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Preliminary communication

PREPARATION AND CRYSTAL STRUCTURE OF DIMERIC DIPHENYLANTIMONY OXIDE BROMIDE $(Ph_2SbBrO)_2$

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Summary

Diphenylantimony(III) bromide and the corresponding chloride can be oxidised to soluble products by t-butyl hydroperoxide; X-ray crystallography shows a discrete dimeric structure containing a planar Sb_2O_2 ring for Ph_2SbBrO.

Phosphoryl halides and their substituted derivatives, $X_nR_{3-n}PO$, exist as discrete molecular species but the corresponding antimony compounds are not known. On the other hand, if such compounds could be obtained they would most likely be polymeric, cf. P_4O_{10} and $(Sb_2O_5)_n$ [1]. A soluble, perhaps monomeric, form of Ph_3SbO has, however, been described [2], and a recent structure determination [3] has shown that triphenylantimony sulphide, Ph_3SbS, exists as discrete tetrahedral molecules with a short Sb—S bond, indicating the presence of significant $(p—d)\pi$-bonding.

We have recently observed that diphenylantimony bromide in dichloromethane solution can be oxidised by atmospheric oxygen, if precautions are taken against hydrolysis, to give a soluble oxide, Ph_2SbBrO. More conveniently, the compound, which melts at 208°C, can be obtained from the monobromide on refluxing with t-butyl hydroperoxide in 1,2-dichloroethane. The compound shows new IR bands at 650 and 495 cm^{-1}, associated with Sb—O stretching, and changes also occur in the 700 and 300 cm^{-1} regions. The corresponding monochloride similarly yields $(Ph_2SbClO)_2$ but in reactions with both $PhSbBr_2$ and $PhSbCl_2$, although oxidation appears to take place, pure products have not been obtained and the compounds may be unstable.

An X-ray crystallographic investigation* of Ph_2SbBrO showed that the

*$(Ph_2SbBrO)_2$, Crystal data: $C_{24}H_{20}Br_2Sb_2$, M = 743.4, monoclinic, a 8.609(4), b 17.556(7), c 16.422(5) Å, β 102.81(3)°, U 2420.3 Å^3. Mo-K_α radiation, space group $P2_1/c$, D_c 2.04 g cm^{-3}, Z = 4, μ 57.7 cm^{-1}, crystal size 0.30 × 0.20 × 0.08 mm. Reflection data corrected for absorption and refinement by full-matrix least-squares with anisotropic thermal parameters and hydrogen atoms in the calculated positions (but not refined) to R = 0.055.

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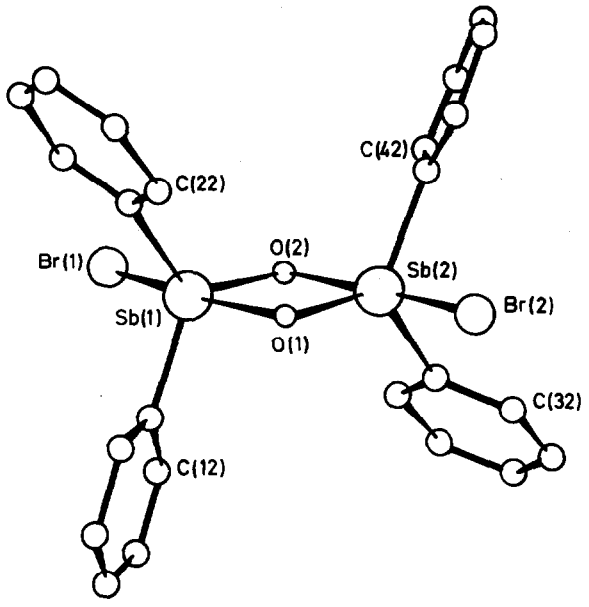

Fig. 1. Structure of $(Ph_2SbBrO)_2$.

molecule has a dimeric structure (see Fig. 1) based on two trigonal bipyramidal units sharing axial and equatorial positions. The four-membered Sb_2O_2 ring so generated is almost planar, with Sb—O distances falling into two sets of two. Those in the longer set, mean 2.04 Å, are associated with axial atoms, while those averaging 1.93 Å are to the equatorial oxygens. The two bromine atoms occupy the remaining axial positions and are mutually *trans*. Constraints imposed by the four-membered ring reduce the axial O—Sb—Br and O—Sb—O angles to ca. 165.5 and 79° respectively. There are no short intermolecular contracts.

Although a monomeric Ph_2SbBrO species might not be expected because of the weakness of Sb—O $(p—d)\pi$-bonding compared with the formation of an extra σ-bond, the formation of a discrete dimer is unexpected. Four membered Sb_2O_2 rings are present in a number of compounds [4,5], but in these one of the ring oxygen atoms is protonated and the antimony atoms are, in fact, triply bridged. The bromide is thus the first example of a compound containing an unmodified Sb_2O_2 ring.

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

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