Diphenylantimony(v) Oxide Halides and Thiocyanate; the Crystal Structures of Dimeric Diphenylantimony(v) Bromide Oxide and Tetrameric Diphenylantimony(v) Oxide Fluoride and Thiocyanate†

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Dimers containing a four-membered Sb_2O_2 ring with antimony atoms in distorted trigonal-bipyramidal co-ordination were obtained when either diphenylantimony(III) chloride or bromide was oxidised with *tert*-butyl hydroperoxide; the crystal structure of $[SbPh_2O(Br)]_2$ has been determined. Related reactions with the corresponding fluoride and thiocyanate gave products with the same stoichiometry but X-ray crystallography showed these are centrosymmetric tetramers, $X_2Ph_2SbO(Ph_2SbO_2SbPh_2)OSbPh_2X_2$, which also contain a central four-membered ring. A possible mechanism for formation of these tetramers is presented. Oxidation of phenylantimony dichloride and dibromide on the other hand gave only rearrangement and decomposition products.

Oxidation of the Group 15 trihalides and their related organo-substituted derivatives with elemental halogens is well established, giving in most cases the expected +5 oxidation-state products. Some of these are unstable (*cf.* the low stabilities of $AsCl_5$[1] and $SbPhCl_4$[2] and the non-existence of $SbBr_5$) and although the products are generally trigonal bipyramidal, other arrangements, notably the ionic forms of PCl_5[3] and PBr_5,[4] are known.

Oxidation with elemental oxygen or peroxides is also well established for the lower members of Group 15 giving π-bonded monomers such as PCl_3O and $AsPh_3O$, but it is interesting that early work on the oxidation of triphenylantimony[5] gave products which, from their high melting points and lack of solubility, were obviously highly polymeric. This type of behaviour can be rationalised naively on the basis of mismatch in orbital size between the antimony 5d and oxygen 2p orbitals, required to produce a monomer *via* Sb–O π bonding. A later report[6] pointed out that triphenylantimony oxide could, in fact, be obtained in a soluble, perhaps monomeric, modification and this was followed by the isolation and structural investigation of a soluble diphenylantimony(v) bromide oxide.[7] The latter, obtained by treating $SbPh_2Br$ with either atmospheric oxygen or better an anhydrous oxidising agent such as *tert*-butyl hydroperoxide, was a cyclic dimer, $[SbPh_2O(Br)]_2$, containing antimony–oxygen single bonds in a four-membered Sb_2O_2 ring, lending credence to the suggestion that species containing $Sb^V{=}O$ double bonds would be unstable. The same Sb_2O_2 unit is also present in the soluble form of triphenylantimony oxide.[8] This paper now reports full details of the preparation and identification of the bromide oxide mentioned above and examines the products of the oxidation of other phenylantimony(III) species. Some of this work was summarised in conference proceedings.[9]

Experimental

All reactions were carried out with dried and redistilled solvents under an atmosphere of nitrogen.

Preparations.—Diphenylantimony bromide oxide **1**. Diphenylantimony bromide (10.8 g, 32 mmol), prepared by redistribution of a 2:1 mixture of $SbPh_3$ and $SbBr_3$,[10] was dissolved in toluene and a solution of *tert*-butyl hydroperoxide (3 mol dm^{-3}, 11.1 cm^3, 33 mmol) also in toluene was added by syringe. The mixture was stirred with cooling in ice for 30 min and then refluxed for 10 min to complete the reaction. Concentration of the solution and subsequent cooling gave white crystals (9.9 g, 26.9 mmol, 84%) which were recrystallised from chloroform, m.p. 208 °C (Found: C, 38.7; H, 2.7. Calc. for $C_{12}H_{10}BrOSb$: C, 38.7; H, 2.9%).

Diphenylantimony chloride oxide. This was prepared similarly from diphenylantimony chloride (19.9 g, 64 mmol), again obtained *via* a redistribution reaction,[10] and *tert*-butyl hydroperoxide (3 mol dm^{-3}, 23.4 cm^3, 70 mmol) to give white crystals of the chloride oxide (yield 82%) which were recrystallised from chloroform, m.p. 168 °C (Found: C, 43.7; H, 3.1. Calc. for $C_{12}H_{10}ClOSb$: C, 44.0; H, 3.1%).

Diphenylantimony fluoride oxide **2**. As for the previous compounds, this was prepared from diphenylantimony fluoride[11] (2.0 g, 7 mmol) and *tert*-butyl hydroperoxide (3 mol dm^{-3}, 2.5 cm^3, 7 mmol) to give white crystals of the fluoride oxide (yield 72%), m.p. 169 °C. Owing to its high solubility in chloroform, the product was recrystallised from toluene (Found: C, 48.4; H, 3.2. Calc. for $C_{12}H_{10}FOSb$: C, 46.3; H, 3.2. Calc. for $C_{12}H_{10}FOSb{\cdot}0.25C_6H_5CH_3$: C, 48.9; H, 3.6%).

Diphenylantimony oxide thiocyanate. (*a*) *By oxidation of diphenylantimony*(III) *thiocyanate.* A solution of *tert*-butyl hydroperoxide (3 mol dm^{-3}, 1.84 cm^3, 0.50 g, 5.52 mmol, 10% excess) in toluene was added by syringe to a solution of diphenylantimony thiocyanate[12] (1.69 g, 5.1 mmol) in dry toluene at 0 °C. After stirring overnight, the solution was filtered, concentrated to one third of its original volume and set aside in a freezer to give white crystals, m.p. 138 °C (Found: C, 47.7; H, 3.2; N, 3.8. Calc. for $C_{13}H_{10}NOSSb$: C, 44.6; H, 2.9; N, 4.0. Calc. for $C_{13}H_{10}NOSSb{\cdot}0.25C_6H_5CH_3$ **3**: C, 47.5; H, 3.2; N, 3.8%). Recrystallisation from chloroform–hexane (1:1) gave needles (1.22 g, 3.5 mmol, 69%) of the unsolvated compound **4**, m.p. 160 °C (Found: C, 44.3; H, 2.9; N, 3.8%).

(*b*) *By metathesis between diphenylantimony bromide oxide and potassium thiocyanate.* A solution of diphenylantimony bromide oxide (1.5 g, 2 mmol) in chloroform (75 cm^3) was

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.

stirred with potassium thiocyanate (0.4 g, 2 mmol) for 1 week in a stoppered vessel at ambient temperature. After filtration to remove precipitated potassium bromide, the solution was evaporated to dryness in a vacuum and the residue recrystallised from toluene to give white crystals (1.0 g, 2.9 mmol, 72%) of the toluene solvate **3**, m.p. 138 °C (Found: C, 47.3; H, 3.1; N, 3.9%).

Attempted preparation of phenylantimony dibromide oxide. Phenylantimony dibromide[10] (2.0 g, 6 mmol) was treated with *tert*-butyl hydroperoxide (3 mol dm^{-3}, 2.2 cm^3, 7 mmol) in toluene, as described above for the monobromide. There was an immediate red coloration and after refluxing for 10 min the solution was cooled. Concentration of the solution gave 1.0 g of an amorphous solid (m.p. > 350 °C) [Found: C, 22.8; H, 2.0. Calc. for $SbPhOBr_2$: C, 19.2; H, 1.3. Calc. for SbPhOBr(OH): C, 23.1; H, 1.8%]. The remaining mother-liquor was then evaporated to dryness giving a white solid (0.8 g), which on recrystallisation from dichloromethane gave diphenylantimony tribromide, m.p. 178 °C (lit.,[13] 171 °C) (Found: C, 27.7; H, 2.2. Calc. for $C_{12}H_{10}Br_3Sb$: C, 27.9; H, 1.9%). The reaction followed effectively the same course when carried out under Schlenk conditions initially at −120 °C but gave an increased yield of $SbPh_2Br_3$.

Attempted preparation of phenylantimony dichloride oxide. Phenylantimony dichloride[10] was treated in refluxing toluene as described above to give a similar unidentified amorphous high-melting solid (Found: C, 14.1; H, 1.7%) and $SbPh_2Cl_3{\cdot}H_2O$, m.p. 176 °C (lit.,[14] 176 °C) (Found: C, 36.0, H, 3.1. Calc. for $C_{12}H_{12}Cl_3OSb$: C, 36.0, H, 3.1%). At −120 °C under Schlenk conditions the only identified product was hydrated diphenylantimony trichloride.

Crystal Structure Determinations.—$[SbPh_2O(Br)]_2$ **1**. *Crystal data.* $C_{24}H_{20}Br_2O_2Sb_2$, $M = 743.4$, monoclinic, space group $P2_1/c$, $a = 8.609(4)$, $b = 17.556(7)$, $c = 11.619(5)$ Å, $\beta = 102.81(5)°$, $U = 2420.3$ Å^3, $Z = 4$, $D_c = 2.04$ g cm^{-3}, $F(000) = 1408$, $\mu = 57.7$ cm^{-1}, Mo-Kα radiation (with graphite monochromator), $\lambda = 0.710\,69$ Å, crystal size 0.3 × 0.2 × 0.08 mm.

