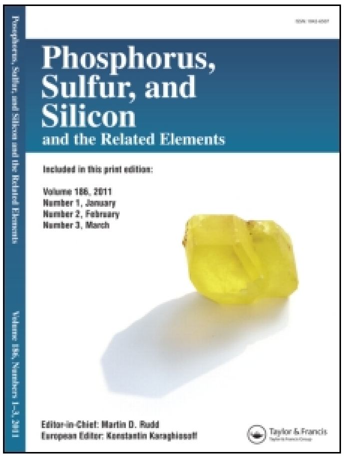

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New Sb_2O_2 Ring Compounds

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NEW Sb_2O_2 RING COMPOUNDS

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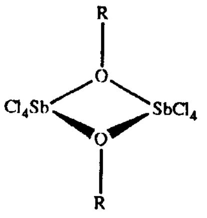
Abstract

Oxidation of diphenylantimony fluoride and thiocyanate with t-butyl hydroperoxide leads to tetrameric products containing a four-membered Sb_2O_2 ring with a further antimony atom, carrying respectively either two fluorine or two thiocyanate substituents, attached via a single oxygen bridge to each of the ring antimony atoms. This is in contrast to the formation of simple four-membered ring compounds when the corresponding bromide and chloride are oxidised. The reaction between $[Ph_2SbOBr]_2$ and silver oxalate is not a simple substitution and the product is a complex salt whose cation contains a planar twelve-membered Sb_6O_6 ring.

INTRODUCTION

Until recently, very few antimony containing ring compounds were known, but a number of Sb-O compounds have now been isolated where the basic unit appears to be a four-membered Sb_2O_2 ring system. This occurs, for example, in dimeric antimony(V) alkoxides (1),[1] and as a protonated form (2) in the compounds obtained by Schmidt and coworkers[2] by partial hydrolysis of antimony(V) chloride in the presence of a carboxylic acid. An unsubstituted Sb_2O_2 ring was, however, first identified in $[Ph_2SbBrO]_2$ (3), obtained by oxidising Ph_2SbBr with t-butyl hydroperoxide in toluene solution[3] and subsequently in the product of the related oxidation of triphenylantimony[4]. We have found that similar dimeric products are obtained by oxidising a range of other antimony triaryls and that Ph_2SbCl behaves in the same way as the monobromide to give $[Ph_2SbClO]_2$ on oxidation. On the other hand, only cyclic diphenyl substituted dimers, $[Ph_2SbXO]_2$, were obtained when phenylantimony dichloride or dibromide were oxidised.

An alternative route to Sb_2O_2 ring compounds, as shown initially by Schmidt[2], is by hydrolysis. We have found difficulty in preventing hydrolysis during isolation of diphenylantimony triacetate[5] from a reaction of the corresponding trichloride and sodium acetate in acetic acid. The triacetate can be obtained but we have not succeeded in obtaining an X-ray structure. The final hydrolysis product is, however, perfectly stable and contains four antimony atoms in an eight-membered



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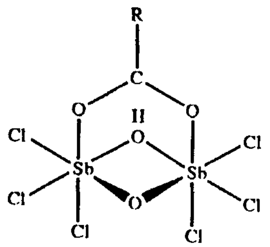

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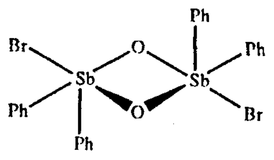

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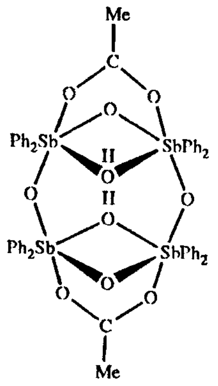


(4)

Sb-O ring system (4)[5]. The antimony atoms are alternately bridged by single and double oxygen bridges, but one of the bridges in the latter is, in fact, a hydroxo group. The antimony atoms linked by double bridges are further bridged by acetate groups and the overall structure can then be thought of as a dimeric derivative of structure (2). To complicate matters, a molecule of acetic acid produced during the hydrolysis reaction, is attached via hydrogen bonds between the hydroxo bridge of one pair of doubly bridged antimony atoms and the bridging oxygen atom of the second pair of antimony atoms.

