

## 07-Crystallography of Organometallic and Coordination Compounds

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Cu(2+) with the carbon atoms of neighbouring molecules. In Cu(acetylacetonate)<sub>2</sub>, for instance, they are arranged in such a way that to form the chains along the shortest unit cell edge. Mixed-ligand complexes of Cu(II) are pseudodimeric and the second form of Y(dipivaloylmethanate)<sub>3</sub> is the dimeric one.

$\beta$ -Diketonate complexes of alkaline-earth-metals are oligomeric ones. Oligomerization extent depends on synthesis conditions. Complexes of the type II and III are "the guest-host complexes". The influence of the additional neutral ligands on oligomerization extent of complexes in condensed phase has been considered by those examples. The Cu complexes with crown ethers are chain polymers. Maxidentant binding of the donor atoms of the additional ligands by the metal atoms has been shown to result in monomeric complexes with high coordination numbers of metal atoms and normal Van-der-Waals interactions between the complexes. Conformation and symmetry changing of the additional ligands in complex formation of this type were considered. The coordination polyhedra of metal atoms in volatile complexes and in the high-T<sub>c</sub> superconducting oxides were compared. It was revealed a lack of direct analogies between them in many cases. Topological features of the central metal atoms arrangement in the complexes were treated. They have been shown to be represented by unclose-packed nets, having, for example, Schläfli symbols, 4<sup>4</sup>, 6<sup>3</sup>, and the shortest distances between metal atoms arranged in the nodes of the nets. A correlation between structures of the complexes and their volatility and thermostability has been discussed. Introduction of additional ligands into guest-host complexes of type II and III has been shown to improve useful qualities of compounds.

**PS-07.04.33** STRUCTURE OF GADOLINIUM COMPLEX WITH ACETYLENE DICARBOXYLIC ACID (ADA). By Yan Xing, Zhong-Sheng Jin, Zhi-Band Duan and Jia-Zuan Ni, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, People's Republic of China

Abstract Gd<sub>2</sub>(ADA) · 8H<sub>2</sub>O, Mr=794.8, triclinic, P $\bar{1}$ , a=8.254(2), b=8.605(2), c=9.066(2) Å,  $\alpha$ =95.38(2),  $\beta$ =115.82(2),  $\gamma$ =110.39(2)°, V=519.8(2) Å<sup>3</sup>, Z=1, D<sub>x</sub>=2.54 g cm<sup>-3</sup>,  $\lambda$ (MoK $\alpha$ )=0.71069 Å, R=0.035 for 2694 observed reflections.

There are one and half ligands in an asymmetric unit. The molecular formula is Gd<sub>2</sub>(ADA) · 8H<sub>2</sub>O. The molecular structure is shown in Fig.1. The ligands are coordinated in three different forms in the molecule, firstly, only one of the two carboxylic oxygen atoms is bonded to a metal ion, and the other one is free, secondly, two carboxylic oxygen atoms are coordinated to two different metal ions, forming a carboxyl bridge, presenting a double chain structure, thirdly, two carboxyl oxygen atoms are bridging tridentate, bonded two Gd atoms, forming a four membered ring. Such the carboxylic groups form

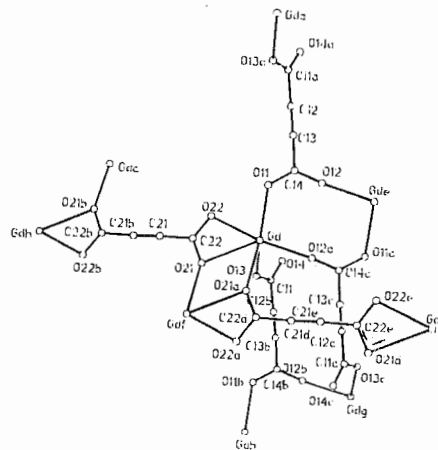


Fig.1. Molecular structure of Gd<sub>2</sub>(ADA) · 8H<sub>2</sub>O.

a single chain, which intersects the double chain above at each Gd atom, presenting a two dimension network structure. The Gd ion is 9-coordinate, bonded to six oxygen atoms from five carboxylic groups and to the three oxygen atoms of water molecules. There are two free water molecules in the unit cell. The Gd-O bond lengths range from 2.34 to 2.64 Å, one distance, namely, the Gd-O(21) of 2.64 Å, being significantly longer than the mean Gd-O bond length, 2.46 Å, the O(21) atom is the upper vertex of the tetragonal pyramid. The Gd-O(bridging bidentate) averaged distance of 2.35 Å is the shortest, but the Gd-O(chelating bidentate in bridging tridentate) averaged one of 2.50 Å is the longest in the three coordination forms. The rest Gd-O(water, unidentate, bridging part in tridentate) range from 2.42 to 2.49 Å with the mean bond length of 2.45 Å. The bond lengths and angles of the ADA in this paper are about the same as those of the literature(Allen and Don, 1973).

## References

Allen, C.L., and Don, T.C.(1973). Acta Cryst. B29, 1579-1583.

**PS-07.04.34** THE STRUCTURE OF AQUOTETRAACETANILIDE OF EDTA COBALT (II) PERCHLORATE. By J.L. Briansó\*<sup>1</sup>, J.F. Piniella<sup>1</sup>, A. Alvarez-Larena<sup>1</sup>, A. Namor<sup>2</sup>, and J. Cárdenas<sup>2</sup>.

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In the context of a study on the use of Tetraacetanilide of EDTA for the recovery and purification of metals, we present here the X-ray crystal structure determination of the title compound.

The crystallographic results show a coordination seven around the cobalt, one water molecule being coordinated with the metal.

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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 <sup>3</sup>	Simm.	R, %
	$\alpha$ , deg	$\beta$	$\gamma$	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 <sub>1</sub> /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 CdL<sub>2</sub> and three compounds of ZnL<sub>2</sub> (L=(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NCS<sub>2</sub><sup>-</sup>) with nitrogen heterocycles (Phen, Bipy, Im) and En: I-CdL<sub>2</sub>Phen; II-CdL<sub>2</sub>(2,2'-Bipy); III-CdL<sub>2</sub>Im; IV-[ZnEn<sub>3</sub>][CdL<sub>3</sub>]<sub>2</sub>; V-ZnL<sub>2</sub>(2,2'-Bipy); VI-[ZnL<sub>2</sub>]<sub>2</sub>(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 <sub>1</sub> /a	20.820	8.576	11.520	4	5(4S+1N)
IV	I4 <sub>1</sub> 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-