09.4–24 SOME METAL TRIFLUOROACETATE STRUCTURES. By T.J. Stillman and R.W.H. Small, Chemistry Department, The University, Lancaster, England.

The trifluoroacetates investigated include the following: Na Ca Zn Mg Mn(II) Co(II) Hg(II)

$Na(CF_3CO_2)\cdot\frac{1}{2}H_2O$, with four independent formula units. The Na have irregular 4 or 5 coordination with ionic Na-O (2.319-2.495Å). The bridging carboxylates, with symmetrical C-O, form an extensive network in which each O binds 2 or 3 Na. There are short Na-F (2.56-2.69Å) in addition to H bonds.

$Ca(CF_3CO_2)_2\cdot 2H_2O$, the Ca have irregular 6 coordinate ionic bonds Ca-O (2.359-2.859Å). Carboxylates are bridging, anti-syn, with symmetrical C-O. H_2O are H bonded to carboxylate O.

$Zn(CF_3CO_2)_2.4H_2O$, isomorphous with Mg, Mn(II) and Co(II) compounds, forms a regular octahedral complex with metal and two H_2O on 2 axis. Metal-oxygen distances Zn-O, 2.055-2.111; Mn-O, 2.122-2.207; Mg-O, mean 2.13Å. The carboxylates are unidentate with the second O H bonded to H_2O.

$Hg(CF_3CO_2)_2$ has two independent molecules, one on $\bar{1}$. Hg are linear 2-covalent; O-Hg-O (1.95, 2.01, 2.10A) with weak bridging Hg-O bonds.

In all these complexes the CF_3 groups show their typical disorder. The conformations of the CF_3CO_2 groups in these and other complexes will be compared.

09.4–25 CRYSTAL STRUCTURES OF SILVER TRIPHENYLARSINE COMPLEXES. By M. Nardelli, C. Pelizzi, G. Pelizzi and P. Tarasconi, Istituto di Chimica Generale della Universita' di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

The silver-triphenylarsine complexes corresponding to the general formulae $[Ag(AsPh_3)_nNO_3]$ and $[Ag(AsPh_3)_4][SnPh_2(NO_3)_2X]$, have been prepared and their crystal structures determined by X-ray diffraction. (I) n = 1: $P2_1/c$, a = 10.405(5), b = 18.895(12), c = 9.138(6) Å, β = 98.35(8)°, Z = 4, R_F(2036) = 0.0450; (II) n = 2: $P\bar{1}$, a = 11.97(1), b = 12.02(1), c = 13.68(1)Å, α = 102.0(1)°, β = 113.3(1)°, γ = 104.0(1)°, Z = 2, R_F(4409) = 0.0468; (III) n = 3: $P2_1/n$, a = 19.193(8), b = 14.003(7), c = 17.893(7)Å, β = 96.4(1)°, Z = 4, R_F(8426) = 0.0478; (IV) X = NO_3, $P\bar{1}$, a = 22.57(2), b = 14.22(1), c = 14.07(1) Å, α = 90.9(1)°, β = 69.9(1)°, γ = 65.6(1)°, Z = 2, R_F(4494) = 0.0635; (V) X = Cl, $P\bar{1}$, a = 22.68(2), b = 14.24(1), c = 14.24(1) Å, α = 90.66(6)°, β = 69.17(5)°, γ = 64.36(4)°, Z = 2, R_F(7108) = 0.0648.

