V. Romanenko, N.V. Pervukhina, and S.V. Borisov, Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, Russia.

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 $(MA_{6-n}X_n)$ or $(MX_{6-n}A_n)$, where $n=0-6$; M-transition metal, A-neutral (H_2O or NH_3), and X-acid (F^- , Cl^- , Br^- , I^- et al.) ligands (N.V. Podberezskaya, T.S. Yudanov, S.A. Magarill, et al., Probl. Kristalloghim. M.: Nauka, 1990, 82-98; Zh. Strukt. Khimii., 1991, 32, No. 6, 137-150). Complex cations or anions are considered to pack as quasi spheres of radii $R_{or} = d(M-X, A) + r_{vdw}(X, A)$, where $d(M-X, A)$ is the distance between the central atom of a complex ion and X or A atoms, and r_{vdw} is the van-der-Waal's radius of these atoms. Structures of inorganic coordination compounds may be divided into structure types as fluorite CaF_2 , anti-

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fluorite $K_2(PtCl_6)$, and NaCl, giving a rough picture. The successive changes from cubic to triclinic symmetry have been observed while preserving the packing rules of complex centers as the most "hard" scattering fragments. It was shown that polyatomic almost linear anions such as NCS^- , N_3^- , ONO^- a.o. of the complex ions $[MA_6X]$ are oriented in the direction of octahedral cavities of 'closest packing'. To estimate lattice parameters of hexagonal ($a_h=2R_{ef}$) and cubic ($a_c=2\sqrt{2}R_{ef}$) unit cells, R_{ef} , 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 cocrystallization and possible isomorphic substitution. It may be used to suggest selective synthesis reactions for complex formation and help to index powder diffraction data.

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

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

Single crystals, the volatile β -diketonates of Cu(2+), Y(3+), and Pb(2+) have been chosen for X-ray analysis. $Cu(zis1)_2-A$, $Cu(zis7)_2-B$, $Y(dpm)_3-C$, $Y_2(dpm)_6-D$, $Pb(gfa)_2-E$, $Pb(pta)_2-F^*$. Molecule configurations of these compounds involve a planar (A,B,E,F) and an isometric (C,D) form. The crystal structures reveal the presence of monomeric (A,B,C), dimeric (D), and chain (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-UM1, $R=192$ mm, $CuK\alpha$ -radiation).

In all cases except A oriented polycrystal 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.

*Hzi1 - pivaloyldimethylmethoxyacetone,
Hzi7 - pivaloylizopropenilacetone,
Hdpm - pivaloylmethane,
Hgfa - hexafluoroacetylacetone,
Hpta - pivaloyltrifluoroacetone.

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A SUBSTRUCTURE-SUPERSTRUCTURE
RELATIONSHIP IN
LITHIUM HYDROGEN MALEATE DIHYDRATE
 $Li(C_4H_2O_4H) \cdot 2H_2O$

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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, manganese, cobalt, nickel, zinc and cadmium derivatives of maleic acid (*cis*-2-butenedioic acid) have been prepared. To properly follow any structural change 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 Buerger precession 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, $b = 6.062(1)$ Å, $c = 9.777(2)$ Å, $\beta = 105.99(2)^\circ$. The geometric disposition of the entire diffraction pattern is described by a *pseudo*-B-centered cell with space group $P2_1/n$ and lattice parameters $a = 5.862(1)$ Å, $b = 6.062(1)$ Å, $c = 18.838(3)$ Å, $\beta = 91.34(1)^\circ$ in good agreement with the results previously reported[1]. The unit cell can be derived from the subcell through the transformation matrix $[a,b,c] = [(1,0,0) (0,1,0) (1,0,2)] [a,b,c]_{sc}$. 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 $C_4H_2O_4H^-$ 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 $Li(C_4H_2O_4H) \cdot 2H_2O$, a structural feature infrequently found in organic and metal-organic materials.

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[1] Popelier, P., Lenstra, A.T.H., and Geise, H.J., *Acta Cryst.*, C45, 1024-1028 (1989)