The Preparation and Crystal Structures of Two Diphenylantimony Triacetate Hydrolysis Products: $[Ph_2Sb(OAc)_2]_2O$ and $[(Ph_8Sb_4O_6)\cdot(HOAc)_3]\cdot CH_2Cl_2$

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Diphenylantimony triacetate undergoes ready hydrolysis to give the oxygen-bridged compound $[Ph_2Sb(OAc)_2]_2O$ containing seven-coordinate antimony(v) atoms, and $[(Ph_8Sb_4O_6)(HOAc)_3]$ containing a non-adamantane Sb_4O_6 cage.

Only two of the possible phenylantimony(v) acetates, Ph_4SbOAc and $Ph_3Sb(OAc)_2$, are known. They are readily prepared as hydrolytically stable, basically trigonal-bipyramidal compounds with respectively one and two axial acetate groups.[1,2] Both structures are distorted by intramolecular Sb · · · O=C interaction leading to an increase in one of the equatorial Ph–Sb–Ph angles to *ca.* 150° and a decrease in the Sb–O–C angle to <108°. The next member of the series, $Ph_2Sb(OAc)_3$, could have a similar structure but with the increased Lewis acidity of the antimony atom and the tendency for acetate groups to bridge, more complex structures may be expected.

Our attempts to prepare the triacetate have been only partially successful in that the room-temperature reaction between Ph_2SbCl_3 and silver acetate in toluene gives a compound with acceptable microanalyses and i.r. spectra. The product is apparently hydrolytically unstable and we have not yet been successful in producing single crystals. Attempts to maintain anhydrous conditions by using acetic anhydride as a recrystallisation solvent gave a product with analytical data close to those for the triacetate. The i.r. spectrum changed and an *X*-ray investigation† showed the compound to be an oxygen-bridged species $[Ph_2Sb(OAc)_2]_2O$, with the structure shown in Figure 1. This structure is unusual as the co-ordination number of each antimony atom is raised to seven by the presence of two asymmetrically chelating acetate groups. The Sb–O (acetate) distances fall into two sets of four with mean values of 2.16 and 2.47 Å; the co-ordination polyhedron is distorted pentagonal bipyramidal. Clearly partial hydrolysis has taken place.

When the original triacetate was recrystallised from dichloromethane with no precautions against hydrolysis by atmospheric moisture, a second product was isolated with different analyses and i.r. spectra. Identification as a tetranuclear basic acetate, $[Ph_8Sb_4O_6\cdot(HOAc)_3]\cdot CH_2Cl_2$, followed

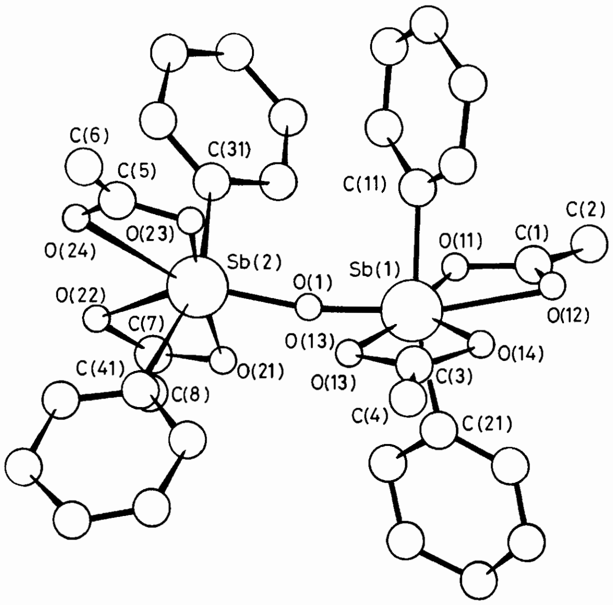

Figure 1. The structure of $[Ph_2Sb(OAc)_2]_2O$.