OXIDATION OF DIPHENYLANTIMONY FLUORIDE AND THIOCYANATE

Two further diphenylantimony derivatives, i.e. Ph_2SbF[7] and $Ph_2Sb(SCN)$[8] have been oxidised using a solution of t-butyl hydroperoxide in toluene. Although analytical data for the products point in each case to the same stoichiometry as that for the bromide, chloride and triaryl oxidation products mentioned above, their infrared spectra each contain an extra band absent in those of the chloride and bromide, and it is likely that the structures of the oxidised fluoride and thiocyanate are different. X-ray crystallographic investigations reveal that the two compounds have similar centrosymmetric structures containing four antimony atoms (see Figures 1 and 2). Two of these atoms, related by

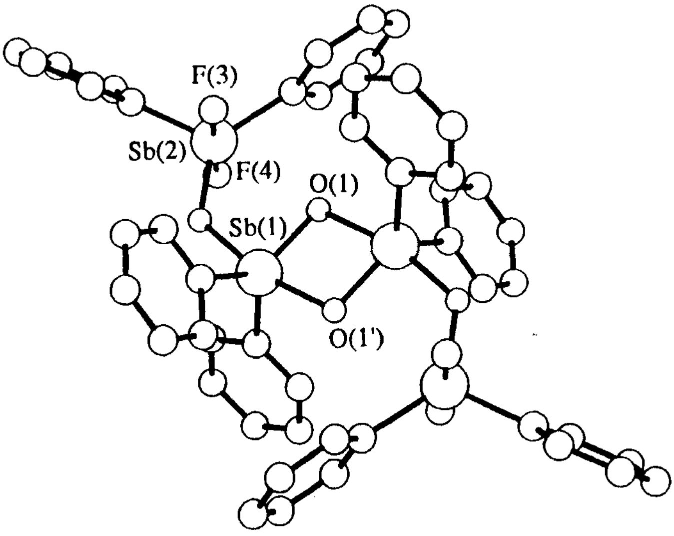


FIGURE 1. STRUCTURE OF $(Ph_2SbO_2)_2(Ph_2SbF_2)_2$

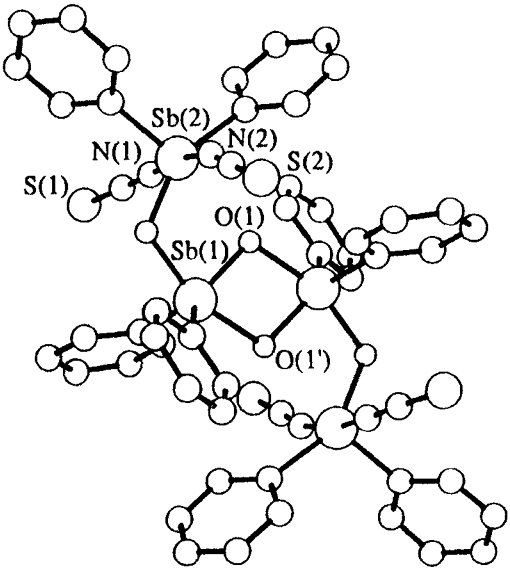


FIGURE 2. STRUCTURE OF $(Ph_2SbO_2)_2[Ph_2Sb(NCS)_2]_2$ (MOLECULE 1)

the centre of symmetry, are linked by double oxygen bridges to form a central Sb_2O_2 unit and each of the heavy atoms is attached by a single oxygen bridge to a second antimony. Rather suprisingly, these singly bridged antimony atoms carry either two fluorine atoms or two isothiocyanate groups and there has clearly been substantial reorganisation.

