Donor Properties of Triphenylantimony Dihalides: Preparation and Crystal Structures of $Ph_3SbCl_2{\cdot}SbCl_3$ and $[Ph_3SbCl][SbCl_6]$ †

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Triphenylantimony dichloride reacts with both antimony(III) and antimony(V) chloride to give addition compounds with the stoicheiometry $Ph_3SbCl_2{\cdot}SbCl_3$ and $Ph_3SbCl_2{\cdot}SbCl_5$, respectively. *X*-Ray analysis of the former shows the presence of only weak interactions between the axial chlorine atoms of Ph_3SbCl_2 and adjacent $SbCl_3$ molecules to give polymeric chains parallel to the *a* axis. The trigonal bipyramidal geometry of Ph_3SbCl_2 is little changed; co-ordination about Sb^{III} is square pyramidal with three short (mean 2.337 Å) and two long (mean 3.262 Å) distances. In the $SbCl_5$ compound there is a chloride ion transfer to $SbCl_5$ giving a structure best described in terms of the ionic formulation $[Ph_3SbCl]^+[SbCl_6]^-$. Residual anion–cation interaction is shown by a Cl • • • Sb contact of 3.231 Å, and the cation geometry is intermediate between the trigonal pyramidal and tetrahedral extremes. Reactions between Ph_3SbX_2 (X = F, Br, or I) and $SbCl_3$, $SbBr_3$, or $SbCl_5$ are also described.

The favoured structure for five-co-ordinate Main Group compounds is the trigonal bipyramid, but in a number of cases alternative solid-state arrangements are found. For example, anion transfer can take place with the formation of tetrahedral and octahedral ions, while with other compounds the central atom achieves octahedral co-ordination by either intra- or inter-molecular interaction. A degree of ' instability ' has thus become associated with the trigonal bipyramidal structure.

Among a group of ' stable ' trigonal bipyramidal compounds, however, are the triorgano-substituted antimony(V) halides, R_3SbX_2. Although it is possible to envisage halide ion transfer giving the tetrahedral and octahedral R_3SbX^+ and $R_3SbX_3^-$ ions, this does not occur in the solid state, nor is there intermolecular association to give, for example, a chlorine-bridged dimeric structure analogous to that in $(Ph_2SbCl_3)_2$.[1] Although the antimony(V) centre is formally unsaturated, its Lewis acidity is insufficient to accept electron density from an axial halogen of a neighbouring molecule.

This work arose from our observation that, while oxidation of triphenylantimony with antimony(V) chloride in toluene gave the expected triphenylantimony dichloride, replacement of toluene by a non-donor solvent such as carbon tetrachloride led to a weakly bonded 1 : 1 addition compound, $Ph_3SbCl_2{\cdot}SbCl_3$. The nature of the interaction between the components was of interest, in view of the weakness of both donor and acceptor properties of Ph_3SbCl_2. It also appeared pertinent to investigate the Ph_3SbCl_2–$SbCl_5$ reaction, as this might lead to a more stable complex if Lewis acidity of the antimony chloride were of major importance in stabilising the complex. Since this work was completed, the formation of $Me_3SbCl_2{\cdot}SbCl_3$ and $Me_3SbBr_2{\cdot}SbBr_3$ has been reported.[2]

Antimony(III) *Halide Compounds*.—The oxidising properties of antimony(V) chloride are well established, and it is not surprising that on reaction in toluene triphenylantimony is converted essentially quantitatively into Ph_3SbCl_2. With a non-donor solvent such as carbon tetrachloride or n-hexane, however, the oxidation product is a well defined 1 : 1 addition compound, $Ph_3SbCl_2{\cdot}SbCl_3$, melting at 126 °C. The compound can also be obtained directly from the components, as can the corresponding bromide, $Ph_3SbBr_2{\cdot}SbBr_3$, melting at 102 °C.

Table 1. Infrared spectra for $Ph_3SbX_2{\cdot}SbX_3$ (X = Cl or Br), with assignments

$Ph_3SbCl_2{\cdot}SbCl_3$	$Ph_3SbBr_2{\cdot}SbBr_3$	Assignment
455 (sh)	460 (sh)	Phenyl *y* mode *
452s	522s	
375s		ν_{sym} ($SbCl_3$)
371 (sh)		
340s		ν_{asym} ($SbCl_3$)
322s		
295s	295s	Phenyl *t* mode
284 (sh)	286 (sh)	
245s	245s	
	230s	ν_{sym} ($SbBr_3$)
	220s	ν_{asym} ($SbBr_3$)
223w		Phenyl *u* mode

* See D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350.

