Phenylchloroantimon(III)ates; their preparations, and the crystal structures of Me$_4$N[PhSbCl$_3$], [Hpy]$_2$[PhSbCl$_4$], and Me$_4$N[Ph$_2$SbCl$_2$]

Michael Hall and D. Bryan Sowerby *

Department of Chemistry, University of Nottingham, Nottingham, NG7 2RD (Great Britain)

(Received December 7th, 1987)

Abstract

Phenylantimony dichloride reacts with ionic chlorides such as Me$_4$NCl or HpyCl to give salts of both the [PhSbCl$_3$]$^-$ and [PhSbCl$_4$]$^{2-}$ anions, whereas the related diphenylantimony chloride will accept only one chloride ion to give [Ph$_2$SbCl$_2$]$^-$ salts. Under similar conditions, no anionic products are formed from Ph$_3$Sb. These results can be rationalised if chloride ion addition takes place *trans* to antimony–chlorine bonds in the starting material and the negative charge is delocalised via three-centre bonding in the resulting Cl–Sb $\cdots$ Cl$^-$ system. Structures have been determined by single crystal X-ray diffraction for Me$_4$N[PhSbCl$_3$] (a 9.214(5), b 11.499(5), c 16.179(6) Å, β 121.65(5)°, space group $P2_1/c$), [Hpy]$_2$[PhSbCl$_4$] (a 8.549(5), b 8.899(5), c 14.509(6) Å, α 100.16(5), β 90.09(4), γ 114.69(5)°, space group $P\bar{1}$) and Me$_4$N[Ph$_2$SbCl$_2$] (a 12.255(5), b 11.078(5), c 14.200(6) Å, β 112.28(5)°, space group $P2_1/n$). Me$_4$N[PhSbCl$_3$] contains a centrosymmetric, double chlorine-bridged dimeric anion, while the anions in both the [PhSbCl$_4$]$^-$ and [Ph$_2$SbCl$_2$]$^-$ salts are monomeric. Antimony–chlorine bond distances are discussed in terms of the delocalisation picture mentioned above.

Introduction

The formation of chloroanions such as [SbCl$_4$]$^-$, [Sb$_2$Cl$_9$]$^{3-}$, [SbCl$_5$]$^{2-}$ and [SbCl$_6$]$^{3-}$ by the successive addition of chloride ions *trans* to one of the original chlorines in SbCl$_3$ has been discussed previously [1], and leads to a rationalisation of the observed anion structures without the need to invoke stereochemical activity of the antimony 5s pair of electrons. Replacement of one or more of the chlorine atoms by phenyl groups will give Ph$_n$SbCl$_{3-n}$, with reduction of antimony Lewis acidity, but anion formation is probably still possible for $n = 1$ and 2. This topic has been little examined, and compounds previously described [2] as diazonium salts, ArN$_2$Cl · Ph$_2$SbCl, and assumed to contain the Ph$_2$SbCl$_2^-$ anion, were subsequently

[3] identified as impure samples of the related antimony(V) species, $ArN_2Cl \cdot Ph_2SbCl_3$. Pyridinium salts of $[RSbCl_3]^-$, where R = m-ClC_6H_4 and α- or β-naphthyl, are known [4], and more recently, among a series of $[PhSbX_3]^-$ salts, both $Me_4N[PhSbCl_3]$ and $Ph_4As[PhSbCl_3]$ were prepared as part of a Mössbauer investigation [5]. Because of the paucity of data in this area, we have systematically examined reactions of $PhSbCl_2$ and Ph_2SbCl with pyridinium chloride and tetramethylammonium chloride as the source of chloride ions, in order to assess the anion-forming capacity of the two phenyl substituted chlorides. Crystal structures have been determined for three of the isolated products.

Experimental

$PhSbCl_2$ and Ph_2SbCl were respectively prepared by interaction of 1/2 and 2/1 mixtures of Ph_3Sb with freshly sublimed $SbCl_3$ [6]. Pyridinium chloride and tetramethylammonium chloride were dried under vacuum.