Reorganisation reactions are fairly common in aryl-antimony chemistry, and one in particular forms the basis of a ready synthetic route to arylantimony(III) bromides and chlorides from mixtures of antimony(III) halides and the appropriate antimony triaryl[9]. The same thiocyanate oxidation compound can also be prepared by substituting the two bromine atoms in $[Ph_2SbBrO]_2$ with potassium thiocyanate in acetonitrile solution.

Although we have no direct evidence for the mechanism of formation of the 'open tetramer' structure of the fluoride and thiocyanate, the initial formation of a four-membered ring compound, analogous to the bromide and chloride, is taken as the starting point. Compared with bromide and chloride, fluoride and thiocyanate are good bridging groups, and this property can serve to bring together the two molecules. Appropriate bond making and breaking to give the observed products are summarised in Figure 3.

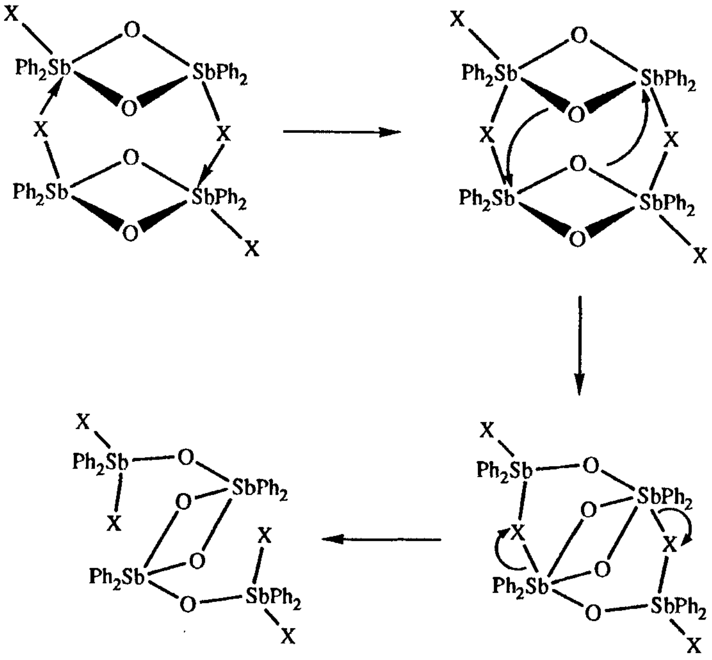
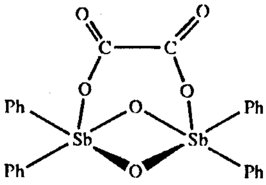


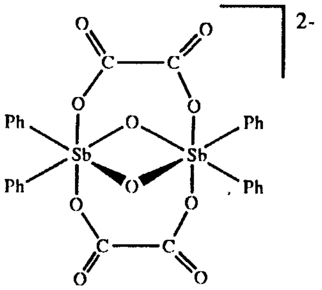
FIGURE 3. POSSIBLE MECHANISM FOR THE FORMATION OF $(Ph_2SbO_2)_2(Ph_2SbX_2)_2$ FOR X = F AND NCS

DIPHENYLANTIMONY OXALATE REACTIONS

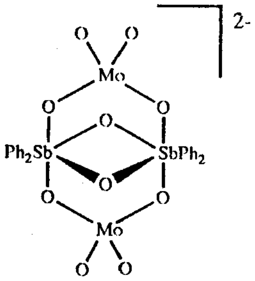
The oxalate ion is one of the best known anionic chelating ligands in classical coordination chemistry and we have attempted to replace the two bromine atoms in $[Ph_2SbBrO]_2$ in the hope of obtaining the triply bridged compound (5). There is also the possibility of adding a second oxalate group, raising the antimony coordination to octahedral, to produce a quadruply bridged species (6), similar to the recently prepared molybdate (7).[10]



(5)



(6)



(7)