Attempts to prepare mixed halogen addition compounds were only partially successful. Although a 1 : 1 compound melting at 112 °C was isolated from equimolar quantities of Ph_3SbCl_2 and $SbBr_3$ in chloroform, decomposition of the adduct with ether led to a solid identified by i.r. spectroscopy as a mixture of Ph_3SbCl_2 and Ph_3SbBr_2. The mother-liquor on addition of dioxan gave a solid whose i.r. spectrum was consistent with it being a mixture of the dioxan adducts of $SbCl_3$ and $SbBr_3$. Reaction between Ph_3SbBr_2 and $SbCl_3$ was similarly ambiguous: halogen exchange again appeared to take place. Mass spectra of the two mixed adducts are dominated by ions from antimony trihalides and their fragments, but it is clear that, although both products show all possible $SbBr_nCl_{3-n}$ ions and fragments, the abundance of bromine-containing species is higher in the $Ph_3SbCl_2{\cdot}SbBr_3$ spectrum. Similarly, antimony–chlorine species dominate the spectrum of $Ph_3SbBr_2{\cdot}SbCl_3$.

No compound formation occurred between either Ph_3SbF_2 or Ph_3SbI_2 and either $SbBr_3$ or $SbCl_3$; in these cases SbF_3 or SbI_3 separated, confirming the ready exchange of halogen atoms.

I.r. spectra for the two well defined adducts in the region below 500 cm^{-1} are listed in Table 1; they arise essentially from a superposition of the spectra of the two starting materials. In free $SbCl_3$ the symmetric and antisymmetric stretches[3] are found at 377 and 356 cm^{-1}, and on complex formation with dioxan, for example, they are lowered in energy to 350 and 325 cm^{-1}, respectively. In the Ph_3SbCl_2 complex there is no change in the position of the symmetric

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† *Supplementary data available* (No. SUP 23565, 67 pp.): structure factors, thermal parameters, calculated hydrogen atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

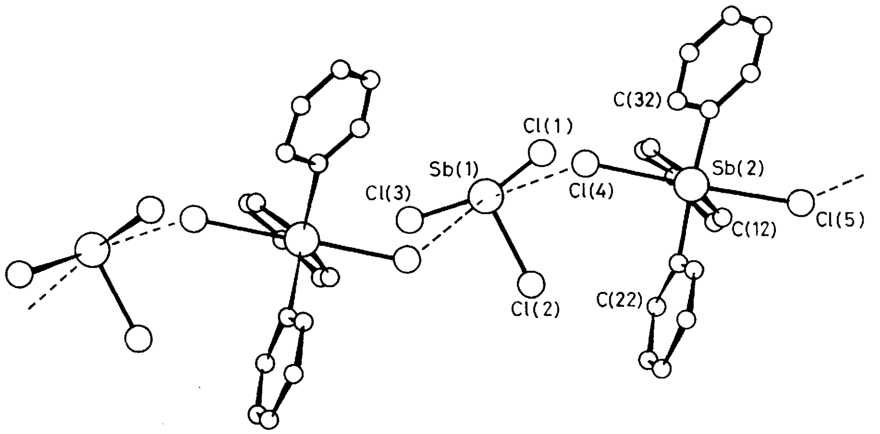

Figure 1. Molecular structure and atom numbering scheme for Ph$_3$SbCl$_2$·SbCl$_3$ (projection onto *ac* plane)

Table 2. Bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for Ph$_3$SbCl$_2$·SbCl$_3$

Sb(1)–Cl(1)	2.354(3)	Sb(2)–Cl(4)	2.512(2)
Sb(1)–Cl(2)	2.309(3)	Sb(2)–Cl(5)	2.474(2)
Sb(1)–Cl(3)	2.347(2)	Sb(2)–C(11)	2.085(4)
Sb(1)–Cl(4)	3.236(3)	Sb(2)–C(21)	2.108(4)
Sb(1)–Cl(5′)	3.287(3)	Sb(2)–C(31)	2.110(4)

