HYDROGEN

This work is part of a study of the properties of a series of quartenary ammonium and phosphonium permanganates. The title compound was recrystallized from a methylenechloride-carbon tetrachloride mixture. Two crystalline forms were found. The first ([a]) is orthorhombic, space group Pbc2₁, with a = 12.826(3) Å, b = 14.832(26) Å, c = 19.806(7) Å. The second form ([a]) is monoclinic, space group P2₁/c. Assuming Z = 4 for the β form, the calculated densities are identical (1.42 g cm⁻³).

The intensity data for the ([a]) form were collected with a Picker four-circle automated diffractometer controlled by the NRC Diffractometer Control System (D.F. Grant, E.J. Gabe, Am. Cryst. Assoc. Abstracts, 2, 245, (1974)). The space group was assumed to be non-centrosymmetric space group Pbc2₁, using the version of the direct methods program MULTAN, contained in the NRCC program system. The structure was refined by block-diagonal least squares with anisotropic temperature factors to a conventional R factor of 0.086, using the 2170 independent reflections with sin 2θ/λ < 0.60 and I/σ(I) > 2.0.

The structure contains two formula units in the form of ions related by a local non-crystallographic center of symmetry. Each of the permanganate ions is found near the methyl group of a cation, which allows the closest approach of the permanganate ion to the positive charge centre. The β form is currently under investigation.

08.2-44 SYNTHESIS AND CRYSTAL STRUCTURES OF CAGED METAL ION COMPLEXES. By R.J. Geue and A.N. Sargeson, Research School of Chemistry, Australian National University, Canberra, Australia and G. Grant, Gainford, Chemistry Division, Department of Scientific and Industrial Research, Private Bag, Petone, New Zealand.

Synthesis of the nitrogen analogues of the parent oxygen cryptands (Lehn, Pure appl. Chem. (1977) 49, 857 and references therein), so-called sephulcrates, was recently achieved utilizing the unique behaviour of bridging ligands, which shows selective binding to metal ions (Karges et al., J. Am. Chem. Soc. (1977) 99, 3181). Other variations of macrocyclic cage ligands have been then developed to be useful in the synthesis of metal complexes (Sargeson et al., J. Am. Chem. Soc. in press). The successful preparation of macrocyclic metal ion complexes of this type has now become a well established route to the preparation of a wide variety of metal complexes, which can be isolated as discrete adducts thereof, with very strong hydrogen bonds linking the atoms into corrugated sheets.

The compound [Co(C₅H₅N$_2$)$_2$]EnCl₄.C₁₇ crystallizes in the monoclinic space group P2₁/c with a = 30.482(2) Å, b = 9.007(1), c = 30.428(1) Å and β = 111.28(1)°. The structure has been refined with full matrix least squares methods to give R=0.049 for the 2683 observed diffractionometer-measured data. In the complex, the two 4-membered CO-Co-CO rings with a common nitrogen atom, show that two ring closures using only one carbon atom occurred in the condensation. As a result, the angles subtended at the metal by the donor nitrogen N₂, N₁ and N₄ are just 72.6 and 73.9°, and the bridging carbon atoms C₁₁, C₁₂ are only 2.47Å from the metal. An expected "nitromethyl" cap closes off the opposite side of the complex, which has in total very approximate mirror symmetry.

The novelty of this structure has prompted a correlative investigation into less suitable crystals of the minor product formed in the same reactions. Analysis and structural details of both compounds and of the synthetic mechanisms will be presented.

08.2-45 PHASE RELATIONS AND CRYSTAL STRUCTURES IN THE SYSTEM WATER - HYDROGEN FLUORIDE.

BY D. Moosz, U. Ohms and W. Poll, Institut für Anorganische Chemie und Strukturforschung, Universität Düsseldorf, D-4000 Düsseldorf, Germany.

In addition to the known liquidus lines of the quasi-binary system H₂O-HF (G. H. Cady and J. H. Hidebrand, J. Am. Chem. Soc. 55, 2843 (1933); G. Pawlanko, Z. anorg. allg. Chem. 328, 155 (1964)) the solidus lines were determined by low temperature difference thermal analysis. They confirm the existence of intermediate solid compounds of 1:1 (melting point -90°C), 1:2 (-75°C, decomposition) and 1:4 (-100°C) stoichiometry and reveal a second 1:2 phase stable below -105°C. Still another, metastable, phase of this composition was found in small samples by X-ray powder analysis with the Guinier-Simon technique.

So far the crystal structures of the 1:1, the high temperature 1:2 and the 1:4 phase were determined from three-dimensional diffractometer data. Single-crystal growth was achieved in a stream of cold nitrogen gas by miniature zone melting using focused radiation of an incandescent lamp (L. Breda and D. Moosz, KAM Meeting, Munich, Germany, 1981). The structures are those of oxonium salts, or HF adducts thereof, with very strong hydrogen bonds linking the atoms into corrugated sheets (1:1 and 1:2) or ribbons only (1:4). The investigations, which will appear in Z. anorg. allg. Chem., are being extended to the system D₂O-HF.