Intensity data were collected on a Hilger and Watts four-circle diffractometer for 4342 reflections in the range $0 < \theta < 25°$ ($0 < h < 11$, $-21 < k < 0$, $-19 < l < 19$) of which 3284 with $I > 3\sigma(I)$ were considered observed. The data were corrected for Lorentz and polarisation effects and for absorption using ABSORB from the XTAL series of programs.[15] Crystallographic calculations used the CRYSTALS programs[16] and scattering factors, including anomalous dispersion contributions, were those for neutral atoms.[17] Possible positions for the two antimony atoms in the asymmetric unit were obtained using MULTAN[18] and the remaining non-hydrogen atoms were revealed by a series of full-matrix least-squares refinements and Fourier-difference syntheses. After refinement with anisotropic thermal parameters, the hydrogen atoms of the phenyl groups were placed at their calculated positions [d(C–H) 1.0 Å], but were not further refined. Application of a four-coefficient Chebyshev weighting scheme led to final convergence (271 least-squares parameters, maximum shift:e.s.d. 0.2:1) at $R = 0.0555$ ($R' = 0.0679$). The final atomic coordinates are collected in Table 6.

$[SbPh_2O(F)]_4{\cdot}C_6H_5Me$ **2**. *Crystal data.* $C_{55}H_{48}F_4O_4Sb_4$, $M = 1335.2$, triclinic, space group $P\bar{1}$, $a = 9.569(5)$, $b = 10.231(4)$, $c = 13.757(6)$ Å, $\alpha = 96.96(3)$, $\beta = 102.27(3)$, $\gamma = 100.90(3)°$, $U = 1273.9$ Å^3, $Z = 1$, $D_c = 1.74$ g cm^{-3}, $F(000) = 650$, $\mu = 21.8$ cm^{-1}, Mo-Kα radiation (as above), crystal size 0.01 × 0.3 × 0.3 mm.

Intensity data were collected as described above for 4475 reflections in the range $0 < \theta < 20°$ ($-12 < h < 12$, $-12 < k < 12$, $0 < l < 16$) of which 3558 with $I > 3\sigma(I)$ were considered observed. Corrections were made for Lorentz and polarisation effects and for absorption using ABSORB[15] (A^* varied between 1.022 and 1.547). The calculated density points to the presence of four possible $SbPh_2OF$ units in the triclinic cell and a Patterson synthesis gave possible positions for the two independent antimony atoms. Subsequent cycles of full-matrix least-squares refinements and Fourier-difference syntheses revealed the other non-hydrogen atoms and showed a centrosymmetric tetrameric structure completely different from that for compound **1**.

Clearly some kind of reorganisation has occurred and, although the product is probably an $SbPh_2OF$ tetramer, more drastic reorganisation to give, say, a mixed-oxidation-state fluoride such as $SbPh_2F{\cdot}SbPh_2F_3$ cannot be completely ruled out. Each antimony carries two phenyl groups and two centrosymmetrically related antimony atoms are bridged by two (oxygen?) atoms to give a four-membered ring while the remaining antimony atoms, which carry two terminal (fluorine?) atoms, are linked by single (oxygen?) bridges to the antimony atoms of the four-membered ring. Owing to the obvious ambiguities in identifying oxygen and fluorine atoms, care was taken in assigning atom types.

Three different arrangements were considered in which: (*a*) oxygen atoms occupied both the bridging positions on Sb(1) and the terminal positions on Sb(2), (*b*) fluorine atoms occupied all these positions and (*c*) oxygen atoms occupied the bridging positions on Sb(1) with terminal fluorines on Sb(2). Refinement with anisotropic thermal parameters assigned to antimony and isotropic parameters to the remaining atoms gave the most satisfactory refinement with option (*c*) and the compound is considered as a rearrangement product with the stoichiometry $(SbPh_2OF)_4$. After convergence with anisotropic thermal parameters for all atoms, the phenyl hydrogen atoms were placed [d(C–H) 1.0 Å] at their calculated positions, but not refined in further cycles. A Fourier-difference synthesis then showed positions for three atoms of a molecule of solvate toluene lying on a centre of symmetry. Distances and angles were constrained [d(C–C) 1.40 Å; C–C–C 120°] and a further Fourier-difference synthesis after refinement of these positions with isotropic thermal parameters revealed the methyl carbon atom, assigned an occupation factor of 0.5. Final convergence occurred at $R = 0.0455$ ($R' = 0.0523$) after application of a four-coefficient Chebyshev weighting scheme (287 least-squares parameters, maximum shift:e.s.d. 0.05:1, maximum and minimum residual electron densities 0.14 and −0.14 e Å^{-3}, with all large peaks in the vicinity of the antimony atoms). The final atomic coordinates are collected in Table 7.

$[SbPh_2O(NCS)]_4{\cdot}C_6H_5Me$ **3**. *Crystal data.* $C_{59}H_{48}N_4O_4S_4Sb_4$, $M = 1491.2$, triclinic, space group $P\bar{1}$, $a = 11.689(6)$, $b = 13.535(5)$, $c = 22.530(9)$ Å, $\alpha = 109.12(3)$, $\beta = 77.50(2)$, $\gamma = 116.24(2)°$, $U = 3010.0$ Å^3, $Z = 2$, $D_c = 1.64$ g cm^{-3}, $F(000) = 1460$, $\mu = 19.7$ cm^{-1}, Mo-Kα radiation (as above), crystal size 0.03 × 0.1 × 0.1 mm.

Suitable crystals were grown from toluene and mounted on a glass fibre. Of the 4146 data collected ($0 < \theta < 18°$, $-11 < h < 11$, $-13 < k < 13$, $0 < l < 21$) 3196 reflections with $I > 3\sigma(I)$ were considered observed and corrected for Lorentz and polarisation effects. Density calculations pointed to an asymmetric unit containing four independent antimony atoms, suggesting the presence of either two dimers similar to that in diphenylantimony bromide oxide or one tetramer as found for compound **2**.

Positions for the four antimony atoms were obtained using MULTAN[18] and the remaining non-hydrogen atoms were revealed by a series of full-matrix least-squares refinements (blocked for each independent molecule) and Fourier-difference syntheses. This showed a unit cell containing two independent centrosymmetric tetramers, analogous to **2**. After refinement with anisotropic thermal parameters, the molecule of toluene of solvation was identified and refinement continued with constraints applied to distances and angles within the C(31) and C(81) phenyl groups and the C(91)–C(97) toluene molecule [C–C (phenyl) 1.40(1), C(96)–C(97) 1.50(1) Å; C–C–C 120.0(1)°]. Placing hydrogen atoms at their calculated positions

[d(C–H) 1.0 Å] and application of a three-coefficient Chebyshev weighting scheme led to convergence at $R = 0.0381$ ($R' = 0.0464$) (677 least-squares parameters, maximum shift:e.s.d. 1.2:1). Table 8 contains the refined atomic coordinates.

$[SbPh_2O(NCS)]_4$ **4**. *Crystal data.* $C_{52}H_{40}N_4O_4S_4Sb_4$, M = 1399.2, triclinic, space group $P\bar{1}$, a = 11.683(6), b = 13.517(6), c = 22.211(9) Å, α = 106.58(3), β = 87.38(3), γ = 116.37(4)°, U = 2998.2 Å^3, Z = 2, D_c = 1.55 g cm^{-3}, F(000) = 1360, μ = 19.8 cm^{-1}, Mo-Kα radiation (as above), crystal size 0.2 × 0.2 × 0.3 mm.

Suitable crystals were grown from chloroform–hexane and mounted on a glass fibre. Of the 7355 originally measured data ($0 < \theta < 22°$, $-12 < h < 12$, $-14 < k < 14$, $0 < l < 23$), 4369 reflections with $I > 5\sigma(I)$ were considered observed and corrected for Lorentz and polarisation effects. The solution, which closely followed that above, showed again the presence of two independent centrosymmetric tetramers. Refinement continued with anisotropic thermal parameters for all atoms except those of the C(81) phenyl group, which were disordered and the bond parameters were constrained. After placing hydrogen atoms at their calculated positions [d(C–H) 1.0 Å] and application of a weighting scheme of the type $w = 1/[1 + (F_o - 16)/20]^2$, refinement converged at $R = 0.0696$ ($R' = 0.1115$) (560 least-squares parameters, maximum shift:e.s.d. 1.2:1). Refined atomic coordinates are collected in Table 9.