Cl(1)–Sb(1)–Cl(2)	94.9(1)	Cl(4)–Sb(2)–Cl(5)	177.3(1)
Cl(1)–Sb(1)–Cl(3)	92.5(1)	Cl(4)–Sb(2)–C(11)	91.1(4)
Cl(1)–Sb(1)–Cl(4)	89.1(1)	Cl(4)–Sb(2)–C(21)	88.8(4)
Cl(1)–Sb(1)–Cl(5′)	177.1(1)	Cl(4)–Sb(2)–C(31)	88.6(3)
Cl(2)–Sb(1)–Cl(3)	94.9(1)	Cl(5)–Sb(2)–C(11)	91.6(4)
Cl(2)–Sb(1)–Cl(4)	83.8(1)	Cl(5)–Sb(2)–C(21)	90.3(3)
Cl(2)–Sb(1)–Cl(5′)	82.1(1)	Cl(5)–Sb(2)–C(31)	89.7(3)
Cl(3)–Sb(1)–Cl(4)	177.9(1)	C(11)–Sb(2)–C(21)	117.8(4)
Cl(3)–Sb(1)–Cl(5′)	87.2(1)	C(11)–Sb(2)–C(31)	121.9(3)
Cl(4)–Sb(1)–Cl(5′)	91.1(1)	C(21)–Sb(2)–C(31)	120.3(4)

stretch but the degeneracy of the antisymmetric stretch is raised, giving two components at 340 and 322 cm^{-1}. The remaining bands can be assigned to Ph$_3$SbCl$_2$ and although they are not shifted in comparison with uncombined Ph$_3$SbCl$_2$, there are some variations in intensity. The Sb–Br stretching modes were not well resolved but occurred at similar energies to those in the SbBr$_3$–dioxan adduct.

These data, together with the fact that the adducts can only form in solvents of very low donor ability, point to there being only very weak interaction between the components. Triphenylantimony dichloride is potentially a Lewis acid, while SbCl$_3$ and SbBr$_3$, each carrying a lone pair of electrons, have potential Lewis base character. However, in neither case is such character well developed. On the contrary, Lewis acidity is a characteristic property of the antimony(III) halides and this, in accepting lone-pair density from a halogen atom in Ph$_3$SbX$_2$, is the more likely interaction leading to the weak adducts. The crystal structure of Ph$_3$SbCl$_2$·SbCl$_3$ has been determined to resolve this bonding problem.

Structure of Ph$_3$SbCl$_2$·SbCl$_3$.—The major feature of the structure is the formation of weak bonds between the two axial chlorine atoms of a Ph$_3$SbCl$_2$ molecule and adjacent SbCl$_3$ molecules to give polymeric chains parallel to the *a* axis. This is illustrated together with the atom numbering scheme in Figure 1. Selected bond distances and angles are collected in Table 2.

Table 3. Torsion angles in Ph$_3$SbCl$_2$·SbCl$_3$

C(11)–Sb(2)–C(21)–C(22)	−14.5°
C(11)–Sb(2)–C(31)–C(32)	138.0°
C(21)–Sb(2)–C(11)–C(12)	−54.8°
C(21)–Sb(2)–C(31)–C(32)	−40.3°
C(31)–Sb(2)–C(11)–C(12)	126.8°
C(31)–Sb(2)–C(21)–C(22)	163.8°

The trigonal bipyramidal geometry of Ph$_3$SbCl$_2$ in the adduct is little different from that in the pure compound,[4] the major difference being in the orientation of the phenyl groups. In the latter, these are related by a pseudo-three-fold axis but in the adduct, the plane of the C(21)—C(26) group is almost coincident with the Sb(2)C(11)C(21)C(31) equatorial plane. The orientation of the phenyl groups is more accurately defined by the torsion angles (Table 3). Such minor changes are perhaps to be expected as a result of decreased non-bonded interactions in the more spacious lattice of the adduct.