[Hpy]₂[PhSbCl₄]

Phenylantimony dichloride (2.7 g, 10 mmol) was dissolved in anhydrous ethanol containing a small amount of anhydrous hydrogen chloride. A solution of pyridine (1.6 g, 20 mmol) in ethanol was added dropwise. The precipitate formed was collected and recrystallised from ethanol. (Found: C, 38.1; H, 3.6; N, 5.6; Cl, 29.0. $[Hpy]_2[PhSbCl_4]$ calc: C, 38.3; H, 3.4; N, 5.6; Cl, 28.3%.

Hpy[PhSbCl₃]

Pyridinium phenyltetrachloroantimonate (1.9 g, 5 mmol) and $PhSbCl_2$ (1.4 g, 5 mmol) were dissolved in the minimum of hot ethanol. Crystals of $Hpy[PhSbCl_3]$ separated on cooling. (Found: C, 33.9; H, 3.0; N, 3.5; Cl, 27.4. $Hpy[PhSbCl_3]$ calc: C, 34.2; H, 2.9; N, 3.6; Cl, 27.6%.)

Me₄N[PhSbCl₃]

This compound was prepared by co-crystallising a 1/1 mixture of Me_4NCl and $PhSbCl_2$ from anhydrous ethanol. (Found: C, 31.5; H, 4.4; N, 3.5. $Me_4N[PhSbCl_3]$ calc: C, 31.7; H, 4.5; N, 3.7%.)

[Me₄N]₂[PhSbCl₄]

Similarly this compound crystallised out from either a 2/1 molar ratio of the components or a mixture in which there was an excess of Me_4NCl. (Found: C, 34.7; H, 6.0; N, 5.9. $[Me_4N]_2[PhSbCl_4]$ calc: C, 34.4; H, 5.9; N, 5.7%.)

Me₄N[Ph₂SbCl₂]

This compound was prepared as above from either a 1/1 mixture of Me_4NCl and Ph_2SbCl or a mixture containing an excess of Me_4NCl. (Found: C, 44.9; H, 5.1; N, 3.5; Cl, 16.6. $Me_4N[Ph_2SbCl_2]$ calc: C, 45.6; H, 4.8; N, 3.3; Cl, 16.9%.)

Et₄N[Ph₂SbCl₂]

The tetraethylammonium salt was prepared as above. (Found: C, 50.0; H, 6.5; N, 2.7; Cl, 15.1. $Et_4N[Ph_2SbCl_2]$ calc: C, 50.3; H, 6.3; N, 2.9; Cl, 14.8%.)

Other experiments

Attempts using the same approach to produce either pyridinium or tetraalkylammonium salts from triphenylantimony or by using a 3/2 ratio of reactants to produce compounds analogous to the $[Sb_2Cl_9]^{3-}$ salts were unsuccessful.

Hydrochlorination of Ph₃Sb

A solution of triphenylantimony in ethanol containing one molar equivalent of pyridine, was cooled to 0 °C and anhydrous hydrogen chloride was passed in. After a considerable induction period, there was an exothermic reaction which raised the solution temperature near to the boiling point. The white solid formed on concentration of the solution and cooling was collected and fractionally crystallised from ethanol, and shown to be a complex mixture of compounds, of which Hpy[PhSbCl₃], [Hpy]₂[PhSbCl₄], Hpy[SbCl₄], [Hpy]₃[Sb₂Cl₉] and [Hpy]₂[SbCl₅] were identified by microanalysis, IR spectroscopy, and X-ray powder diffraction. The reaction is difficult to control and the ratio of monophenyl to inorganic antimony anions varied from ca. 1/1 to ca. 1/100 in ostensibly identical reactions. In no case was it possible to isolate anions containing two phenyl groups per antimony atom.

Vibrational spectra

IR data for the series Ph_nSbCl_{3-n} in the region below 500 cm^{-1} are listed for comparison purposes in Table 1, and the IR and Raman data for the compounds reported in this study are summarised in Table 2.

