A New Diphenylantimony Oxide Containing a Planar Sb_6O_6 Ring

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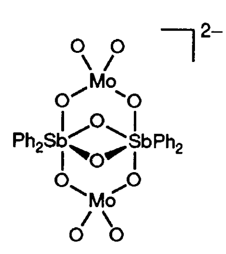
Treatment of diphenylantimony bromide oxide, $(Ph_2SbBrO)_2$, with silver oxalate leads to a novel ionic product, containing a planar twelve-membered cyclic antimony–oxygen dication in which two pairs of adjacent antimony atoms are further linked by hydroxy bridges to give Sb_2O_2 rings and a quadridentate oxalate is coordinated between the two remaining antimony atoms of the ring; the counter ions are two *cis*-dioxalatodiphenylantimony anions.

Liu and coworkers[1] have recently reported the preparation of a salt of the quadruply bridged diantimony(v) anion **1**, from a reaction between triphenylantimony diiodide and bis(tetrabutylammonium)molybdate. The mechanism of preparation is unknown but it must involve both hydrolysis, to insert the two bridging oxygen atoms, and phenyl group reorganisation, to obtain a product with two phenyl groups per antimony atom from a reactant containing three such groups.

A more realistic precursor for species such as **1** would be $(Ph_2SbBrO)_2$ **2**, the dioxygen bridged product obtained by oxidising diphenylantimony bromide under anhydrous conditions[2] and we have indeed obtained compound **1**, melting at 255 °C, using two moles of bis(tetrabutylammonium)molybdate in chloroform solution. We report now the results of a reaction between **2** and silver oxalate which, with a 1 : 1 ratio of reactants, was expected to produce a neutral triply bridged monooxalate analogue of **1** or a direct anionic dioxalate analogue when a 1 : 2 ratio was used.

A white solid, melting at 163 °C, was obtained when a mixture of equimolar quantities of **2** and silver oxalate were stirred in benzene for 48 h in the dark at room temperature. Analytical data were not satisfactory for the expected neutral product, but IR and mass spectroscopy showed clearly the presence of both oxalate groups and Sb_2O_2 rings.† The material was therefore characterised by X-ray analysis‡ on crystals obtained from a chloroform–acetonitrile mixture.

This analysis showed that the compound was ionic, consisting of a doubly charged cation and two singly charged dioxalatodiphenylantimony(v) anions. Fig. 1 shows that the anion is the *cis*-isomer. The cation (see Fig. 2) is centrosymmetric and the main feature is a previously unknown planar twelve-membered Sb_6O_6 ring system. Two pairs of antimony atoms are linked by a further oxygen atom to produce two four-membered Sb_2O_2 rings. One of these oxygen atoms carries a hydrogen atom, which forms a hydrogen bond to an



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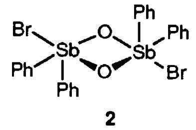

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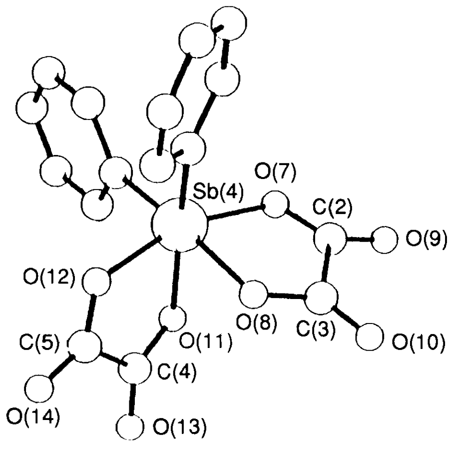