Co-ordination about the antimony(III) atom is square pyramidal (or octahedral if the antimony lone pair is considered to be stereochemically active), showing three short Sb–Cl distances (mean 2.337 Å, *cf.* 2.359 Å in SbCl$_3$ [5]) and two longer contacts (mean 3.262 Å). The latter are well within the sum of the van der Waals radii, and should be considered as secondary bonds. It is significant that the apical Sb–Cl bond, *i.e.* that with no *trans* secondary Sb $\cdots$ Cl interaction, is significantly shorter (2.309 Å) than the two remaining Sb–Cl distances. This bonding pattern is also found in the ionic compound [S$_4$N$_3$][SbCl$_5$],[6] but [SbCl$_5$]$^{2-}$ salts with other cations show different bond lengths.[7]

There are strong similarities between this structure and that of the related methyl derivative,[2] where again the two halogens of Me$_3$SbCl$_2$ form weak secondary bonds with adjacent SbCl$_3$ molecules. In the latter, however, there is a further secondary bond which links the chains, giving distorted octahedral co-ordination about the antimony(III) atom. In the Ph$_3$SbCl$_2$·SbCl$_3$ structure, there are no further Sb $\cdots$ Cl contacts within 4.0 Å; here it is most likely the larger size of the phenyl group that precludes the formation of the third secondary bond.

Antimony(V) *Chloride Compounds.*—It is perhaps not surprising that antimony(III) chloride does not abstract a chloride ion from Ph$_3$SbCl$_2$ but, as Me$_4$SbCl has been converted into [Me$_4$Sb][SbCl$_6$] by antimony(V) chloride,[8] chloride

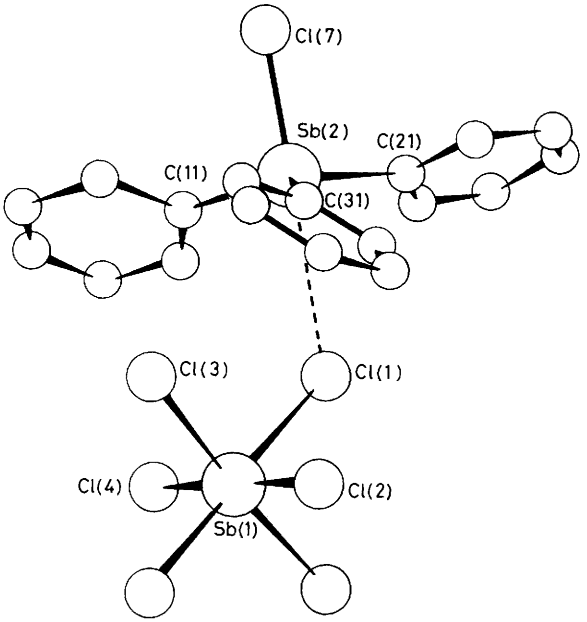

Figure 2. Molecular structure and atom numbering scheme for $[Ph_3SbCl]^+[SbCl_6]^-$

ion abstraction may be possible with the stronger Lewis acid. In fact, a 1 : 1 addition compound can be isolated as moisture-sensitive crystals melting at 155—156 °C from a reaction between equimolar quantities of the components in carbon tetrachloride solution. The product crystallizes unchanged from chloroform solution, but with donor solvents only uncomplexed Ph_3SbCl_2 could be recovered.

Reactions of either Ph_3SbBr_2 or Ph_3SbI_2 with antimony(V) chloride liberated the free heavier halogen to give $Ph_3SbCl_2\cdot SbCl_5$. With Ph_3SbF_2, the product appeared to be more consistent with the composition $Ph_3SbFCl\cdot SbCl_5$ than with $Ph_3SbF_2\cdot SbCl_5$, and although it was crystalline it was not possible to index the single-crystal *X*-ray data; it is probably considerably disordered.

When 2 mol equiv. of $SbCl_5$ reacted with Ph_3SbCl_2 in chloroform, the product was initially an oil with the stoicheiometry $Ph_3SbCl_2\cdot 2SbCl_5$; this solidified on recrystallisation from carbon tetrachloride.

I.r. spectra of $Ph_3SbCl_2\cdot SbCl_5$ below 600 cm^{-1} show bands at 451s, 443 (sh), 347vs, 330 (sh), 295s, and 286 (sh) cm^{-1}. Those at 451 and 286 cm^{-1} are characteristic phenyl group modes, while the sharp, intense Sb–Cl stretching band at 347 cm^{-1} could well be assigned to $SbCl_6^-$. In $K[SbCl_6]$ and $[NO][SbCl_6,]$ for example, the degenerate stretch occurs at, respectively, 346 and 353 cm^{-1}.[9] The 1 : 2 adduct gives a more complicated spectrum in the 350 cm^{-1} region, with peaks at 374ms, 355vs, 343vs, and 330s cm^{-1}. If the 1 : 1 adduct is $[Ph_3SbCl]^+[SbCl_6]^-$, a related ionic structure is possible for $Ph_3SbCl_2\cdot 2SbCl_5$. A dipositive cationic species, $[Ph_3Sb]^{2+}2[SbCl_6]^-$, is unlikely, but formulation as $[Ph_3SbCl]^+[Sb_2Cl_{11}]^-$ would be consistent with the more complex spectrum.