Additional data available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Discussion

Preparations.—Using *tert*-butyl hydroperoxide, it has been possible to oxidise four diphenylantimony(III) compounds to the corresponding antimony(V) oxides as summarised in equation (1) (X = F, Cl, Br or SCN). The oxide thiocyanate

$$SbPh_2X + Bu^tO_2H \longrightarrow SbPh_2O(X) + Bu^tOH \quad (1)$$

can also be obtained by a simple metathesis between potassium thiocyanate and $[SbPh_2O(X)]_2$, where X = Cl or Br. The oxidation products, which are soluble in a number of organic solvents, can be recrystallised from chloroform, though the chloride and bromide are, at the most, sparingly soluble. The oxide fluoride and thiocyanate both crystallise from toluene as solvates [one toluene per four $SbPh_2O(X)$ units]; this was identified initially by microanalysis and ^1H NMR spectroscopy and later confirmed by X-ray studies.

Oxidation of the related monophenylantimony dichloride and dibromide (the corresponding difluoride and dithiocyanate are unknown) is not straightforward and the expected oxidation products, $SbPhOX_2$ for X = Cl or Br, are apparently unstable and cannot be isolated. The actual products appear to result from rearrangement and hydrolysis. One product is polymeric with a formula close to SbPhO(X)(OH) and the second is a phenyl rearrangement product, $SbPh_2X_3$ for X = Cl or Br; the former is isolated as the monohydrate. In some respects, the apparent instability of the $SbPhOX_2$ species parallels that of the halogen oxidation products, $SbPhX_4$,[2] which yield similar phenyl rearrangement products.

Mass Spectrometry.—Electron-impact (EI) mass spectra were recorded for all four products, supplemented by FAB spectra for the fluoride and thiocyanate. The highest-mass peaks (m/z 617 and 661, respectively) in the EI spectra of the chloride and bromide could be assigned to $Sb_2Ph_4O_2X$ fragments, suggesting halogen loss from $Sb_2Ph_4O_2X_2$ parent ions. Low-intensity peaks associated with $Sb_2Ph_3O_2X_2$ species were also observed (m/z 575 and 663, respectively), but the major fragments were single antimony-containing species.

The EI mass spectra of the fluoride **2** at both 70 and 20 eV showed no evidence for oxygen-containing fragments and the most intense ion was $SbPh_2F_2$. This fragment is unexpected when the starting material has a 1:1 ratio of Sb:F and, while it may arise by recombination in the ion source, it could also imply reorganisation during oxidation. The FAB spectrum was highly complex but units containing both two (*e.g.* Sb_2Ph_3O) and three antimony atoms could be identified.

The EI spectra of the thiocyanate **3** were dominated by phenylantimony fragments and the only thiocyanate-containing ions, *i.e.* $SbPh_2O(NCS)$, $SbPh_2(NCS)$, $SbPh(NCS)_2$ and Sb(NCS) were of very low intensity. There was no evidence from FAB spectra for fragments containing more than two antimony atoms, but species such as $Sb_2Ph_4O_2(NCS)_2$ (m/z 657) and fragments resulting from the further loss of either one (m/z 581) or two (m/z 505) thiocyanate groups were observed. In general, thiocyanate-containing fragments were of low intensity.

Infrared Spectra.—All compounds gave complex spectra but a large number of bands are common and are associated with the phenyl groups.[19] Comparisons of the spectra with those of the starting materials clearly show the appearance of new bands at *ca.* 500, 650 and 670 cm^{-1} (see Table 1); similar bands are also present in the spectra of triarylantimony oxides.[8,20] These are assigned to Sb–O vibrations, most probably associated with an Sb_2O_2 ring. Spectra of the fluoride **2** and thiocyanate **3** and **4** both show an additional band at *ca.* 770 cm^{-1} [*cf.* bands at 762, 769 and 764, 772 cm^{-1} for $(SbPh_3X)_2O$, where X = Cl or Br[21]] in the region associated with the stretching of single oxygen bridges.

The spectra of both compounds **3** and **4** also contained a strong broad band at *ca.* 2030 cm^{-1}, characteristic of N-bonded thiocyanate groups, but the lower-energy C–S stretch could not be identified although a shoulder at 445 cm^{-1} on the phenyl 'y' mode[19] at 450 cm^{-1} is probably the NCS deformation mode.

NMR Spectra.—Proton NMR spectroscopy confirmed that both compounds **2** and **3** crystallised from toluene as solvates, showing increased complexity in the δ 7.2–8.0 region and the presence of a signal at δ 2.3 from the toluene methyl group. Nitrogen-14 NMR spectroscopy for **3** and **4** showed a band at δ −227 (linewidth 3 ppm at half peak height) associated with N-bonded thiocyanate.[22] This shows both a downfield shift and line sharpening when compared with the signal for $SbPh_2(NCS)$ (δ −260, peak width 12 ppm),[12] but is comparable to the signal (δ −237, peak width 2 ppm) of $SbPh_3(NCS)_2$.[23]

Structure of $[SbPh_2O(Br)]_2$ **1**.—Important bond distances and angles are collected in Table 2 and a diagram of the

Table 1 Infrared bands (cm^{-1}) due to Sb–O vibrations

Assignment	$[SbPh_2O(Cl)]_2$	$[SbPh_2O(Br)]_2$	$[SbPh_2O(F)]_4$	$[SbPh_2O(NCS)]_4$	
		1	**2**	**3**	**4**
$\nu(SbOSb)$			770	772	769
$\nu(Sb_2O_2)$	667	666	667	671	670
$\nu(Sb_2O_2)$	646	647	645	655	652
$\delta(Sb_2O_2)$	493	495	512	517	512

structure, showing the atom numbering scheme, is in Fig. 1. The compound is a dimer in which two $SbPh_2OBr$ units form a four-membered Sb_2O_2 ring with Sb–O σ bonds, rather than a discrete π-bonded monomer. The two antimony atoms are in distorted trigonal-bipyramidal co-ordination with equatorial sites occupied by two phenyl substituents and an oxygen atom of the four-membered ring and axial sites by bromine and the second oxygen atom of the ring. Selected parameters for this compound and the fluoride and thiocyanate are summarised in Table 3 and Fig. 2(*a*). As expected, distances to equatorial oxygens [Sb(1)–O(2) 1.936(6) and Sb(2)–O(1) 1.918(6) Å] are shorter (*ca.* 6%) than those to axial atoms [Sb(1)–O(1) 2.061(6) and Sb(2)–O(2) 2.030(6) Å] but it is noticeable that all four Sb–O separations are different. Corresponding distances in $(SbPh_3O)_2$, which contains two independent centrosymmetric dimers, are 1.928(4), 1.929(4) and 2.071(4), 2.080(4) Å, respectively.[8]

Angles at oxygen are constrained to a mean of 101.5° but reduction of the endocyclic angle at antimony to a mean of 78.5° leads to Sb_2O_2 ring planarity. There are also slightly different degrees of distortion at the two antimony atoms, *e.g.* the equatorial angles, C(11)–Sb(1)–C(21) 117.3(4) and C(31)–Sb(2)–C(41) 111.3(4)°, are not only substantially different but both are less than the ideal 120°, though the equatorial angles at Sb(1) and Sb(2) sum to 358.9 and 359.5°, respectively. The axial O–Sb–Br angles are also reduced from the ideal value to *ca.* 165.5° and the two Sb–Br separations are significantly different [2.554(1) and 2.589(1) Å]. There are, however, no close Sb···Br intermolecular interactions within 4.5 Å, which might account for these differences.

