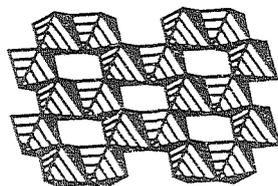


## 09.4-20 CRYSTAL STRUCTURE OF THE SODIUM AND CHROMIUM SALTS OF DIETHYLDITHIOPHOSPHINATE.

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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 $\alpha$ . (I)  $P\bar{1}$ ,  $a=6.1202(5)$ ,  $b=6.5908(8)$ ,  $c=14.443(1)$  Å,  $\alpha=98.49(1)$ ,  $\beta=95.07(1)$ ,  $\gamma=115.55(1)^\circ$ ,  $V=512.25(7)$  Å<sup>3</sup>,  $Z=2$ ,  $\mu=9.1$  cm<sup>-1</sup>,  $R=0.035$  for 1294 independent reflections.



Each Na<sup>+</sup> 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,  $\alpha=86.25(1)$ ,  $\beta=75.15(1)$ ,  $\gamma=66.95(1)^\circ$ ,  $V=1199(2)$  Å<sup>3</sup>,  $Z=2$ ,  $\mu=11.86$  cm<sup>-1</sup>,  $R=0.036$  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, D.W. Jones, H.J. 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)- $\mu$ -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,  $\beta=107.70(1)^\circ$ ,  $V=1311(4)$  Å<sup>3</sup>,  $D_x=1.69$  gr. cm<sup>-3</sup> 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 $\alpha$  graphite monochromated radiation. The atomic coordinates of all non-hydrogen atoms and their anisotropic thermal parameters were