It was not possible to grow crystals of the 1 : 2 compound, but rather poor quality single crystals were obtained for $Ph_3SbCl_2\cdot SbCl_5$ and a structure determination was carried out.

Structure of $Ph_3SbCl_2\cdot SbCl_5$.—The *X*-ray investigations show that the compound is best represented in terms of $[Ph_3SbCl]^+$ and $[SbCl_6]^-$ ions, but there is significant cation–anion interaction. A diagram of the ion pair is shown in Figure 2, which also gives the atom numbering scheme; important bond distances and angles are collected in Table 4.

Table 4. Bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for $[Ph_3SbCl][SbCl_6]$

Sb(1)–Cl(1)	2.414(6)	Sb(2)–Cl(1′)	3.231(6)
Sb(1)–Cl(2)	2.362(6)	Sb(2)–Cl(7)	2.325(7)
Sb(1)–Cl(3)	2.331(7)	Sb(2)–C(11)	2.11(2)
Sb(1)–Cl(4)	2.341(6)	Sb(2)–C(21)	2.08(2)
Sb(1)–Cl(5)	2.343(7)	Sb(2)–C(31)	2.07(3)
Sb(1)–Cl(6)	2.344(7)		
Cl(1)–Sb(1)–Cl(2)	87.4(2)	Cl(1′)–Sb(2)–Cl(7)	177.6(3)
Cl(1)–Sb(1)–Cl(3)	89.2(2)	Cl(1′)–Sb(2)–C(11)	78.8(6)
Cl(1)–Sb(1)–Cl(4)	89.2(2)	Cl(1′)–Sb(2)–C(21)	84.5(6)
Cl(1)–Sb(1)–Cl(5)	179.0(3)	Cl(1′)–Sb(2)–C(31)	81.7(7)
Cl(1)–Sb(1)–Cl(6)	90.1(2)		
Cl(2)–Sb(1)–Cl(3)	89.6(3)	Cl(7)–Sb(2)–C(11)	99.4(7)
Cl(2)–Sb(1)–Cl(4)	176.5(3)	Cl(7)–Sb(2)–C(21)	97.7(6)
Cl(2)–Sb(1)–Cl(5)	91.7(3)	Cl(7)–Sb(2)–C(31)	97.9(7)
Cl(2)–Sb(1)–Cl(6)	89.1(3)	C(11)–Sb(2)–C(21)	112.8(9)
Cl(3)–Sb(1)–Cl(4)	90.4(3)	C(11)–Sb(2)–C(31)	118.7(10)
Cl(3)–Sb(1)–Cl(5)	90.8(3)	C(21)–Sb(2)–C(31)	122.4(9)
Cl(3)–Sb(1)–Cl(6)	178.5(3)		
Cl(4)–Sb(1)–Cl(5)	91.8(3)	Sb(1′)–Cl(1′)–Sb(2)	121.7(2)
Cl(4)–Sb(1)–Cl(6)	90.9(3)		
Cl(5)–Sb(1)–Cl(6)	89.9(3)		

Table 5. Torsion angles in $[Ph_3SbCl]^+[SbCl_6]^-$

C(11)–Sb(2)–C(21)–C(22)	−27.6°
C(11)–Sb(2)–C(31)–C(32)	−158.5°
C(21)–Sb(2)–C(11)–C(12)	−36.7°
C(21)–Sb(2)–C(31)–C(32)	51.1°
C(31)–Sb(2)–C(11)–C(12)	170.2°
C(31)–Sb(2)–C(21)–C(22)	124.4°

The antimony atom Sb(1) in the anion is in distorted octahedral co-ordination to chlorine with the Sb(1)–Cl(1) bond significantly longer (2.414 Å) than the remainder, which are equal (mean 2.344 Å) within the limits of the determinations. Bond angle deviations from the ideal values are consistent with the presence of this longer bond with a reduction of the Cl(1)–Sb(1)–Cl(2) angle to 87.4°, leading to a decrease in the Cl(2)–Sb(1)–Cl(4) angle to 176.5° and a compensating increase in the Cl(2)–Sb(1)–Cl(5) angle to 91.7°.

