08.2-43 THE CRYSTAL STRUCTURE OF METHYLTRIPHENYL-
PHOSPHONIUM PERMANGANATE, C₁₇H₁₅₃P'MnO₇. By Hassan
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This work is part of a study of the properties of a se-
ries of quaternary ammonium and phosphonium permangana
tes. The title compound was recrystallized from a methylene-
chloride-carbon tetrachloride mixture. Two crystalline
forms were found. The first [α] is orthorhombic, space
group Pbc₂₁, a = 12.826(3)Å), b = 14.832(2)Å, c =
19.806(7)Å, Z = 8. The second form [α] 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 [α] form were collected with a
Picker four-circle automated diffractometer controlled by
the MAD diffractometer automation control system (D.F.
The space group was assumed to be Pcm (C2-D = 0.94,
C<α = 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 Pbc₂₁ using the ver-
sion of the direct methods program MULTAN, contained in
the NRCC program system. The structure
was refined by the block-diagonal least squares with anisotropic tempera-
ture factors to a conventional R factor of 0.086,
and I/F(I) > 2.0.

The structure contains two formula units in the form of
ion pairs related by a local non-crystallographic cen-
ter 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
positve charge centre. The δ 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,
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versity, Canberra, Australia and G. Grant,
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Zealand.

Synthesis of the nitrogen analogues of the exo-
dentate oxygen cryptands (Lehn, Pure appl. Chem. (1977)
49, 857 and references therein), so-called sepulchromes,
was recently achieved utilizing the unique behaviour of
block-linear metal ions (Karges et al., J. Am. Chem. Soc.
1977, 99, 3181). Other variations of macrocyclic cage ligands
which have been used to prepare separchromes (Grant
1979, 101, 25). The successful preparation of macrocyclic metal
ion compounds has now been achieved via the condensa-
tion reactions of Co(tame)₂³⁺ (tame = tris(aminomethyl)
ethane), HCON and CH₃NO₂. Suitable crystals for X-ray
study of the major product have finally been prepared
and the structure (Figure) of one of these, (1,7-
8-dimethyl-14-nitro-3,5,9,13,16,19-hexamethylcyclono-
9.3.3.3.3.7)icosacosaebi(III) determined as its
tetrachlororosinate, chloride salt.

The compound [Co(C₂H₅)₃P₂]⁺Cl₄Cl₁₋₁ crystallizes in the
monoclinic space group C2/c with a = 30.482(2) Å,
b = 9.007(1), c = 30.482(2) Å and β = 111.35(1)°.
The structure has been refined by full matrix least squares
methods to give R = 0.049 for the 2683 observed diffraction-
eter data. The structure, which shows two ring closures both
parallel to one another, contains four nitrogen atoms.

The crystal structures of the 1:1, the high temperature
1:2 and the 1:4 phase were determined from three-dimensional diffracto-
meter data. Single-crystal growth was achieved via a stream of cold nitrogen gas by miniature
zone melting using focused radiation of an in-
candeascent lamp (J. Brodalla and D. Mootz,
KEM Meeting, Munich, Germany, 1981). The
structures are those of onoxonium 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 inves-
tigations, which will appear in Z. anorg.
al., Chem., are being extended to the system
D₂O · HF.

08.2-45 PHASE RELATIONS AND CRYSTAL STRUCTURES
IN THE SYSTEM WATER - HYDROGEN FLUORIDE.
BY P. Mootz, U. Ochs and W. Poll, Institut für
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tät 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.
Hildebrand, J. Am. Chem. Soc. 52, 2343 (1930); S. Pawlenko,
Z. anorg. allg. Chem. 328, 155
(1964)) the solidus lines were determined by
low temperature difference thermal analysis.
They confirm the existence of intermediate so-
lid compounds of 1:1 (melting point -65°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 diffracto-
meter data. Single-crystal growth was achieved via
a stream of cold nitrogen gas by miniature
zone melting using focused radiation of an in-
candeascent lamp (J. Brodalla and D. Mootz,
KEM Meeting, Munich, Germany, 1981). The
structures are those of onoxonium 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 inves-
tigations, which will appear in Z. anorg.
al., Chem., are being extended to the system
D₂O · HF.