Reaction of the bromide oxide with one mol of silver oxalate in benzene at room temperature produced a solid, which could be crystallised from a chloroform-acetonitrile mixture, and which according to its infrared spectrum contained coordinated oxalate groups. An X-ray investigation, however, showed that the product was far removed from the expected simple substitution product. In the first instance, the product is ionic, containing the diphenyldioxalato-antimony(V) anion (Figure 4), but it is the centrosymmetric cation (Figure 5) which is most surprising. This is based on a planar twelve-membered Sb_6O_6 ring system, and as in the acetate structure (4), two pairs of antimony atoms are linked by double oxygen bridges; one of these is protonated and hydrogen bonds to an oxygen atom of one of the chlelating oxalate groups in the anion. The two extra oxygen atoms also effectively lie in the plane of the twelve-membered ring. Four of the antimony atoms, like those in the other cyclic species discussed above, are in trigonal bipyramidal coordination, while for the remaining two the coordination number is raised to six by the presence of a quadridentate oxalate group, which is orientated at right angles to the major ring plane.

Reorganisation here is substantially greater than in the case of the fluoride and thiocyanate oxidation reactions, but the probable first step in any rational mechanism will be formation of the expected substitution product. Subsequent steps will probably depend on the power of the oxalate group to chelate.

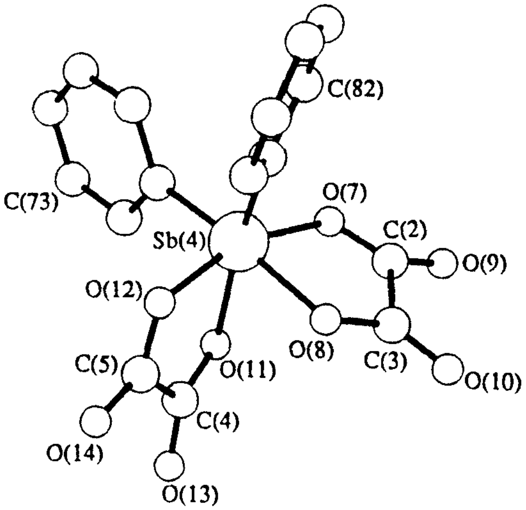


FIGURE 4. THE BIS(DIOXALATO)DIPHENYL ANTIMONY ANION

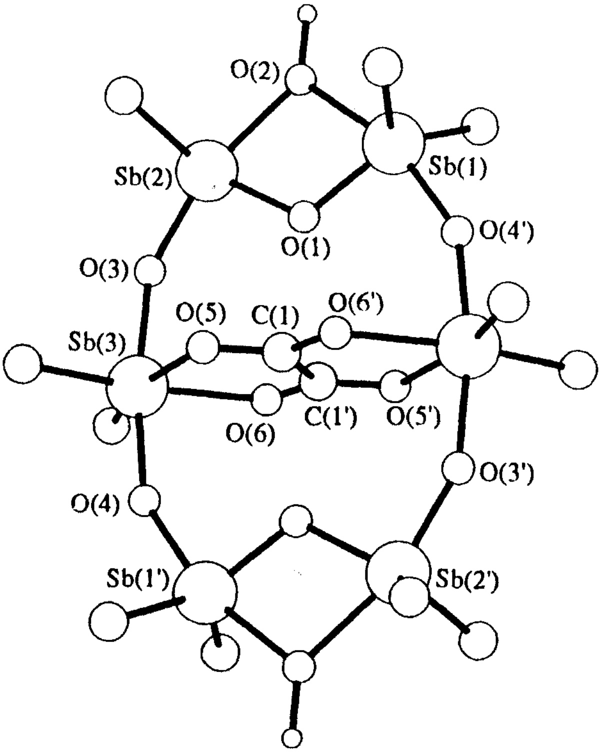


FIGURE 5. STRUCTURE OF THE COMPLEX CATION
(PHENYL GROUPS OMITTED FOR CLARITY)

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