The anion and cation are bridged by Cl(1), but, while the Cl(1′)–Sb(2) distance is long (3.231 Å), it falls well within the sum of the van der Waals radii (4.00 Å), implying the presence of a weak secondary bond. From the Pauling formula[10] for partial bond orders, the Cl(1) · · · Sb(2) distance is equivalent to a bond order of 0.06.

The geometry of the cation could be described either as a distorted trigonal pyramid if the secondary bond is omitted, or as a distorted trigonal bipyramid if Cl(1) is considered still bonded to Sb(2). The structure does in fact represent a point on the reaction co-ordinate between a regular trigonal bipyramidal structure and the tetrahedral geometry observed for the cation in $[Me_4Sb]^+[SbCl_6]^-$. In view of the great disparity in the Sb(2)–Cl(1) and Sb(2)–Cl(7) distances, formulation as a stibonium salt is the more realistic alternative.

This is supported by (*a*) the decrease in Sb(2)–Cl(7) length from *ca.* 2.48 Å in Ph_3SbCl_2 to 2.325 Å, (*b*) an increase in all three Cl(7)–Sb(2)–C angles from 90° to *ca.* 98.3°, and (*c*) a decrease in the C(11)–Sb(2)–C(21) equatorial angle to 112.8°; the other two equatorial angles are, however, 118.7 and 122.4°.

There is also confirmation from the fact that Sb(2) is displaced 0.30 Å in the direction of Cl(7) from the plane through C(11), C(21), and C(31).

The torsion angles for the phenyl groups (see Table 5) indicate that the C(11)–C(16) phenyl group is tilted in the opposite sense to the C(21) and C(31) groups. This is in contrast to the situation in both free Ph_3SbCl_2 and the $SbCl_3$ adduct.

Experimental

All reactions were carried out with exclusion of moisture in dried solvents under nitrogen. Antimony(v) chloride was vacuum distilled before use and antimony(III) halides were sublimed. All products were handled in a dry box.

Oxidation of Ph_3Sb.—Solutions of triphenylantimony (1.1 g, 0.003 mol) and antimony(v) chloride (0.4 cm^3, 0.003 mol) in toluene were mixed. Cooling to −20 °C gave white crystals of Ph_3SbCl_2, which were collected and recrystallized from carbon tetrachloride; yield 1.0 g (75%), m.p. 142 °C (lit.,[11] 143 °C) (Found: C, 50.8; H, 3.2. Calc. for $C_{18}H_{15}Cl_2Sb$: C, 50.9; H, 3.5%).

Preparation of $Ph_3SbCl_2{\cdot}SbCl_3$.—Addition of a solution of triphenylantimony (3.5 g, 0.01 mol) in carbon tetrachloride to antimony(v) chloride (1.3 cm^3, 0.01 mol) in the same solvent led to the immediate precipitation of $Ph_3SbCl_2{\cdot}SbCl_3$. After recrystallization from CCl_4 the compound had m.p. 126 °C (Found: C, 33.2; H, 2.6; Cl, 27.4. Calc. for $C_{18}H_{15}Cl_5Sb_2$: C, 33.1; H, 2.3; Cl, 27.2%). An immediate precipitate of the addition compound was formed when solutions of triphenylantimony dichloride (4.2 g, 0.01 mol) and antimony(III) chloride (2.3 g, 0.01 mol) in n-hexane were mixed (Found: C, 33.0; H, 2.2%).

Preparation of $Ph_3SbBr_2{\cdot}SbBr_3$.—Solutions of triphenylantimony dibromide (1.9 g, 0.004 mol) and antimony tribromide (1.4 g, 0.004 mol) in chloroform were mixed and the volume of the solution was reduced until crystallisation occurred; m.p. 102 °C (Found: C, 24.6; H, 1.8. Calc. for $C_{18}H_{15}Br_5Sb_2$: C, 24.7; H, 1.7%).

Preparation of $Ph_3SbCl_2{\cdot}SbBr_3$.—Equimolar solutions of the components in chloroform were mixed and white crystals, m.p. 112 °C, were obtained (Found: C, 27.6; H, 1.9; Br, 29.9. Calc. for $C_{18}H_{15}Br_3Cl_2Sb_2$: C, 27.5; H, 1.9; Br, 30.5%).