Structure of $[SbPh_2O(F)]_4 \cdot C_6H_5Me$ **2**.—The X-ray determination shows that the unit cell for this compound contains an unexpected centrosymmetric tetramer, illustrated in Fig. 3, rather than two dimers as might have been expected from the results for **1**. Important bond distances and angles are listed in Table 4. The structure consists of a central four-membered Sb_2O_2 ring containing one pair of symmetry-related antimony atoms, connected *via* Sb–O–Sb bridges to the other pair of antimony atoms. Each antimony carries two phenyl substituents

Table 2 Important bond lengths (Å) and angles (°) for compound **1**, with estimated standard deviations (e.s.d.s) in parentheses

Sb(1)–Br(1)	2.554(1)	Sb(2)–Br(2)	2.589(1)
Sb(1)–O(1)	2.061(6)	Sb(2)–O(1)	1.918(6)
Sb(1)–O(2)	1.936(6)	Sb(2)–O(2)	2.030(6)
Sb(1)–C(11)	2.100(9)	Sb(2)–C(31)	2.105(10)
Sb(1)–C(21)	2.115(11)	Sb(2)–C(41)	2.124(9)
Br(1)–Sb(1)–O(1)	165.8(2)	O(1)–Sb(2)–C(31)	124.5(3)
Br(1)–Sb(1)–O(2)	87.9(2)	O(1)–Sb(2)–C(41)	123.7(3)
Br(1)–Sb(1)–C(11)	95.4(3)	O(2)–Sb(2)–C(31)	93.6(3)
Br(1)–Sb(1)–C(21)	97.3(3)	O(2)–Sb(2)–C(41)	91.3(3)
O(1)–Sb(1)–O(2)	78.0(3)	C(31)–Sb(2)–C(41)	111.3(4)
O(1)–Sb(1)–C(11)	89.9(3)	Sb(1)–O(1)–Sb(2)	101.2(3)
O(1)–Sb(1)–C(21)	92.0(4)	Sb(1)–O(2)–Sb(2)	101.7(3)
O(2)–Sb(1)–C(11)	118.2(4)	Sb(1)–C(11)–C(12)	121.3(8)
O(2)–Sb(1)–C(21)	123.4(3)	Sb(1)–C(11)–C(16)	117.6(7)
C(11)–Sb(1)–C(21)	117.3(4)	Sb(1)–C(21)–C(22)	117.3(8)
Br(2)–Sb(2)–O(1)	86.3(2)	Sb(1)–C(21)–C(26)	122.6(9)
Br(2)–Sb(2)–O(2)	165.1(2)	Sb(2)–C(31)–C(32)	121.1(8)
Br(2)–Sb(2)–C(31)	97.5(3)	Sb(2)–C(31)–C(36)	118.4(8)
Br(2)–Sb(2)–C(41)	94.0(3)	Sb(2)–C(41)–C(42)	114.6(7)
O(1)–Sb(2)–O(2)	79.2(3)	Sb(2)–C(41)–C(46)	123.4(8)

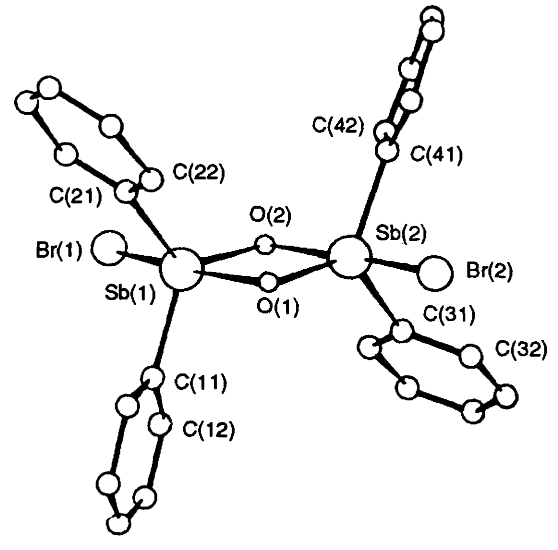


Fig. 1 Structure of $[SbPh_2O(Br)]_2$ **1** showing the atom numbering scheme

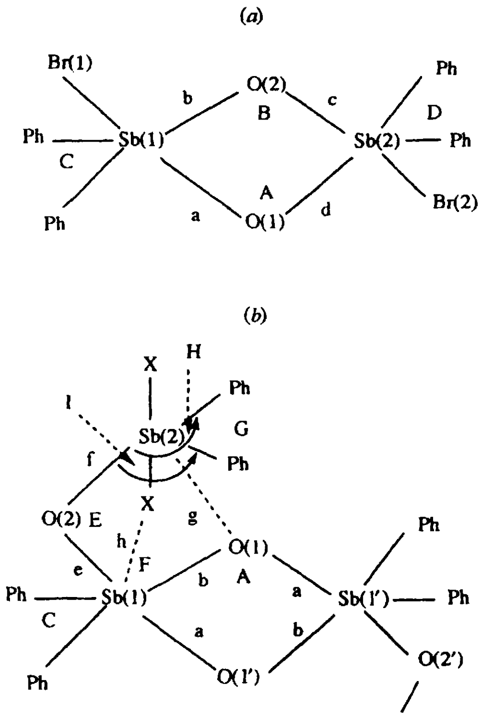


Fig. 2 Schematic diagrams for (*a*) $[SbPh_2O(Br)]_2$ **1** and (*b*) $[SbPh_2O(X)]_4$ **2** and **3**

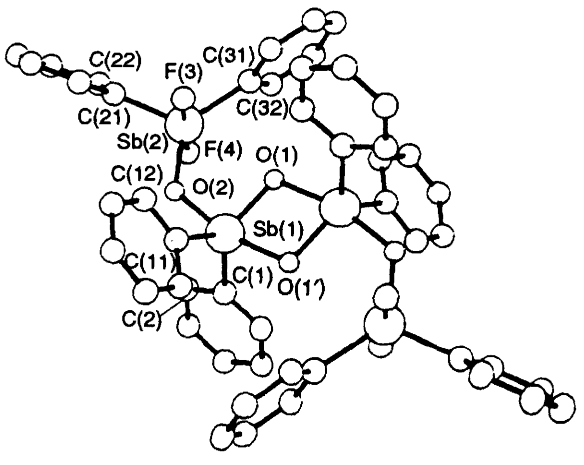


Fig. 3 Structure of $[SbPh_2O(F)]_4$ **2** showing the atom numbering scheme

Table 3 Important bond lengths (Å) and angles (°) in compounds **1**–**3**

Compound	Label[a]	**1**	**2**	**3a**[b]	**3b**[c]
Sb(1)–O_{ax}	a	2.061(6)	2.048(5)	2.068(8)	2.077(8)
	c	2.030(6)			
Sb(1)–O_{eq}	b	1.936(6)	1.921(4)	1.925(8)	1.952(8)
	d	1.918(6)			
Sb(1)–O(2)	e		1.987(5)	2.012(8)	1.987(8)
Sb(2)–O(2)	f		1.901(5)	1.888(8)	1.896(8)
Sb(2) ··· O(1)	g		3.076(5)	2.636(8)	2.527(8)
Sb(1) ··· X	h		3.690(4)	3.71(1)	3.73(1)
Sb(1)–O(1)–Sb(1′)	A	101.2(3)	100.9(2)	103.3(4)	104.0(3)
	B	101.7(3)			
C–Sb(1)–C	C	117.3(4)	120.6(3)	119.2(7)	115.5(6)
	D	111.3(4)			
Sb(1)–O(2)–Sb(2)	E		127.0(2)	116.7(4)	115.8(4)
O(1)–Sb(1)–O(2)	F		166.4(2)	159.6(3)	156.6(3)
C–Sb(2)–C	G		119.6(3)	107.0(6)	108.6(5)
O(2)–Sb(2)–C	H		107.8(2)	103.6(4)	100.2(3)
O(2)–Sb(2)–C	I		132.7(2)	149.5(5)	151.2(5)

[a] See Fig. 2. [b] The Sb(1)/Sb(2) molecule. [c] The Sb(3)/Sb(4) molecule.

Table 4 Important bond lengths (Å) and angles (°) for compound **2**, with e.s.d.s in parentheses *

Sb(1)–O(1)	1.921(4)	Sb(2)–O(2)	1.901(5)
Sb(1)–O(1′)	2.048(5)	Sb(2)–F(3)	1.965(4)
Sb(1)–O(2)	1.987(5)	Sb(2)–F(4)	1.952(4)
Sb(1)–C(1)	2.113(7)	Sb(2)–C(21)	2.095(8)
Sb(1)–C(11)	2.123(6)	Sb(2)–C(31)	2.090(7)
O(1)–Sb(1)–O(1′)	79.1(2)	F(3)–Sb(2)–C(21)	91.5(2)
O(1)–Sb(1)–O(2)	87.4(2)	F(3)–Sb(2)–C(31)	91.5(2)
O(1)–Sb(1)–C(1)	117.7(2)	F(4)–Sb(2)–C(21)	91.1(3)
O(1)–Sb(1)–C(11)	121.5(3)	F(4)–Sb(2)–C(31)	89.0(2)
O(1′)–Sb(1)–O(2)	166.4(2)	C(21)–Sb(2)–C(31)	119.6(3)
O(1′)–Sb(1)–C(1)	93.4(2)	Sb(1)–O(1)–Sb(1′)	100.9(2)
O(1′)–Sb(1)–C(11)	92.4(2)	Sb(1)–O(2)–Sb(2)	127.0(2)
O(2)–Sb(1)–C(1)	94.7(2)	Sb(1)–C(1)–C(2)	118.7(5)
O(2)–Sb(1)–C(11)	92.9(2)	Sb(1)–C(1)–C(6)	120.1(5)
C(1)–Sb(1)–C(11)	120.6(3)	Sb(1)–C(11)–C(12)	120.8(5)
O(2)–Sb(2)–F(3)	88.2(2)	Sb(1)–C(11)–C(16)	117.9(5)
O(2)–Sb(2)–F(4)	89.0(2)	Sb(2)–C(21)–C(22)	121.4(6)
O(2)–Sb(2)–C(21)	107.8(2)	Sb(2)–C(21)–C(26)	119.7(6)
O(2)–Sb(2)–C(31)	132.7(2)	Sb(2)–C(31)–C(32)	121.9(6)
F(3)–Sb(2)–F(4)	176.7(2)	Sb(2)–C(31)–C(36)	119.1(6)

* Atoms carrying a prime are related to unprimed atoms by the symmetry operation 1 − x, 1 − y, 1 − z.