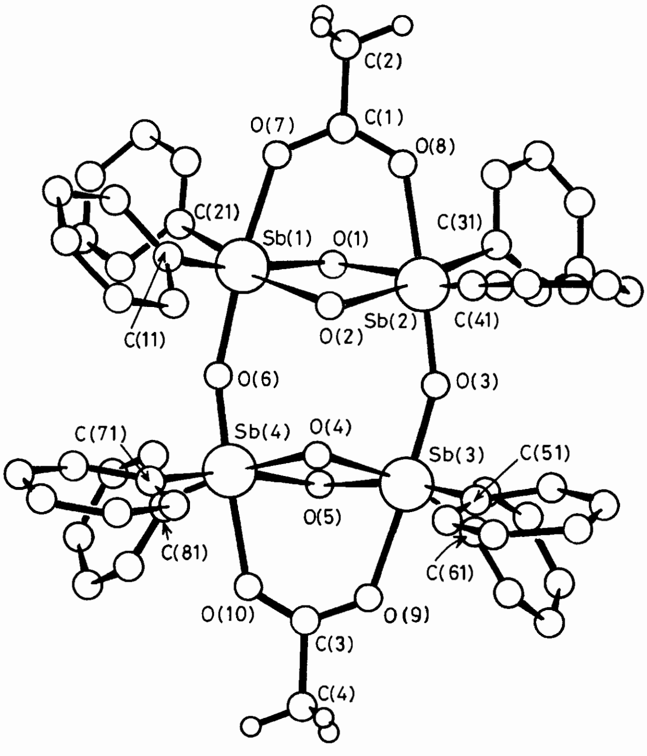

Figure 2. The cage structure in $[(Ph_8Sb_4O_6)\cdot(HOAc)_3]\cdot CH_2Cl_2$.

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† $[Ph_2Sb(OAc)_2]_2O$, *Crystal data:* $C_{32}H_{32}O_9Sb_2$, M = 804.1, monoclinic, a = 8.676(4), b = 16.554(6), c = 11.619(5) Å, β = 104.21(2)°, U = 1618.2 Å^3, Mo-K_α radiation, space group $P2_1$, D_c = 1.65 g cm^{-3}, Z = 4, μ = 13.5 cm^{-1}, crystal size 0.25 × 0.25 × 0.40 mm. Refinement by full-matrix least-squares, with anisotropic thermal parameters and hydrogen atoms in the calculated positions (but not refined), to R 0.029.

$[(Ph_8Sb_4O_6)\cdot(HOAc)_3]\cdot CH_2Cl_2$, *Crystal data:* $C_{55}H_{54}Cl_2O_{12}Sb_4$, M = 1464.2, triclinic, a = 11.465(5), b = 12.719(6), c = 20.541(8) Å, α = 97.74(2), β = 94.92(2), γ = 109.42(2)°, U = 2771.8 Å^3, Mo-K_α radiation, space group $P\bar{1}$, D_c = 1.75 g cm^{-3}, Z = 2, μ = 21.0 cm^{-1}, crystal size 0.20 × 0.10 × 0.10 mm. Refinement by full-matrix least-squares (hydrogen atoms of the phenyl and methyl groups in the calculated positions but not refined) with anisotropic thermal parameters for all atoms, except O(11), O(12), C(5), and C(6), *i.e.* those of the hydrogen-bonded acetic acid molecule, to R 0.054.

The atomic co-ordinates for both structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

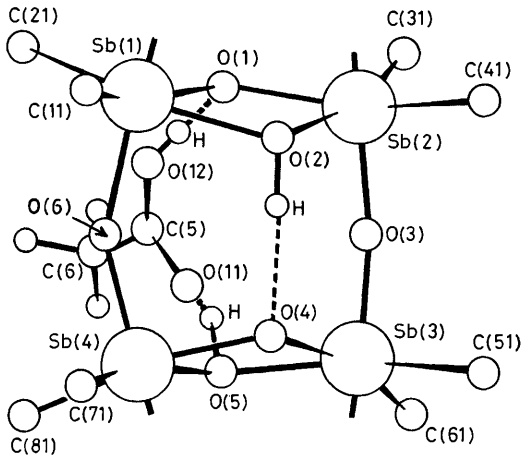

Figure 3. Hydrogen bonding across the Sb_4O_6 cage.

from an X-ray crystallographic analysis.† As shown in Figure 2, the basic structural unit is an Sb_4O_6 cage in which each antimony atom carries two phenyl groups; acetate groups bridge between two pairs of antimony atoms. One of the oxygen atoms in each of the four-membered Sb_2O_2 ring systems is, in fact, a hydroxy group and the structure is completed (see Figure 3) by a direct hydrogen bond between O(2) and O(4) and by incorporation of a hydrogen-bonded acetic acid molecule between O(1) and O(5). The lattice also contains a molecule of dichloromethane of solvation.

The 'non-adamantane' geometry of the Sb_4O_6 cage is at first sight perhaps a little unusual but such a structure is found in one form of the phosphorus(III) derivative, $P_4(NPr^i)_6$.[3] On heating, however, this compound rearranges to the isomeric adamantane form. In the present case, the non-adamantane form is likely to be stable, a major factor being the basically octahedral co-ordination about each antimony atom and the possibility for acetate groups to bridge between pairs of antimony atoms brought sufficiently close together by the double oxygen bridges. It is interesting to note that the structure in Figure 2 is a derivative of the triply bridged diantimony structures recently investigated by Schmidt and his co-workers.[4]

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