Attempted Preparation of $Ph_3SbBr_2{\cdot}SbCl_3$.—Equimolar solutions in chloroform treated as above gave white crystals, m.p. 121 °C [Found: C, 30.3; H, 2.1; Br, 14.0. Calc. for $C_{18}H_{15}Br_2Cl_3Sb_2$ ($Ph_3SbBr_2{\cdot}SbCl_3$): C, 29.1; H, 2.0; Br, 21.6. Calc. for $C_{18}H_{15}Br_{1.25}Cl_{3.75}Sb_2$ ($Ph_3Sb_2Br_{1.25}Cl_{3.75}$): C, 30.5; H, 2.1; Br, 14.1%].

Preparation of $Ph_3SbCl_2{\cdot}SbCl_5$.—A solution of antimony(v) chloride (0.9 cm^3, 0.007 mol) in carbon tetrachloride was added dropwise to a solution of triphenylantimony dichloride (3.0 g, 0.007 mol) in the same solvent. Extremely moisture sensitive crystals, which could be recrystallised from chloroform solution, were slowly deposited; m.p. 115—116 °C (Found: C, 29.9; H, 2.0; Cl, 34.7. Calc. for $C_{18}H_{15}Cl_7Sb_2$: C, 29.9; H, 2.1; Cl, 34.4%).

Preparation of $Ph_3SbCl_2{\cdot}2SbCl_5$.—Triphenylantimony dichloride (4.2 g, 0.01 mol) in chloroform solution was added dropwise to a solution of antimony(v) chloride (2.5 cm^3, 0.02 mol) in the same solvent, leading to separation of a pale yellow oil. Crystallisation from carbon tetrachloride gave a white solid (Found: C, 21.5; H, 1.3; Cl, 40.9. Calc. for $C_{18}H_{15}Cl_{12}Sb_3$; C, 21.1; H, 1.8; Cl, 41.6%).

Table 6. Fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses, for $Ph_3SbCl_2{\cdot}SbCl_3$

Atom	*X/a*	*Y/b*	*Z/c*
Sb(1)	7 617.9(4)	2 873.0(3)	1 422.0(2)
Cl(1)	6 143(2)	4 440(2)	1 754(1)
Cl(2)	6 507(2)	2 920(2)	438.6(8)
Cl(3)	9 514(2)	4 254(1)	1 272.7(9)
Sb(2)	2 301.3(3)	766.3(3)	1 233.3(1)
Cl(4)	5 030(1)	920(1)	1 587.1(7)
Cl(5)	−395(1)	721(1)	889.1(6)
C(11)	2 414(5)	−1 157(5)	1 253(2)
C(12)	1 540(7)	−1 851(5)	823(3)
C(13)	1 677(8)	−3 116(6)	828(3)
C(14)	2 657(8)	−3 684(6)	1 256(4)
C(15)	3 517(8)	−3 015(6)	1 688(4)
C(16)	3 410(7)	−1 742(5)	1 684(3)
C(21)	2 651(5)	1 650(5)	433(2)
C(22)	3 255(7)	1 009(6)	6(3)
C(23)	3 495(8)	1 610(8)	−523(3)
C(24)	3 163(9)	2 809(8)	−606(3)
C(25)	2 561(10)	3 444(7)	−168(4)
C(26)	2 294(8)	2 868(6)	358(3)
C(31)	1 910(5)	1 793(5)	1 993(2)
C(32)	2 714(6)	2 856(5)	2 135(3)
C(33)	2 404(8)	3 552(7)	2 624(3)
C(34)	1 314(10)	3 178(8)	2 956(3)
C(35)	522(9)	2 123(7)	2 807(3)
C(36)	825(7)	1 431(6)	2 324(3)

Attempted Preparation of $Ph_3SbF_2{\cdot}SbCl_5$.—An immediate white precipitate separated when solutions of triphenylantimony difluoride and antimony(v) chloride were mixed. The solid was recrystallized from a 1 : 1 mixture of chloroform and carbon tetrachloride [Found: C, 30.4; H, 2.1; Cl, 28.4. Calc. for $C_{18}H_{15}Cl_5F_2Sb_2$ ($Ph_3SbF_2{\cdot}SbCl_5$): C, 31.3; H, 2.2; Cl, 25.7. Calc. for $C_{18}H_{15}Cl_6FSb_2$ ($Ph_3SbFCl{\cdot}SbCl_5$): C, 30.1; H, 2.1; Cl, 30.0%].