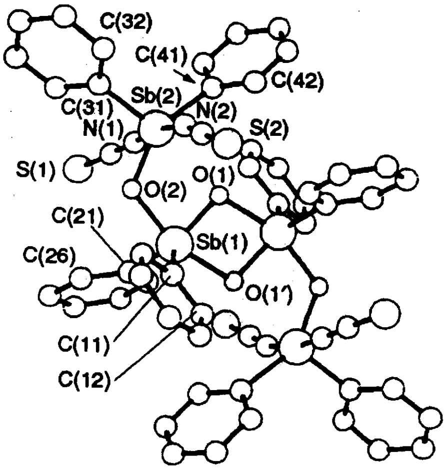


Fig. 4 Structure of $[SbPh_2O(NCS)]_4{\cdot}C_6H_5Me$ **3** showing the atom numbering scheme

but reorganisation has clearly taken place so that one set of antimony atoms is attached to three oxygen atoms while the second carries one oxygen and two fluorine substituents. The reorganisation, which is reminiscent of a disproportionation, gives a product formulated as $F_2Ph_2SbO(Ph_2SbO_2SbPh_2)OSbPh_2F_2$. The unit cell also contains a molecule of toluene of crystallisation.

The co-ordination about the two independent antimony atoms is distorted trigonal bipyramidal with the equatorial plane at Sb(1) containing the phenyl groups and O(1); O(2) and the symmetry-related O(1′) occupy the axial sites. As for **1**, distortion leads to a reduction in the axial angle at Sb(1) to 166.4(2)° but the equatorial angles are more normal ranging between 121.5(3) and 117.7(2)°. The more electronegative fluorines occupy axial positions at Sb(2) with a small but significant difference (0.013 Å) in the Sb–F separations and the axial angle [F(3)–Sb(2)–F(4) 176.7(2)°] is closed slightly. There is little distortion in the C(21)–Sb(2)–C(31) equatorial angle [119.6(3)°] but the O(2)–Sb(2)–C(21) and O(2)–Sb(2)–C(31) angles are, respectively, closed to 107.8(2) and increased to 132.7(2)°, maintaining planarity.

The Sb–O distances [see Table 3 and Fig. 2(*b*)] range between 1.901(5) and 2.048(5) Å where the two shorter separations, 1.901(5) and 1.921(4) Å, are to oxygen atoms in equatorial sites at Sb(2) and Sb(1), respectively, and the longer ones, 1.987(5) and 2.048(5) Å, to oxygens in axial sites at Sb(1). In each set, the longer bonds, comparable with those in **1** and $(SbPh_3O)_2$, probably result from inclusion of the atoms in the Sb_2O_2 ring.

As in compound **1**, angles in the four-membered ring are constrained [Sb–O–Sb 100.9(2), O–Sb–O 79.1(2)°] but it is surprising that the Sb(1)–O(2)–Sb(2) angle is as low as 127.0(2)°. Typically angles in singly oxygen-bridged $(SbPh_3X)_2O$ compounds are *ca.* 140° [139.8, 136.5, 139.0(3) and 139.8(4)°, respectively, for X = $PhSO_3$,[24] CF_3SO_3, Cl[25] and N_3[26]] though higher values [170.2, 176.6° for X = Br[27] and 180.0° for X = 2-hydroxyethanesulfonate[28]] are also known.

There are a number of weak intramolecular secondary interactions and that between Sb(2) and the ring oxygen atom O(1) at 3.076(5) Å (*cf.* 3.60 Å, the sum of the antimony and oxygen van der Waals radii) is most probably associated with both the decrease in the Sb(1)–O(1)–Sb(2) angle and the increase in the O(2)–Sb(2)–C(31) angle. The presence of this weak interaction provides information on a possible mechanism for formation of this tetrameric product (see later). There are two further close intramolecular contacts, *i.e.* between Sb(1) and F(3) and F(4) at 3.690(4) and 3.916(4) Å, respectively, and although less

Table 5 Important bond lengths (Å) and angles (°) for compounds **3** and **4**, with e.s.d.s in parentheses*

	3	**4**		**3**	**4**
Sb(1)–O(1)	1.925(8)	1.97(1)	Sb(3)–O(3)	1.952(8)	1.94(1)
Sb(1)–O(1′)	2.068(8)	2.06(1)	Sb(3)–O(3″)	2.077(8)	2.07(1)
Sb(1)–O(2)	2.012(8)	2.01(1)	Sb(3)–O(4)	1.987(8)	1.97(1)
Sb(1)–C(11)	2.08(2)	2.13(2)	Sb(3)–C(51)	2.09(2)	2.11(2)
Sb(1)–C(21)	2.12(2)	2.12(2)	Sb(3)–C(61)	2.06(1)	2.08(2)
Sb(2)–O(2)	1.888(8)	1.89(1)	Sb(4)–O(4)	1.896(9)	1.92(1)
Sb(2)–N(1)	2.13(1)	2.13(2)	Sb(4)–N(3)	2.10(1)	2.10(2)
Sb(2)–N(2)	2.08(2)	2.11(2)	Sb(4)–N(4)	2.09(1)	2.08(2)
Sb(2)–C(31)	2.08(1)	2.06(2)	Sb(4)–C(71)	2.11(1)	2.08(2)
Sb(2)–C(41)	2.09(2)	2.10(2)	Sb(4)–C(81)	2.06(1)	1.99(2)
N(1)–C(1)	1.13(2)	1.11(3)	N(3)–C(3)	1.15(2)	1.15(3)
C(1)–S(1)	1.57(2)	1.59(3)	C(3)–S(3)	1.55(2)	1.55(3)
N(2)–C(2)	1.14(2)	1.12(3)	N(4)–C(4)	1.13(2)	1.13(3)
C(2)–S(2)	1.59(2)	1.57(3)	C(4)–S(4)	1.60(2)	1.64(3)
O(1)–Sb(1)–O(1′)	76.7(4)	77.2(6)	O(3)–Sb(3)–O(3″)	76.0(3)	75.7(5)
O(1)–Sb(1)–O(2)	82.9(3)	82.4(6)	O(3)–Sb(3)–O(4)	81.3(3)	82.3(5)
O(1)–Sb(1)–C(11)	121.4(5)	122.1(8)	O(3)–Sb(3)–C(51)	129.1(4)	129.0(6)
O(1)–Sb(1)–C(21)	119.4(6)	117.8(9)	O(3)–Sb(3)–C(61)	115.2(5)	113.9(7)
O(1′)–Sb(1)–O(2)	159.6(3)	159.5(5)	O(3″)–Sb(3)–O(4)	156.6(3)	157.2(5)
O(1′)–Sb(1)–C(11)	96.0(6)	94.5(9)	O(3″)–Sb(3)–C(51)	95.0(6)	95.1(6)
O(1′)–Sb(1)–C(21)	94.9(6)	93.4(8)	O(3″)–Sb(3)–C(61)	95.6(4)	96.0(6)
O(2)–Sb(1)–C(11)	93.9(6)	95.0(9)	O(4)–Sb(3)–C(51)	95.0(6)	94.0(7)
O(2)–Sb(1)–C(21)	95.7(6)	97.6(8)	O(4)–Sb(3)–C(61)	99.1(4)	98.4(6)
C(11)–Sb(1)–C(21)	119.2(7)	120(1)	C(51)–Sb(3)–C(61)	115.5(6)	116.9(8)
Sb(1)–O(1)–Sb(1′)	103.3(4)	102.8(6)	Sb(3)–O(3)–Sb(3″)	104.0(3)	104.3(5)
O(2)–Sb(2)–N(1)	87.2(5)	87.3(8)	O(4)–Sb(4)–N(3)	86.7(5)	85.9(7)
O(2)–Sb(2)–N(2)	87.6(5)	87.8(8)	O(4)–Sb(4)–N(4)	88.5(5)	89.4(7)
O(2)–Sb(2)–C(31)	103.6(4)	101.5(8)	O(4)–Sb(4)–C(71)	151.2(5)	149.7(7)
O(2)–Sb(2)–C(41)	149.5(5)	151.8(8)	O(4)–Sb(4)–C(81)	100.2(3)	99.5
N(1)–Sb(2)–N(2)	171.3(5)	171.7(9)	N(3)–Sb(4)–N(4)	171.2(6)	170.6(8)
N(1)–Sb(2)–C(31)	94.6(4)	93.7(9)	N(3)–Sb(4)–C(71)	89.6(6)	90.1(9)
N(1)–Sb(2)–C(41)	90.4(7)	90.1(9)	N(3)–Sb(4)–C(81)	94.4(6)	94.7
N(2)–Sb(2)–C(31)	93.4(5)	93.9(9)	N(4)–Sb(4)–C(71)	91.0(7)	89.9(9)
N(2)–Sb(2)–C(41)	90.5(7)	91.1(9)	N(4)–Sb(4)–C(81)	93.7(6)	94.0
C(31)–Sb(2)–C(41)	107.0(6)	106.7(9)	C(71)–Sb(4)–C(81)	108.6(5)	110.7
Sb(1)–O(2)–Sb(2)	116.7(4)	114.8(7)	Sb(3)–O(4)–Sb(4)	115.8(4)	115.2(6)
Sb(2)–N(1)–C(1)	158(1)	156(2)	Sb(4)–N(3)–C(3)	168(1)	168(2)
N(1)–C(1)–S(1)	179(1)	177(2)	N(3)–C(3)–S(3)	178(2)	177(2)
Sb(2)–N(2)–C(2)	165(2)	171(2)	Sb(4)–N(4)–C(4)	151(1)	151(2)
N(2)–C(2)–S(2)	178(2)	179(2)	N(4)–C(4)–S(4)	178(2)	178(2)
Sb(1)–C(11)–C(12)	120(2)	117(2)	Sb(3)–C(51)–C(52)	119(2)	120(2)
Sb(1)–C(11)–C(16)	120(2)	119(2)	Sb(3)–C(51)–C(56)	120(1)	119(2)
Sb(1)–C(21)–C(22)	119(2)	122(2)	Sb(3)–C(61)–C(62)	120(1)	119(2)
Sb(1)–C(21)–C(26)	119(2)	120(2)	Sb(3)–C(61)–C(66)	119(1)	118(2)
Sb(2)–C(31)–C(32)	120(1)	119(2)	Sb(4)–C(71)–C(72)	120(2)	121(2)
Sb(2)–C(31)–C(36)	120(1)	122(2)	Sb(4)–C(71)–C(76)	119(2)	119(2)
Sb(2)–C(41)–C(42)	123(1)	123(2)	Sb(4)–C(81)–C(82)	120(1)	124
Sb(2)–C(41)–C(46)	117(2)	116(2)	Sb(4)–C(81)–C(86)	120(1)	115