In (I) the structure is polymeric with silver surrounded by the triphenylarsine moiety (Ag-As = 2.471(2) Å), by a symmetrically bidentate NO_3^- (Ag-O = 2.560(6), 2.618(8) Å), and by an adjacent NO_3^- asymmetrically bidentate (Ag-O = 2.355(6), 2.829(6) Å) in such a way that all the three oxygen atoms of the nitrate group are involved in coordination to metal. In (II) the silver atom is five-coordinated by two As atoms from two $AsPh_3$ moieties (Ag-As = 2.535(5), 2.521(3) Å) and by three oxygen atoms from two symmetry related NO_3^- ions (Ag-O = 2.409(6), 2.684(7), 2.737(6) Å). The nitrate ligand is bidentate with one O atom bridging asymmetrically two Ag atoms related by a centre of symmetry, so that centrosymmetric dimers are formed. In (III) monomeric units are present where silver is coordinated by one NO_3^- symmetrically bidentate (Ag-O = 2.607(16), 2.544(14) Å) and three As atoms from the $AsPh_3$ groups at distances 2.608(3), 2.617(2), and 2.678(2) Å.

The crystal structures of (IV) and (V) are built up of discrete ions: the tetrahedral cation $[Ag(AsPh_3)_4]^+$, equal in both compounds (Ag-As is in the ranges 2.643(4) - 2.700(5) Å in (IV), 2.657(3) - 2.698(3) Å in (V)), an hexagonal bipyramidal anion $[SnPh_2(NO_3)_3]^-$ in (IV) and a pentagonal bipyramidal anion $[SnPh_2(NO_3)_2Cl]^-$ in (V). In both these anions the phenyl groups are apical (Sn-C = 2.09(2), 2.12(2) Å in(IV) and 2.13(2), 2.14(2) Å in (V)), while the NO_3^- ligands are bidentate equatorial (Sn-O is in the range 2.30(2) - 2.60(1) Å in (IV) and 2.26(1) - 2.69(1) Å in (V)). In (V) an equatorial position is occupied by Cl (Sn-Cl = 2.443(5) Å).

09.4–26 EVIDENCE OF OXYGEN UPTAKE BY A Mo(VI) COMPOUND: THE CRYSTAL STRUCTURE OF THE 1:1:1 COMPLEX OF 18-CROWN-6 ETHER WITH A MOLYBDENUM PEROXIDE $[MoO(O_2)_2(H_2O)_2]$ and H_2O. By C. Brink Shoemaker, L. V. McAfee, C. W. DeKock, and D. P. Shoemaker, Department of Chemistry, Oregon State University, Corvallis, OR 97331, USA.

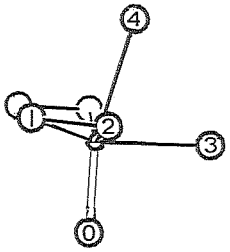
The title compound, $MoC_{12}H_{30}O_{14}$, was formed in an attempt to make a coordination compound of 18-crown-6 ether with MoO_3. MoO_3 and freshly distilled tetrahydrofuran were co-condensed in a "metal vapor" reactor at -196°C. The resulting gray-green solid was stirred at room temperature with THF in the presence of air. A yellow solution was obtained from the slurry by the addition of a small amount of H_2O. Addition of 18-crown-6 ether to this solution and slow evaporation yielded crystals from which a specimen was selected for X-ray diffraction. The structure analysis unexpectedly showed that this compound contains a diperoxo complex of Mo(VI).

Crystal data: $MoO(O_2)_2(H_2O)_2.18\text{-crown-6}.H_2O$. Orthorhombic, $A2_1ma$, a = 12.882(2), b = 13.683(2), c = 12.020(2) Å, D_m = 1.57, D_x = 1.55 g cm^{-3}, Z = 4, R = 0.028. MoKα radiation, heavy-atom method, full-matrix least-squares refinement.

The Mo atom, situated on the mirror plane, has a distorted pentagonal bipyramidal seven-coordination with the two peroxo groups and one H_2O roughly in the equatorial plane, and the double bonded oxygen and one H_2O at the apices. Two oxygens of the 18-crown-6 are on the mirror plane, but the symmetry of the crown is actually close to D_{3d} with the configurations at C-C gauche, at C-O trans. Four oxygen atoms of the crown are hydrogen bonded in pairs to two H_2O molecules, one of which is

the "free" H_2O and the other the apical H_2O of the Mo moiety. A fifth oxygen of the crown is hydrogen bonded to the equatorial H_2O of the Mo moiety, which is itself also hydrogen bonded to the "free" H_2O; the sixth crown oxygen does not participate in hydrogen bonding.

