

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

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(CF₃CO₂)₂·4H₂O, 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(CF₃CO₂)₂·2H₂O, the Ca have irregular 6 coordinate ionic bonds Ca-O (2.359-2.859Å). Carboxylates are bridging, anti-syn, with symmetrical C-O. H₂O are H bonded to carboxylate O.

Zn(CF₃CO₂)₂·4H₂O, isomorphous with Mg, Mn(II) and Co(II) compounds, forms a regular octahedral complex with metal and two H₂O 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 H₂O.

Hg(CF₃CO₂)₂ has two independent molecules, one on $\bar{1}$. Hg are linear 2-covalent; O-Hg-O (1.95, 2.01, 2.10Å) with weak bridging Hg-O bonds.

In all these complexes the CF₃ groups show their typical disorder. The conformations of the CF₃CO₂ 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 Università di Parma, Centro di Studio per la Strutturistica Diffraattometrica del CNR, Parma, Italy.

The silver-triphenylarsine complexes corresponding to the general formulae [Ag(AsPh₃)_nNO₃] and [Ag(AsPh₃)₄][SnPh₂(NO₃)₂X], have been prepared and their crystal structures determined by X-ray diffraction. (I) \bar{n} = 1: $\bar{P}2_1/\bar{C}$, \bar{a} = 10.405(5), \bar{b} = 18.895(12), \bar{c} = 9.138(6) Å, β = 98.35(8)°, \bar{Z} = 4, $R_F(2036)$ = 0.0450; (II) \bar{n} = 2: $\bar{P}\bar{1}$, \bar{a} = 11.97(1), \bar{b} = 12.02(1), \bar{c} = 13.68(1) Å, α = 102.0(1)°, β = 113.3(1)°, γ = 104.0(1)°, \bar{Z} = 2, $R_F(4409)$ = 0.0468; (III) \bar{n} = 3: $\bar{P}2_1/\bar{n}$, \bar{a} = 19.193(8), \bar{b} = 14.003(7), \bar{c} = 17.893(7) Å, β = 96.4(1)°, \bar{Z} = 4, $R_F(8426)$ = 0.0478; (IV) X = NO₃, $\bar{P}\bar{1}$, \bar{a} = 22.57(2), \bar{b} = 14.22(1), \bar{c} = 14.07(1) Å, α = 90.9(1)°, β = 69.9(1)°, γ = 65.6(1)°, \bar{Z} = 2, $R_F(4494)$ = 0.0635; (V) X = Cl, $\bar{P}\bar{1}$, \bar{a} = 22.68(2), \bar{b} = 14.24(1), \bar{c} = 14.24(1) Å, α = 90.66(6)°, β = 69.17(5)°, γ = 64.36(4)°, \bar{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 NO₃⁻ (Ag-O = 2.560(6), 2.618(8) Å), and by an adjacent NO₃⁻ 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 AsPh₃ moieties (Ag-As = 2.535(5), 2.521(3) Å) and by three oxygen atoms from two symmetry related NO₃⁻ 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 NO₃⁻ symmetrically bidentate (Ag-O = 2.607(16), 2.544(14) Å) and three As atoms from the AsPh₃ 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(AsPh₃)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 [SnPh₂(NO₃)₃]⁻ in (IV) and a pentagonal bipyramidal anion [SnPh₂(NO₃)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 NO₃⁻ 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(O₂)₂(H₂O)₂] and H₂O. 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, MoC₁₂H₃₀O₁₄, was formed in an attempt to make a coordination compound of 18-crown-6 ether with MoO₃. MoO₃ 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 H₂O. 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(O₂)₂(H₂O)₂·18-crown-6·H₂O. Orthorhombic, A2₁ma, 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. MoK α 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 peroxy groups and one H₂O roughly in the equatorial plane, and the double bonded oxygen and one H₂O 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 H₂O molecules, one of which is