* Atoms carrying primes and double primes are related to unprimed atoms by the symmetry operations 2 − *x*, 1 − *y*, 1 − *z* and −*x*, 1 − *y*, 2 − *z*, respectively, for compound **3** and 1 − *x*, 1 − *y*, −*z* and 1 − *x*, −*y*, 1 − *z*, for **4**.

significant they could be implicated in distortion of the F(3)–Sb(2)–F(4) axial angle.

Structures of [SbPh$_2$O(NCS)]$_4$·C$_6$H$_5$Me **3** *and* [SbPh$_2$O(NCS)]$_4$ **4**.—Both compounds contain two independent, but closely similar, centrosymmetric tetramers, with structures similar to that of **2**. As refinement proceeded more smoothly for **3** this will be discussed first, but for comparison important bond distances and angles for both compounds are collected in Table 5. A diagram of the Sb(1)/Sb(2) molecule of **3**, showing the atom numbering scheme, is in Fig. 4; the Sb(3)/Sb(4) molecule is similarly numbered.

As in compound **2**, all four antimony atoms are in trigonal-bipyramidal co-ordination with the equatorial plane about Sb(1) [Sb(3) atoms in brackets] occupied by the C(11) and C(21) phenyl groups [C(51) and C(61)] and the O(1) [O(3)] oxygen atom of the Sb$_2$O$_2$ ring. Two further oxygen atoms, O(1′) [O(3′)], which is also part of the four-membered ring, and O(2) [O(4)] which bridges to Sb(2) [Sb(4)] are in the axial sites. Equatorial sites at Sb(3) [Sb(4)] accommodate the C(31) and C(41) phenyl groups [C(71) and C(81)] and the singly bridging oxygen atom O(2) [O(4)], with two N-bonded thiocyanate groups, N(1) and N(2) [N(3) and N(4)] in axial positions.

The Sb–O distances and angles follow the pattern established in compound **2** [see Table 3 and Fig. 2(*b*)], but it is noteworthy that the angle at O(2) [O(4)] is reduced even further from 'normal' values to 116.7(4)° [115.8(4)°]. Equally important is the increased secondary interaction between Sb(2) and O(1) at 2.636 Å [Sb(4)–O(3) 2.527 Å], with concomitant opening of the C(41)–Sb(2)–O(2) angle to 149.5(5)° [C(71)–Sb(4)–O(4) 151.2(5)°], while planarity is maintained at antimony by closing the C(31)–Sb(2)–O(2) and C(31)–Sb(2)–C(41) angles to, respectively, 103.6(4) and 107.0(6)° [C(81)–Sb(4)–O(4) and C(81)–Sb(4)–C(71) 100.2(3) and 108.6(5)°].

Two effectively linear N-bonded thiocyanate groups occupy axial positions at Sb(2)[Sb(4)] and, as with the increased Lewis acidity of Sb(2), the Sb–N distances (mean 2.10 Å) are slightly shorter than in $SbPh_3(NCS)_2$ (2.14 Å). Bond lengths within the thiocyanate groups show no unusual features with C–N distances of 1.13(2) and 1.14(2) Å and C–S distances of 1.57(2) and 1.59(2) Å compared with average values of 1.14 and 1.58 Å, respectively, in $SbPh_3(NCS)_2$. Distortion of the N(1)–Sb(2)–N(2) angle from 180° to 171.3(5)° [N(3), Sb(4)–N(4) 171.2(6)°] can be correlated with the presence of weak secondary interactions between both N(1) and N(2) and Sb(1) at respectively, 3.71(1) and 3.90(1) Å [N(3),N(4) and Sb(4) 3.82(1) and 3.73(1) Å]. There is also a broad correlation between the strengths of these interactions and the extent of closing of the Sb–N–C angles, which vary between 151(1) and 168(1)°.

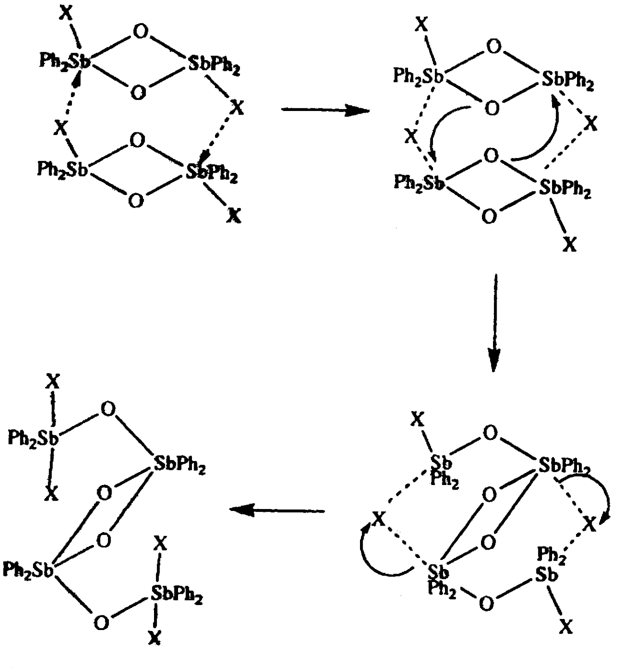
With the exception of the molecule of toluene of solvation, compounds **3** and **4** are almost identical with the same secondary contacts and small differences between the independent molecules. Differences do occur in (*a*) the Sb(2)–N(1)–C(1) and Sb(2)–N(2)–C(2) angles, 158(1) and 165(2)° in **3** and 156(2) and 171(2)° in **4**, (*b*) the angle at O(2), 116.7(4) and 114.8(7)° for **3** and **4**, respectively, and (*c*) the Sb(1)–O(1) distance, 1.925(8) and 1.97(1) Å for **3** and **4**. Following these there are necessarily corresponding small changes in the secondary bond lengths.

Mechanism of Tetramer Formation.—It is curious that while oxidation of diphenylantimony chloride and bromide leads to simple dimers containing a four-membered Sb_2O_2 ring, the corresponding fluoride and thiocyanate give rearranged tetramers. It is unlikely that this is a consequence of the oxidation reaction as the thiocyanate can also be obtained by metathesis. It is therefore probable that cyclic dimers analogous to those in the bromide are formed initially and reaction mechanisms in the two cases are similar.

