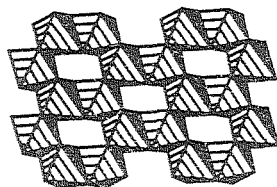


09.4-20 CRYSTAL STRUCTURE OF THE SODIUM AND CHROMIUM SALTS OF DIETHYLDITHIOPHOSPHINATE.

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As a part of our investigation of metal complexes with sulphur-containing ligands we are working with dithiophosphinates. The chemistry of transition metal dithiophosphinates was reviewed some years ago (W. Kuchen and H. Hertel, *Angew. Chem.* 81, (1969) 127-135). The crystal structures of sodium diethyldithiophosphate hydrate $[(C_2H_5)_2PS_2Na \cdot 2H_2O]$ (I) and tris(diethyldithiophosphate)chromium(III) $[Cr(S_2P(C_2H_5)_2)_3]$ (II) were determined. The measurements were carried out on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated MoK α . (I) $P\bar{1}$, $a=6.1202(5)$, $b=6.5908(8)$, $c=14.443(1)$ Å, $\alpha=98.49(1)$, $\beta=95.07(1)$, $\gamma=115.55(1)^\circ$, $V=512.25(7)$ Å³, $Z=2$, $\mu=9.1$ cm⁻¹, $R=0.035$ for 1294 independent reflections.



Each Na⁺ ion is surrounded by four water O and two S atoms forming a distorted octahedron. These polyhedra are connected by edge sharing parallel to the *ab*-plane. The average Na-S and Na-O distances are 2.999(1) and 2.44(5) Å respectively.

(II) $P\bar{1}$, $a=9.638(1)$, $b=10.017(3)$, $c=13.983(3)$ Å, $\alpha=86.25(1)$, $\beta=75.15(1)$, $\gamma=66.95(1)^\circ$, $V=1199(2)$ Å³, $Z=2$, $\mu=11.86$ cm⁻¹, $R=0.036$ for 3209 independent reflections. The chromium ion is surrounded by six sulphur in a slightly distorted octahedron with the average Cr-S distance 2.442(8) Å.

09.4-21 X-RAY AND NEUTRON DIFFRACTION STUDIES OF HEXACYANOMETALLATES (III): CRYSTAL STRUCTURES OF $Cs_2LiM(CN)_6$ [M = Cr, Mn].

By B.M. Chadwick, Jones, Wilde and J. Yerkess, Schools of Chemistry and Chemical Technology, University of Bradford, Bradford, West Yorkshire, BD7 1DP, England.

Bonding changes along the series of first-row transition-metal hexacyanides, $Cs_2LiM(CN)_6$ [M = Cr, Mn, Fe or Co], are of considerable structural and spectroscopic interest. From X-ray and neutron-diffraction measurements, we have shown that any deviations of the room-temperature structures of the Fe and Co compounds from the cubic ($Fm\bar{3}m$) elpasolite structure are extremely small (Chadwick, Jones, Wilde and Yerkess, *J. Cryst. Spectros. Res.* 1985, 15, 129). Deviations are rather greater at room temperature for the Mn compound and more so for $Cs_2LiCr(CN)_6$, such that different symmetries have been proposed (Chowdhury, et al., *Acta Cryst.*, 1977, B33, 46; Ryan and Swanson, *Inorg. Chem.*, 1974, 13, 1681 and *Acta Cryst.*, 1978, B34, 1398).

Examination by X-ray and neutron (powder and single crystal) diffraction of the Mn and Cr compounds (prepared by improved methods) confirms that departures from the full $Fm\bar{3}m$ symmetry are small for $Cs_2LiMn(CN)_6$: there are very few weak extra reflections ($N^* = 2, 10, 14$, with $N = 26$ on the neutron powder patterns) and some line splittings ($N = 16, 20, 40, 44, 56$). Although the Cr compound showed some further weak neutron reflections ($N = 1, 30, 42$), refinements of single-crystal neutron data, carried out in $Fm\bar{3}m$, were not improved by resorting to primitive cubic or tetragonal space groups. Accordingly least-squares neutron refinements in $Fm\bar{3}m$ are reported to $R = 0.064$ over 69 reflections for a $Cs_2LiMn(CN)_6$ crystal quenched in liquid nitrogen and to $R = 0.113$ over 76 reflections for a quenched

$Cs_2LiCr(CN)_6$ crystal.