Computational support from the OSU Computer Center is acknowledged.



Mo-O distances (Å) :		
=O (ap.)	(0)	1.647(5)
-O (peroxo)	(1)	1.900(4)
-O (peroxo)	(2)	1.920(3)
$-OH_2$ (eq.)	(3)	2.084(5)
$-OH_2$ (ap.)	(4)	2.325(4)
Mo to L.S. plane of equatorial O and H_2O (Å)		0.359

09.4–27 CRYSTAL STRUCTURE OF A BASIC THORIUM DICHLOROACETATE $[Th_6(O_2CCHCl_2)_{12}(OH)_{12}(OH_2)_2]$, A NOVEL OLIGOMERIC STRUCTURE. By E.Towns and A.J. Smith, Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, England.

While studying carboxylate compounds of thorium, we obtained crystals of the title compound by reacting thorium hydroxide with excess dichloroacetic acid and recrystallising the product from ethanol. *Crystal data* Monoclinic $P2_1/n$, a = 15.087(9)Å, b = 15.111(11), c = 16.084(5) Å, β = 99.73(4)°, V = 3614 Å^3, Z = 4, μ = 158.6 cm^{-1} D_m = 2.85, D_x = 2.90 g cm^{-3}; 1950 unique data with $2\theta < 50°$ and $I > 3\sigma(I)$ collected on Syntex R3 diffractometer and corrected for crystal decay and X-ray absorption. The structure was solved by Patterson and difference Fourier methods and refined to a current R of 0.061. H atoms have not been detected and so OH and H_2O are distinguished only on chemical grounds.

The complex forms discrete molecules (Fig.3). The thorium atoms are at the vertices of a nearly regular octahedron, with an oxygen (presumed to be OH) above the centre of each face. These thorium and oxygen atoms together mark the 14 vertices of a rhombic dodecahedron (Fig.1). Each edge of the octahedron is spanned by a dichloroacetate group (Fig.5). The relationship of these bridges is more clearly seen in Fig.2 (carbon and chlorine omitted). Each of the remaining 6 oxygens (4OH & $2H_2O$) is attached to one of the octahedron vertices. The 6 thorium atoms with all their attached oxygens are shown in Fig.4. Each thorium atom is coordinated to 9 oxygens at the vertices of a monocapped square antiprism (1.4/4) having $\theta_1 = 64.9°$ and $\theta_2 = 127.5°$.

We thank the SERC and the Chemistry Division of AERE Harwell for a CASE Studentship awarded to one of us (ET).

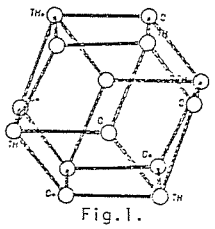
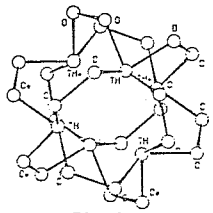


Fig.1.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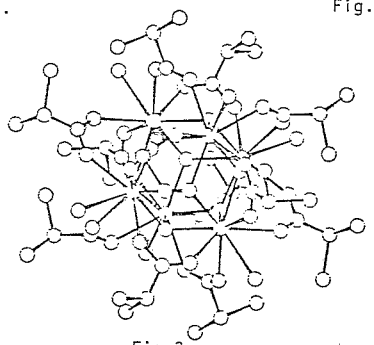
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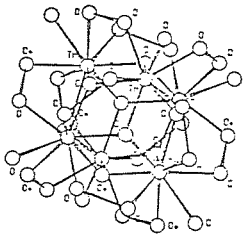
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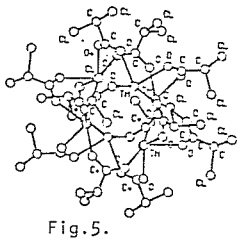
Fig.5.