The mechanism shown in Scheme 1 has the merit of simplicity. The first step is formation of either thiocyanate or fluoride bridges between two dimeric $[SbPh_2O(X)]_2$ units and it is assumed that, as bridging is less effective with chloride and bromide, these compounds are stable as simple dimers. As both groups in the thiocyanate product are N-bonded, bridging is considered to involve nitrogen only. Such 1,1-μ-N bridged

Table 6 Fractional atomic coordinates for compound **1** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.346 24(7)	0.425 40(3)	0.833 26(4)
Sb(2)	0.175 47(7)	0.329 13(3)	0.683 57(3)
Br(1)	0.261 1(1)	0.449 93(7)	0.970 32(7)
Br(2)	0.260 5(1)	0.309 20(7)	0.543 33(6)
O(1)	0.367 2(7)	0.387 6(4)	0.717 4(4)
O(2)	0.154 1(7)	0.365 6(4)	0.797 9(4)
C(11)	0.558(1)	0.368 4(5)	0.888 1(6)
C(12)	0.558(1)	0.308 1(7)	0.942 6(7)
C(13)	0.701(2)	0.268 8(8)	0.971 0(7)
C(14)	0.837(2)	0.292 7(9)	0.948 8(8)
C(15)	0.837(1	0.351 8(9)	0.896 2(8)
C(16)	0.697[illegible]	0.391 0(7)	0.864 7(7)
C(21)	0.36[illegible])	0.540 6(6)	0.799 1(6)
C(22)	0.4[illegible]2)	0.554 7(7)	0.724 8(8)
C(23)	0[illegible]3(2)	0.629 2(8)	0.700 9(9)
C(24)	[illegible]07(2)	0.688 3(8)	0.750 9(9)
C(25)	[illegible].365(2)	0.673 5(7)	0.823 2(8)
C(26)	0.345(2)	0.599 3(7)	0.849 3(8)
C(31)	0.153(1)	0.213 5(6)	0.712 8(6)
C(32)	0.141(2)	0.157 2(7)	0.651 9(7)
C(33)	0.110(2)	0.084 8(7)	0.671 3(9)
C(34)	0.089(2)	0.064 7(8)	0.747 4(9)
C(35)	0.100(2)	0.119 9(9)	0.808 9(9)
C(36)	0.131(2)	0.195 2(7)	0.791 0(7)
C(41)	−0.049(1)	0.377 2(5)	0.626 5(6)
C(42)	−0.167(1)	0.363 5(7)	0.667 6(6)
C(43)	−0.320(1)	0.390 5(7)	0.634 1(8)
C(44)	−0.347(1)	0.430 9(7)	0.562 9(9)
C(45)	−0.228(2)	0.445 6(8)	0.520 3(9)
C(46)	−0.074(1)	0.418 9(7)	0.554 3(7)



Scheme 1 Possible mechanism for the formation of $[SbPh_2O(X)]_4$, where X = F or NCS

Table 7 Fractional atomic coordinates for compound **2** with e.s.d.s in parentheses

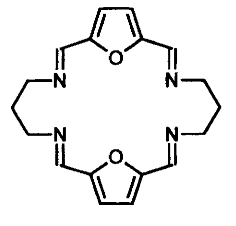
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.573 95(4)	0.411 61(4)	0.567 36(3)
Sb(2)	0.729 38(5)	0.633 48(4)	0.793 85(3)
O(1)	0.553 8(5)	0.595 5(4)	0.573 8(4)
O(2)	0.688 7(5)	0.462 2(5)	0.710 0(4)
F(3)	0.522 3(4)	0.598 5(4)	0.799 3(3)
F(4)	0.931 5(5)	0.662 6(5)	0.780 4(4)
C(1)	0.748 9(7)	0.359 6(7)	0.511 4(5)
C(2)	0.876 0(7)	0.350 5(8)	0.580 5(6)
C(3)	0.993 2(8)	0.323 6(8)	0.543 3(7)
C(4)	0.984 8(9)	0.306 2(8)	0.442 3(7)
C(5)	0.859 5(9)	0.316 3(9)	0.375 6(7)
C(6)	0.740 6(8)	0.343 9(8)	0.409 9(6)
C(11)	0.415 1(7)	0.260 8(7)	0.601 5(5)
C(12)	0.379 0(8)	0.275 7(8)	0.692 4(6)
C(13)	0.275(1)	0.174 8(9)	0.711 5(7)
C(14)	0.208 9(9)	0.064 1(9)	0.640 9(8)
C(15)	0.244(1)	0.049 2(9)	0.550 4(8)
C(16)	0.348 0(9)	0.149 0(9)	0.528 5(6)
C(21)	0.795 3(8)	0.605 8(7)	0.943 8(6)
C(22)	0.939(1)	0.657(1)	1.000 4(7)
C(23)	0.975(1)	0.633(1)	1.098 4(8)
C(24)	0.880(1)	0.564(1)	1.141 0(7)
C(25)	0.738(1)	0.512(1)	1.085 0(7)
C(26)	0.696 3(9)	0.534 4(9)	0.987 6(6)
C(31)	0.723 4(8)	0.827 4(7)	0.762 4(5)
C(32)	0.843(1)	0.911 6(8)	0.748 4(8)
C(33)	0.840(1)	1.041 9(9)	0.731 8(8)
C(34)	0.715(1)	1.087 7(9)	0.729 6(8)
C(35)	0.595(1)	1.007 2(9)	0.744 3(8)
C(36)	0.595 4(9)	0.874 5(9)	0.761 0(6)
C(41)	0.456(2)	0.121(1)	−0.011(2)
C(42)	0.604(2)	0.122(1)	0.020(2)
C(43)	0.648 8(8)	0.001(2)	0.032(2)
C(44)	0.806(2)	0.002(4)	0.065(4)

Table 8 Fractional atomic coordinates for compound **3** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.894 3(1)	0.376 04(8)	0.480 62(4)	N(3)	0.248(1)	0.816(1)	0.967 3(6)
Sb(2)	1.004 4(1)	0.341 99(8)	0.329 77(4)	C(3)	0.211(2)	0.884(1)	0.996 3(7)
O(1)	1.036 2(8)	0.485 5(7)	0.443 0(4)	S(3)	0.159 2(6)	0.976 8(5)	1.033 6(3)
O(2)	0.876 8(9)	0.280 6(7)	0.390 7(4)	N(4)	0.327(1)	0.523(1)	0.899 7(7)
N(1)	1.121(1)	0.284(1)	0.357 8(6)	C(4)	0.306(1)	0.435(2)	0.867 6(8)
C(1)	1.147(1)	0.223(1)	0.371 2(7)	S(4)	0.280 6(5)	0.309 2(4)	0.822 3(3)
S(1)	1.183 9(5)	0.138 8(5)	0.389 2(3)	C(51)	−0.047(2)	0.359(2)	0.859 3(8)
N(2)	0.887(1)	0.411(1)	0.316 9(7)	C(52)	0.014(2)	0.365(2)	0.800(1)
C(2)	0.816(2)	0.452(1)	0.323 4(8)	C(53)	−0.018(2)	0.267(3)	0.751 9(9)
S(2)	0.720 6(6)	0.510 1(5)	0.330 4(3)	C(54)	−0.107(3)	0.164(2)	0.760(1)
C(11)	0.711(2)	0.372(1)	0.493 2(9)	C(55)	−0.165(2)	0.163(2)	0.819(2)
C(12)	0.673(2)	0.438(2)	0.549 0(9)	C(56)	−0.130(2)	0.263(2)	0.870 2(8)
C(13)	0.552(3)	0.432(2)	0.556(1)	C(61)	−0.115(1)	0.599(1)	0.941 2(8)
C(14)	0.469(2)	0.366(2)	0.512(1)	C(62)	−0.131(2)	0.674(1)	0.998 4(8)
C(15)	0.509(2)	0.305(2)	0.456(1)	C(63)	−0.209(2)	0.733(1)	1.004(1)
C(16)	0.630(2)	0.306(2)	0.447(1)	C(64)	−0.268(2)	0.712(2)	0.954(1)
C(21)	0.927(2)	0.262(2)	0.513 7(7)	C(65)	−0.255(2)	0.639(2)	0.898(1)
C(22)	1.029(2)	0.303(2)	0.548 0(9)	C(66)	−0.178(2)	0.580(2)	0.891 3(8)
C(23)	1.054(2)	0.233(3)	0.569 7(9)	C(71)	0.396(1)	0.727(2)	1.012 1(7)
C(24)	0.971(3)	0.122(3)	0.557(1)	C(72)	0.402(2)	0.645(2)	1.034(1)
C(25)	0.868(3)	0.071(2)	0.520(2)	C(73)	0.466(2)	0.679(2)	1.086(1)
C(26)	0.848(2)	0.149(2)	0.499(1)	C(74)	0.524(2)	0.795(3)	1.116(1)
C(31)	0.959(1)	0.211 3(9)	0.247 3(5)	C(75)	0.517(2)	0.878(2)	1.095(1)
C(32)	0.926(2)	0.228(1)	0.197 1(6)	C(76)	0.455(2)	0.842(2)	1.041(1)
C(33)	0.902(3)	0.142(2)	0.140 9(6)	C(81)	0.433 0(9)	0.745(1)	0.862 2(5)
C(34)	0.905(2)	0.039(1)	0.136 3(6)	C(82)	0.560(1)	0.807(2)	0.873 8(8)
C(35)	0.939(2)	0.023(1)	0.186 3(8)	C(83)	0.649(1)	0.847(2)	0.827(1)
C(36)	0.967(2)	0.110(1)	0.241 7(6)	C(84)	0.611(2)	0.825(2)	0.768 2(7)
C(41)	1.167(2)	0.478(2)	0.306 8(6)	C(85)	0.484(2)	0.772(3)	0.758 4(8)
C(42)	1.166(2)	0.580(2)	0.310 6(8)	C(86)	0.394(1)	0.731(3)	0.805 5(8)
C(43)	1.278(3)	0.660(2)	0.290(1)	C(91)	0.661(3)	0.944(4)	0.312(2)
C(44)	1.386(3)	0.643(2)	0.269(1)	C(92)	0.580(5)	0.993(3)	0.311(2)
C(45)	1.386(2)	0.542(3)	0.264(1)	C(93)	0.478(4)	0.987(3)	0.356(2)
C(46)	1.278(2)	0.458(2)	0.284 0(7)	C(94)	0.462(5)	0.940(6)	0.405(2)
Sb(3)	−0.005 74(9)	0.509 55(8)	0.932 42(4)	C(95)	0.547(5)	0.896(3)	0.407(1)
Sb(4)	0.301 40(9)	0.676 58(8)	0.930 38(5)	C(96)	0.644(4)	0.895(3)	0.360(2)
O(3)	0.112 3(7)	0.571 4(7)	0.997 6(4)	C(97)	0.734(7)	0.845(6)	0.362(4)
O(4)	0.151 0(8)	0.600 8(8)	0.886 9(4)				