Although the 2.02(1) Å Cr-C bond length determined is slightly shorter than found in $Cs_2LiCr(CN)_6$ from X-ray diffraction by Swanson & Ryan and by Figgis et al (*Acta Cryst.*, 1983, C39, 1587) in $Cs_2KCr(CN)_6$, it is the longest in the steadily increasing M-C sequence Co-Fe-Mn-Cr (from 1.89(1) Å in the Co compound). The C-N bond lengths of 1.14(1) Å are much the same as Swanson and Ryan reported, both above and below the transition, and as in the other $Cs_2LiM(CN)_6$; neutron diffraction can give marginally longer C-N bonds than X-ray diffraction.

At 4.2 K, neutron powder data indicate the presence of further non-face-centred reflections for both Cr and Mn compounds and there are small contractions 10.60 - 10.55(1) Å (M = Mn) and 10.69 - 10.67 Å (M = Cr) in the apparent cubic unit-cell parameters.

09.4-22 CRYSTAL STRUCTURE OF BINUCLEAR HEXAAQUABIS-(ETHYLENEDIAMINE)- μ -PYROMELITATO-DINICKEL (II) TETRAHYDRATE.

By D. Poletti*, B. Prelesnik**, R. Herak** and Dj. Stojaković*, * Faculty of Technology and Metallurgy, University of Belgrade, Kernegijeva 4, 11000 Belgrade, ** Laboratory of Solid State Physics and Radiation Chemistry "Boris Kidrič" Institute, P.O.Box 522, 11001 Belgrade, Yugoslavia.

In continuation of our studies of structures and properties of transition metal complexes with aromatic polycarboxylate ligands the synthesis and the crystal structure determination of the title compound were carried out. The complex was prepared by sedimentation from diluted solution containing $Ni(en)^{2+}$ and pyr^{4-} ions (en = ethylenediamine, pyr^{4-} = anion of pyromelic acid). Single crystals suitable for x-ray crystal structure analysis were grown by recrystallization from water. The pale blue crystals belong to monoclinic system, space group $P2_1/c$, $a=9.192(1)$, $b=13.919(2)$, $c=10.754(1)$ Å, $\beta=107.70(1)^\circ$, $V=1311(4)$ Å³, $D_x=1.69$ gr. cm⁻³ for $Z=2$. The structure was solved by the heavy atom methods on the basis of 1908 intensities of independent reflexions measured on CAD-4 diffractometer using MoK α graphite monochromated radiation. The atomic coordinates of all non-hydrogen atoms and their anisotropic thermal parameters were

refined by full-matrix least-squares method to an R value of 0.035.

The crystal structure consists of $[(en)(H_2O)_3 - Ni - pyr - Ni(H_2O)_3(en)]$ units and molecules of water. Pyromellitate ion behaves here as a bridging ligand with its two COO^- groups coordinated to the metal in *ortho* position. Remaining two COO^- groups are involved in hydrogen bonding. The metal atom is octahedrally coordinated by two nitrogen atoms belonging to ethylenediamine ligand, oxygen atom from coordinated COO^- group of pyromellitate ion and three molecules of water.

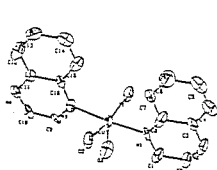
Complex molecules are inclined to the XY crystallographic plane at about 30° and are forming layers parallel to the XZ crystallographic plane. These layers are mutually connected by the system of hydrogen bonds.

09.4-24 THE STRUCTURE OF COMPLEXES OF Cu(II) AND Co(III) WITH TWO- AND THREEBASIC AMINOALCOHOLS. By T.I. Malinowsky, M.D. Mazus, Yu.A. Simonov, A.L. Kovalenko, V.N. Polyakov, The Institute of Applied Physics Academy of Sciences Moldavian SSR, Kishinev- 277028, USSR.

