

08.2-43 THE CRYSTAL STRUCTURE OF METHYLTRIPHENYL-PHOSPHONIUM PERMANGANATE, $C_{19}H_{18}P^+MnO_4^-$. By Hassan Karaman, Richard J. Barton, Donald G. Lee and Beverly E. Robertson, Faculty of Science, University of Regina, Regina, Saskatchewan, Canada S4S 0A2.

This work is part of a study of the properties of a series of quaternary ammonium and phosphonium permanganates. The title compound was recrystallized from a methylene-chloride-carbon tetrachloride mixture. Two crystalline forms were found. The first (α) is orthorhombic, space group $Pbc2_1$, $a = 12.626(3) \text{ \AA}$, $b = 14.832(26) \text{ \AA}$, $c = 19.806(7) \text{ \AA}$, $Z = 8$. The second form (β) is monoclinic, space group $P2_1/c$. Assuming $Z = 4$ for the β form, the calculated densities are identical (1.42 g cm^{-3}).

The intensity data for the (α) form were collected with a Picker four-circle automated diffractometer controlled by the NRCC Diffractometer Control System (D.F. Grant, E.J. Gabe, Am. Cryst. Assoc. Abstracts, 2, 245, (1974)). The space group was assumed to be $Pbcm$ ($\langle E^2-1 \rangle = 0.94$, $\langle E \rangle = 0.81$). However, the Patterson map did not show the expected peaks of the form (00w), associated with the mirror plane. A solution was then attempted in the non-centrosymmetric space group $Pbc2_1$, 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 2110 independent reflections with $\sin \theta/\lambda \leq 0.60$ and $I/\sigma(I) > 2.0$.

The structure contains two formula units in the form of ion pairs 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.

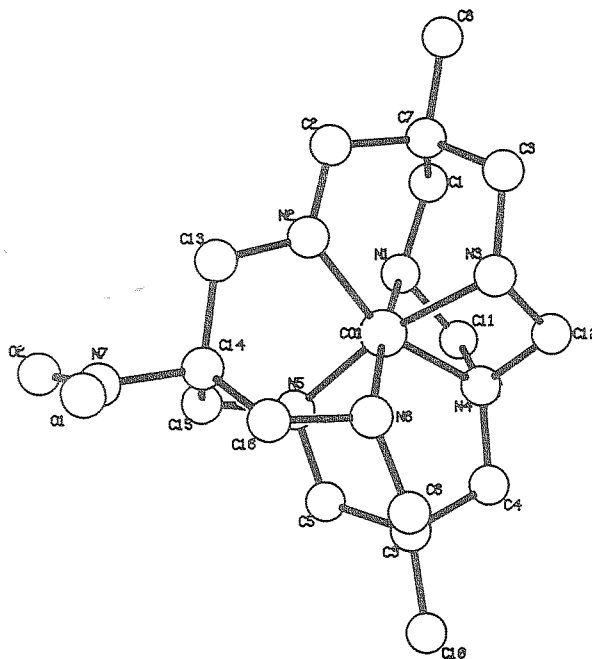
08.2-44 SYNTHESIS AND CRYSTAL STRUCTURES OF CAGED METAL ION COMPLEXES. By R.J. Geue and A.M. Sargeson, Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia and G.J. Gainsford, Chemistry Division, Department of Scientific and Industrial Research, Private Bag, Petone, New Zealand.

Synthesis of the nitrogen analogues of the sexadentate oxygen cryptands (Lehn, Pure appl. Chem. (1977) 49, 857 and references therein), so-called sepulchrates, was recently achieved utilizing the unique behaviour of bound imino nitrogen atoms to metal ions (Sargeson et al., J. Am. Chem. Soc. (1977) 99, 3181). Other variations of macrobicyclic cage ligands were then able to be prepared (Sargeson, Chem. in Britain (1979) 15, 23). The successful preparation of macrotricyclic metal ion cage compounds has now been achieved via the condensation reactions of $Co(\text{tame})_2^{3+}$ (tame = tris(aminomethyl) ethane), HCHO and CH_3NO_2 . Suitable crystals for X-ray study of the major product have finally been prepared and the structure (Figure) of one of these, (1,7-dimethyl-11-nitro-3,5,9,13,16,19-hexaazatricyclo-[9.3.3.3^{3,7}]eicosane)cobalt(III) determined as its tetrachlorozincate, chloride salt.

The compound $[Co(C_{16}H_{33}N_7O_2)]ZnCl_4 \cdot Cl$ crystallizes in the monoclinic space group $C2/c$ with $a = 30.482(2)$, $b = 9.007(1)$, $c = 20.428(1) \text{ \AA}$ and $\beta = 111.28(1)^\circ$. The structure has been refined by full matrix least squares methods to give $R=0.049$ for the 2683 observed diffractometer-measured data. The most unusual feature of the complex, the two 4-membered Co-N-C-N rings with a common nitrogen atom, shows that two ring closures both using only one carbon atom occurred in the condensation. As a result, the angles subtended at the metal by the donor nitrogens N1, N3 and N4 are just 72° & 73° , and the bridging carbon atoms C11, C12 are only 2.47 \AA 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 corroborative 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.

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In addition to the known liquidus lines of the quasi-binary system $H_2O - HF$ (G.H. Cady and J.H. Hildebrand, J. Am. Chem. Soc. 52, 3843 (1930); S. Pawlenko, Z. anorg. allg. Chem. 328, 133 (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 $-36^\circ C$), 1:2 (-78° , decomposition) and 1:4 (-100°) stoichiometry and reveal a second 1:2 phase stable below -103° . 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 (D. Brodalla and D. Mootz, KSAM 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 $D_2O - DF$.