Fig. 1 Structure of the dioxalato diphenylantimony(v) anion

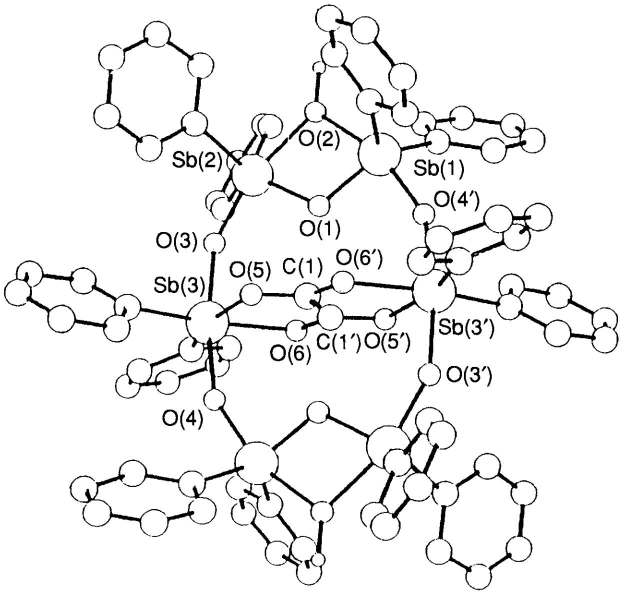

Fig. 2 Structure of the complex cation. Selected bond distances (Å) and angles (°) are as follows: Sb(1)–0(1), 1.903; Sb(1)–0(2), 2.127; Sb(1)–0(4), 1.934; Sb(2)–0(2), 2.147; Sb(2)–0(1), 1.957; Sb(2)–0(3), 1.904; Sb(3)–0(3), 1.984; Sb(3)–0(4), 1.945; Sb(3)–0(5), 2.178; Sb(3)–0(6), 2.173; Sb(1)–0(2)–Sb(2), 100.0; 0(2)–Sb(2)–0(3), 162.8; Sb(2)–0(3)–Sb(3), 151.0; 0(3)–Sb(3)–0(4), 169.5; Sb(3)–0(4)–Sb(1′), 153.6; 0(4)–Sb(1)–0(2), 161.7.

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† Analysis for carbon and hydrogen gave values of 43.3 and 2.9%, respectively, compared with 46.6 and 3.0% for the expected product $(Ph_2SbO)_2ox$ and 43.4 and 2.9% for the solvated ionic compound identified by X-ray crystallography. The IR spectrum showed oxalate bands at 1730, 1640, 1350 and 1305 cm^{-1}, Sb_2O_2 ring modes at 560 and 480 and a band at 770 cm^{-1} associated with the single Sb–O–Sb bonds.

‡ *Crystal data*: $C_{112}H_{90}Cl_6N_2O_{28}Sb_8$, $M = 3097.4$, triclinic, space group $P\bar{1}$, $a = 13.624(5)$, $b = 13.869(5)$, $c = 17.753(6)$ Å, $\alpha = 67.13(2)$, $\beta = 74.73(2)$, $\gamma = 72.39(2)°$, $V = 2905.6$ Å^3, $Z = 1$, μ(Mo-Kα) = 20.6 cm^{-1}, $D_c = 1.77$ g cm^{-3}, $F(000) = 1350$. Intensity data for 5643 reflections were measured of which 3834 reflections with $I > 3\sigma(I)$ were used in the refinement. Data were corrected for Lorentz and polarisation effects but an absorption correction was not necessary. Possible positions for the four antimony atoms in the asymmetric unit were obtained using MULTAN, and the other non-hydrogen atoms were revealed by a series of full-matrix least-squares refinements and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the phenyl groups were placed at calculated positions and were not refined; positions of the hydrogen atoms of the hydroxy groups were obtained from a difference Fourier map and final convergence occurred at $R = 5.35\%$ ($R_w = 5.42\%$) after application of a three coefficient Chebyshev weighting scheme. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

oxalate oxygen of the anion. This cation structure is completed by a quadridentate oxalate group, lying on the centre of symmetry, which coordinates to the two opposite singly bridged antimony atoms. These atoms are in distorted octahedral coordination, while coordination at the doubly bridged antimony atoms is distorted trigonal bipyramidal. Each antimony atom carries two phenyl substituents. The asymmetric unit also contains one molecule each of chloroform and acetonitrile of crystallisation and the molecular formula of the compound is therefore $[(Ph_2Sb)_6O_6(OH)_2(ox)][Ph_2Sb(ox)_2]_2 \cdot 2CHCl_3 \cdot 2MeCN$.

Twelve-membered rings are not, *per se*, unusual but planarity within such a system is. Dodecanes and related compounds, for example, are invariably puckered,[3] as are the P_6O_6 rings in hexametaphosphates, such as $Na_6P_6O_{18} \cdot 6H_2O$[4] and $Cu_2Li_2P_6O_{18}$[5] and the P_6N_6 rings in the cyclohexaphosphazenes, $N_6P_6X_{12}$ where X = Me[6] and OMe.[7] The related cyclohexasilicate ion in beryl, $Be_3Al_2Si_6O_{18}$,[8] on the other hand, is accurately planar as the angles at oxygen are reentrant. There are three other compound types, each containing six main group atoms, of relevance in this type of comparison. In $(HAlNPr)_6$,[9] and a range of organotin(IV) oxide carboxylates,[10] the structures are three dimensional with aluminium and nitrogen or tin and oxygen atoms occupying the corners of a distorted hexagonal prism, while the six bismuth atoms in $[Bi_6O_4(OH)_4]^{6+}$,[11] occupy the corners of an octahedron with oxygen and hydroxy groups above the eight triangular faces.

In the present case, formation of a planar, monocyclic system rather than a three dimensional structure is a consequence of two factors. First, a twelve-membered ring without reentrant angles is possible as the angle at each antimony is large. This arises as coordination about Sb(1) and Sb(2) is basically trigonal bipyramidal (with the ring oxygen atoms in axial sites) and octahedral about Sb(3) (with the ring oxygen atoms in *trans* positions). Secondly, the presence of the oxalate group coordinated between the two octahedral antimony atoms effectively prevents the structure from being extended into three diemsions.

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