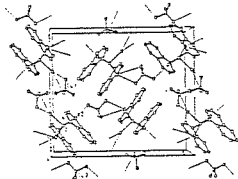
Various types of complexes are formed by aminoalcohols (AA) with transition metals by acting as both chelate and chelate-bridge ligands. The nature of the bonding of AA to metals depends on the metal-ligand ratio, the medium of synthesis and the extent of AA deprotonation. The structures of AA complexes with Cu(II) and Co(III) of the following composition: $[Cu(TRIS_2-H)H_2O]ClH_2O$ (I), $[Cu(TRIS-H)_2] \cdot 5H_2O$ (II), $[Cu(RDEA-H)Cl]_2$ (III), $K[Co(RDEA-H)_2] \cdot 7H_2O$ (IV), were determined by X-ray analysis methods. In compounds I-IV, AA is coordinated through the nitrogen atoms and oxygen atoms of alcohol. The participation of the latter in coordination is determined by the link with the metal of competing neutral- and acido- ligands. The framework of the structure is realized in I with ramification system of hydrogen bonds. The two chemically equivalent but crystallographically independent molecules in the crystal, form pseudodimers with the short $O-H \cdots O = 2.54 \text{ \AA}$ hydrogen bonds. The two AA molecules in the complex cation are in the *cis*-configuration; one of them is deprotonated, another - neutral. The dentation of the AA molecules is two and three respectively. The mononuclear structure with bidentate molecules of AA is realized in II. The centrosymmetric complex has a *trans*-configuration. The dimers where the distances $Cu-Cu = 2.952 \text{ \AA}$ form quadrimers through hydrogen bonds in III. The symmetry of the dimer is C_2 , the fragment Cu_2O_2 is not flat essentially. The coordination polyhedron of Co is a tetragonal pyramid with N-atom, two bridge-atoms, linked by C_2 -symmetry, and Cl-ion in the base. The O of the nonprotonated alcohol group is situated on the apex of the polyhedron. The magnetic properties of I-III are in fair agreement with the peculiarities of the complexes' structure. In IV the structure is realized with octahedral coordination of Co(III) formed by two mono-deprotonated molecules of AA.

09.4-23 CRYSTAL AND MOLECULAR STRUCTURE, MAGNETIC AND SPECTRAL PROPERTIES OF TRIAQUABIS(QUINOXALINE)COPPER(II) PERCHLORATE. By P.O. Lumme, S. Lindroos and E. Lindell, Department of Inorganic Chemistry, University of Helsinki, Vuorik. 20, SF-00100 Helsinki, Finland.

The crystal and molecular structure of triaquabis(quinoxaline)copper(II) perchlorate was determined by direct and Fourier methods. The compound crystallized in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 8.263(2)$, $b = 17.259(7)$, $c = 15.307(5)$ Å, $\beta = 90.07(2)^\circ$, $Z = 4$. The molecular structure of the title compound consists of a cation $[Cu(C_8N_2H_6)_2(H_2O)_3]^{2+}$, where the copper atom is coordinated to two nitrogen atoms of the quinoxaline molecules and to three oxygen atoms of the water molecules. The coordination polyhedron around the copper atom is a trigonal bipyramid, the oxygen atoms forming the basal plane and the nitrogen atoms at the apical positions. The water molecules are involved in hydrogen bonding to perchlorate anions and to two uncoordinated nitrogen atoms of the quinoxaline ligands. The magnetic, infrared and reflectance spectral data are compared with those found for other copper quinoxaline complexes.



ORTEP drawing at 50% probability level for non-hydrogen atoms of the cation unit.



View of the unit cell down *a*.

	The Crystal Data							
	a(Å)	b(Å)	c(Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	space group	R
I	19.785	11.798	6.489	90.13	96.39	91.81	P1	0.050
II	12.925	10.116	6.367	90	90	95.8	$P2_1/n$	0.051
III	19.459	18.202	13.251	90	90	67.21	$P2_1/a$	0.073
IV	15.488	14.812	7.632	90	90	86.34	$A2/a$	0.053