C-184 09. STRUCTURES OF ORGANIC AND COORDINATION COMPOUNDS

09.4-20 CRYSTAL STRUCTURE OF THE SODIUM AND CHROMIUM SALT OF DITHIYLTHIOPHOSPHINATE.

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As a part of our investigation of metal complexes with sulphur-containing ligands we are working with dithiolphosphinates. The chemistry of transition metal dithiolphosphinates was reviewed some years ago (W. Kuchen and H. Hertel, Angew. Chem. 81, (1969) 127-135). The crystal structures of sodium

dithiylthiophosphinate hydrate [(CH₃)₂PS₂Na₂H₂O] (I) and tris(dithiylthiophosphinate)chromium(III) [Cr(S₂P(CH₃)₂)₃] (III) were determined. The measure­
ments were carried out on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated MoKα. P = 90.49(1), b = 95.07(1), c = 115.55(1)°. V = 512.25(7) Å³, Z = 2, μ = 0.035 for 1294 independent reflections.

Each Na ion is surrounded by four water molecules 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) P₁, a = 90.638(1), b = 10.017(3), c = 13.983(3) Å.

a = 86.25(1), b = 75.15(1), γ = 66.95(1)°, V = 1199.2(2) Å³, Z = 2, μ = 1.89 cm⁻¹, R = 0.036 for 3209 independent reflections. The chromium ion is surrounded by six sulphur atoms, forming 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 (II) CRYSTAL STRUCTURES OF Cs₂LiCr(CN)₆ [M = Cr, Mn, Fe or Co], are of considerable structural and spectroscopic interest. From X-ray and neutron-diffractions. The deviations from the ideal cubic structure are extremely small (Chadwick, D.W. Jones, H.J. Wilde and J. Yerkes, J. Cryst. Spectrosc. Res., 1985, 15, 193). Deviations are rather greater at room temperature for the Mn compound and some for Cs₂LiCr(CN)₆, such that different symmetry have been proposed (Chadwick, et al., Acta Cryst., 1977, B33, 461; Ryan and Swanson, Inorganic Chemistry, 1974, 13, 1892 and Acta Cryst., 1978, B34, 2399).

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 Fm3m symmetry are small for Cs₂LiCr(CN)₆; there are very few weak extra reflections (N = 2,10,12, with N = 25 on the neutron powder patterns) and some line splittings (N = 15,20,40,44,56). Although the Cr compound showed some further weak neutron reflections (N = 3,10,42), refinements of single-crystal neutron data, carried out in Fm3m, were not improved by resorting to primitive cubic or tetragonal space groups. Accordingly least-squares neutron refinements in Fm3m are reported to R = 0.084 over 69 reflections for a Cs₂LiCr(CN)₆ crystal quenched in liquid nitrogen and to R = 0.113 over 76 reflections for a Cs₂LiCr(CN)₆ crystal.

Although the 2.02(1) Å Cr-C bond length determined is slightly shorter than found in Cs₂LiCr(CN)₆, from X-ray diffraction by Swanson & Ryan and by Flégé et al. (Acta Cryst., 1983, C41, 1849) in Cs₂KCr(CN)₆, it is the longest in the steadily increasing M-C sequence (Oe-Fe-Mn-Cr (from 1.89(1) Å in the Cr compound). The Cr-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 Cs₂LiCr(CN)₆; neutron diffraction can give marginally longer Cr-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 10.50 - 10.55(1) Å (M = Mn) and 10.59 - 10.87 Å (M = Cr) in the apparent cubic unit-cell parameters.

09.4-22 CRYSTAL STRUCTURE OF BINUCLEAR HEXAQUABIS-(ETHYLENEDIAMINE)-μ - PYROMELITATO - DINICKEL (II) TETRAHYDRATE. By D. Poleti*, B. Prelesnik**, R. Hrask** and D. Stojskovic*, * Faculty of Technology and Metallurgy, University of Belgrade, Kneževina 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 poly- carboxylate ligands the synthesis and the crystal structure determination of the title compound were carried out. The complex was prepared by precipitation from diluted solution containing Ni(en)₂⁺ and pyr₄⁻ ions (en = ethylenediamine, pyr₄⁻ = anion of pyromelitic 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 P2₁/c, a = 9.192(1), b = 10.319(2), c = 10.754(1) Å, V = 1107.70(1) Å³, Z = 13914(4) Å³, D = 1.69 gr.cm⁻³ for Z = 2. The structure was solved by the heavy atom methods on the basis of 1108 intensities of independent reflections measured on CAD-4 diffractometer using MoKα graphite monochro­mated radiation. The atomic coordinates of all non-hydro­gen atoms and their anisotropic thermal parameters were...