

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 axis 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 CdL_2 and three compounds of ZnL_2 ($L=(C_2H_5)_2NCS_2^-$) with nitrogen heterocycles (Phen, Bipy, Im) and En: I- CdL_2 Phen; II- $CdL_2(2,2'$ -Bipy); III- CdL_2 Im; IV- $[ZnEn_3][CdL_3]_2$; V- $ZnL_2(2,2'$ -Bipy); VI- $[ZnL_2]_2(4,4'$ -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. Yudanova, 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. Yudanova, 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-