Table 9 Fractional atomic coordinates for compound **4** with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.392 1(2)	0.390 9(1)	0.015 59(7)	Sb(3)	0.494 0(1)	0.077 3(1)	0.567 64(6)
Sb(2)	0.499 7(1)	0.505 8(1)	0.165 97(7)	Sb(4)	0.801 2(1)	0.249 7(1)	0.571 93(7)
O(1)	0.538(1)	0.540(1)	0.057 8(6)	O(3)	0.611(1)	0.075(1)	0.503 0(6)
O(2)	0.374(1)	0.379(1)	0.104 2(7)	O(4)	0.648(1)	0.215(1)	0.614 8(6)
N(1)	0.621(2)	0.424(2)	0.140(1)	N(3)	0.744(2)	0.349(2)	0.535(1)
C(1)	0.645(2)	0.350(2)	0.127(1)	C(3)	0.707(2)	0.388(2)	0.505(1)
S(1)	0.688(1)	0.250 0(8)	0.109 5(5)	S(3)	0.656(1)	0.442 9(9)	0.467 6(5)
N(2)	0.376(2)	0.584(2)	0.178(1)	N(4)	0.830(2)	0.129(2)	0.601(1)
C(2)	0.310(3)	0.623(2)	0.176(1)	C(4)	0.812(2)	0.074(2)	0.634(1)
S(2)	0.219 0(9)	0.681(1)	0.174 4(6)	S(4)	0.785 4(8)	−0.009 2(8)	0.678 8(4)
C(11)	0.205(2)	0.375(2)	0.001(1)	C(51)	0.455(2)	−0.001(2)	0.640 8(9)
C(12)	0.173(3)	0.382(3)	−0.055(1)	C(52)	0.515(2)	0.061(2)	0.699(1)
C(13)	0.055(4)	0.372(4)	−0.066(2)	C(53)	0.487(3)	0.016(3)	0.748(1)
C(14)	−0.032(3)	0.354(4)	−0.018(2)	C(54)	0.400(4)	−0.095(3)	0.738(2)
C(15)	0.006(3)	0.356(4)	0.036(2)	C(55)	0.335(3)	−0.159(3)	0.678(2)
C(16)	0.127(3)	0.364(3)	0.050(2)	C(56)	0.362(3)	−0.114(2)	0.629(1)
C(21)	0.429(3)	0.246(2)	−0.024(1)	C(61)	0.384(2)	0.159(2)	0.558(1)
C(22)	0.543(3)	0.259(3)	−0.047(1)	C(62)	0.374(2)	0.176(2)	0.502(1)
C(23)	0.559(4)	0.157(3)	−0.070(1)	C(63)	0.302(3)	0.231(3)	0.494(1)
C(24)	0.467(5)	0.055(3)	−0.069(2)	C(64)	0.238(3)	0.264(3)	0.543(2)
C(25)	0.358(5)	0.042(3)	−0.048(3)	C(65)	0.235(3)	0.233(3)	0.598(2)
C(26)	0.338(4)	0.136(3)	−0.023(3)	C(66)	0.317(3)	0.184(3)	0.607(1)
C(31)	0.452(2)	0.453(2)	0.246(1)	C(71)	0.891(2)	0.216(2)	0.491(1)
C(32)	0.430(4)	0.523(3)	0.297(2)	C(72)	0.903(2)	0.114(2)	0.470(1)
C(33)	0.405(6)	0.489(5)	0.356(2)	C(73)	0.965(3)	0.095(3)	0.416(2)
C(34)	0.403(5)	0.395(5)	0.358(2)	C(74)	1.023(3)	0.180(4)	0.388(2)
C(35)	0.419(4)	0.320(4)	0.310(3)	C(75)	1.019(3)	0.285(3)	0.410(2)
C(36)	0.446(3)	0.350(3)	0.249(2)	C(76)	0.950(3)	0.302(3)	0.461(2)
C(41)	0.661(2)	0.668(2)	0.193(1)	C(81)	0.925 7	0.384 0	0.639 5
C(42)	0.659(3)	0.769(2)	0.191(1)	C(82)	1.058 9	0.435 3	0.637 4
C(43)	0.765(4)	0.873(2)	0.214(2)	C(83)	1.140 0	0.523 3	0.693 3
C(44)	0.875(4)	0.878(3)	0.239(2)	C(84)	1.080 7	0.569 5	0.741 1
C(45)	0.885(3)	0.784(3)	0.241(2)	C(85)	0.944 4	0.537 4	0.733 1
C(46)	0.769(3)	0.671(2)	0.218(1)	C(86)	0.871 3	0.427 6	0.688 4



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systems are known, for example, in $\{[SnMe_2(NCS)]_2O\}_2$,[29] $[Re_2(NCS)_{10}]^{3-}$[30] and a macrocyclic cobalt complex, $[Co_2L(OEt)(NCS)_3]$,[31] but are less widespread than conventional 1,3-μ-NS bridged systems. Interaction of an oxygen lone pair with a diagonally related antimony atom, followed by rearrangement of bonds as shown in Scheme 1 and migration of either fluoride or thiocyanate, then leads to the final product.

This mechanism gains support from the secondary intramolecular interactions in compounds **3** and **4**. Those between Sb(2) and O(1) and Sb(4) and O(3) can be regarded as remaining from incomplete disruption of the original Sb_2O_2 ring, while the Sb(1) ··· F(3), Sb(1) ··· N(1) and Sb(3) ··· N(4) interactions may be residues of the original Sb–X–Sb bridges. The latter, on the other hand, may simply arise as a consequence of Sb–O interactions which necessarily bring electron-donating F or NCS groups close to a co-ordinatively unsaturated antimony atom.

To obtain support for this mechanism, IR spectra (2500–1800 cm^{-1} in chloroform) were recorded during the course of a metathesis reaction between diphenylantimony bromide oxide and potassium thiocyanate in chloroform. Normal 1,3-μ-NS bridged compounds show bands at *ca.* 2100 cm^{-1} compared with *ca.* 1950 cm^{-1} for those with 1,1-μ-N bridges. Although growth of a thiocyanate band at 2038 cm^{-1}, which broadened and intensified as the reaction proceeded, was observed, there was no evidence for a lower-energy band associated with N,N-bridge formation. This could be due to insensitivity of the method and/or the low concentration of any bridged thiocyanate species, but the solution spectra are dominated by the broad band at 2038 cm^{-1} from N-bonded thiocyanate in both the final tetramer and the proposed dimeric starting material, which would effectively mask bands due to bridged intermediates.

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