Structure of $Ph_3SbCl_2{\cdot}SbCl_3$.—*Crystal data.* $C_{18}H_{15}Cl_5Sb_2$, $M = 652.1$, monoclinic, $a = 9.118(4)$, $b = 10.888(4)$, $c = 22.435(8)$ Å, $\beta = 97.84(2)°$, $U = 2\,207$ Å^3, $Z = 4$, $D_c = 1.96$ g cm^{-3}, $F(000) = 1\,240$, space group $P2_1/c$ from systematic absences, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 30.7$ cm^{-1}, $\mu R = 0.90$.

Structure determination. Data for 3 396 reflections with $I > 3\sigma(I)$ were collected on a Hilger and Watts four-circle diffractometer for a crystal sealed in a thin-walled capillary and corrected for Lorentz and polarisation effects; no absorption correction was necessary. For data reduction and subsequent calculations the CRYSTALS programs [12] were used; scattering factors were those for neutral atoms.[13] The structure was solved by Patterson and Fourier methods and refined by full matrix, least-squares methods to $R = 0.078$ with isotropic and 0.044 with anisotropic thermal parameters. A difference-Fourier synthesis revealed the hydrogen atom positions. In subsequent cycles, however, these were not refined; application of a four-coefficient Chebyshev weighting scheme gave final convergence at $R = 0.038$.

Refined atomic co-ordinates for the heavy atoms are collected in Table 6.

Structure of $Ph_3SbCl_2{\cdot}SbCl_5$.—*Crystal data.* $C_{18}H_{15}Cl_7Sb_2$, $M = 723.0$, monoclinic, $a = 25.033(8)$, $b = 10.147(4)$, $c =$

Table 7. Fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses, for $[Ph_3SbCl][SbCl_6]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	981.4(8)	633(1)	2 029.4(8)
Cl(1)	202(3)	−998(6)	1 913(3)
Cl(2)	1 533(4)	942(8)	3 207(3)
Cl(3)	114(4)	2 244(7)	1 657(4)
Cl(4)	388(4)	230(7)	855(3)
Cl(5)	1 748(4)	2 221(7)	2 162(4)
Cl(6)	1 859(4)	−997(7)	2 430(4)
Sb(2)	3 981.9(9)	2 387(2)	459.5(8)
Cl(7)	3 072(4)	1 229(8)	−578(4)
C(11)	3 891(13)	1 484(24)	1 126(12)
C(12)	4 088(16)	146(30)	1 260(15)
C(13)	4 002(16)	−508(30)	1 650(15)
C(14)	3 725(15)	86(27)	1 892(14)
C(15)	3 559(15)	1 386(29)	1 764(14)
C(16)	3 661(15)	2 039(27)	1 389(14)
C(21)	4 880(12)	1 707(21)	634(11)
C(22)	5 486(14)	1 241(24)	1 301(12)
C(23)	6 101(17)	842(31)	1 452(16)
C(24)	6 127(17)	1 012(31)	944(17)
C(25)	5 531(18)	1 521(31)	282(17)
C(26)	4 929(14)	1 899(25)	147(13)
C(31)	3 553(13)	4 265(25)	78(13)
C(32)	3 385(15)	4 668(27)	−546(14)
C(33)	3 112(18)	5 942(33)	−797(17)
C(34)	3 031(17)	6 725(31)	−454(16)
C(35)	3 194(15)	6 399(28)	141(15)
C(36)	3 471(14)	5 166(26)	415(13)

26.043(8) Å, $\beta = 133.46(3)°$, $U = 4\,802$ Å^3, $Z = 8$, $D_c = 2.00$ g cm^{-3}, $F(000) = 2\,752$, space group $C2/c$ from systematic absences and subsequent refinement, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 30.5$ cm^{-1}, $\mu R = 0.76$.

Structure determination. Data were collected and treated as in the foregoing determination, for 2 746 observed reflections. During data collection, the intensity of the standard reflections decreased substantially, probably as a consequence of crystal deterioration in the *X*-ray beam. The refinement converged at $R = 0.119$ with isotropic and 0.084 with anisotropic thermal parameters and the hydrogen atoms fixed at their calculated positions.

Refined atomic co-ordinates for the heavy atoms are collected in Table 7.

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