Crystal structures

Crystal structures were determined for Me₄N[PhSbCl₃], [Hpy]₂[PhSbCl₄] and Me₄N[Ph₂SbCl₂] using crystals grown by slow recrystallisation from ethanol and mounted on glass fibres. Crystal data for the three compounds are summarised in Table 3. Data were collected using a Hilger and Watts four circle diffractometer with Mo-K_α radiation and corrected for Lorentz and polarisation effects; no absorption correction was considered necessary. Data reduction and subsequent calculations used the CRYSTALS programs [7]; scattering factors were those for

Table 1

Infrared spectra (cm^{-1}) for the chlorides Ph_nSbCl_{3-n} with $n = 0$–3

Ph₃Sb	Ph₂SbCl	PhSbCl₂	SbCl₃	Assignment
460vs	460vs	450s		y modes
443sh			375vs ⎱ 355vsvbr ⎰	$\nu(SbCl_3)$
		340s 320vs	⎱ ⎰	$\nu(SbCl_2)$
	290vs			$\nu(SbCl)$
280vs			⎱	
272sh	272s		⎰	t modes
247m	250m	260s		
230w	230w			u modes
215,205m				

62

Table 2

IR spectral data (cm^{-1}) for phenylchloroantimonates

Ph$_2$SbCl$_2^-$			PhSbCl$_3^-$			PhSbCl$_4^{2-}$			Assignment
Et$_4$N$^+$	Me$_4$N$^+$		pyH	Me$_4$N$^+$		pyH$^+$	Me$_4$N$^+$		
IR	IR	R	IR	IR	R	IR	IR	R	
468s	463sh	462w	460s	460s	457w	463s	463s	456mw	y
452s	460s	454w							
			395vw			398vw			cation
		369vw			366vw			366vw	
			305s	300s	307s				ν(SbCl)
270m	278s	268m	255s	260s	251s	268s	262m	257s	t
255m	255s	248m							
232s	225s	228vs	240m	232s	225s	240vs	240vs	230sh	ν(SbCl)
		207vs					218s	225vs	
					217sh			204sh	u
					205m				
		175m			184w			186vw	
					157m			126sh	
		114s			112s			113sh	
		90vs			83s			90vs	
		86sh						78sh	
		64vs							
		44s							
		35vs							

neutral atoms [8]. The structures were each solved by Patterson and Fourier methods and refined by full-matrix least squares. In no case was it possible to define a complete set of hydrogen atom positions from the appropriate difference Fourier

Table 3

Crystal data

	Me$_4$N[PhSbCl$_3$] C$_{10}$H$_{17}$Cl$_3$NSb	[Hpy]$_2$[PhSbCl$_4$] C$_{16}$H$_{17}$Cl$_4$N$_2$Sb	[Me$_4$N][Ph$_2$SbCl$_2$] C$_{16}$H$_{22}$Cl$_2$NSb
M	379.4	500.9	421.0
a (Å)	9.214(5)	8.549(5)	12.255(5)
b (Å)	11.499(5)	8.899(5)	11.078(5)
c (Å)	16.179(6)	14.509(6)	14.200(6)
α (°)	90.0	100.16(5)	90.0
β (°)	121.65(5)	90.09(4)	112.28(5)
γ (°)	90.0	114.69(5)	90.0
U (Å^3)	1459.2	876.6	1796.4
D_c (g cm^{-3})	1.73	1.90	1.56
Z	4	2	4
$F(000)$	744	492	840
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
μ(cm^{-1})	24.3	21.9	18.4
μR	0.7	0.6	0.6
Observed reflections	2319	3203	2185
R	0.055	0.044	0.036

Table 4

Fractional coordinates ($\times 10^4$) for Me$_4$N[PhSbCl$_3$] with e.s.d.'s in parentheses

Atom	x/a	y/b	z/c
Sb(1)	3901.0(4)	1616.6(3)	174.1(2)
Cl(1)	4030(2)	3643(1)	−188(1)
Cl(2)	5682(2)	1042(1)	−629(1)
Cl(3)	2006(2)	2177(2)	815(1)
N(1)	7164(5)	1051(4)	3461(3)
C(1)	7085(12)	2239(7)	3106(6)
C(2)	7981(9)	1089(8)	4526(4)
C(3)	5443(10)	591(10)	3051(6)
C(4)	8111(14)	299(8)	3205(7)
C(11)	1623(6)	1279(4)	−1179(3)
C(12)	1186(7)	1958(5)	−1978(4)
C(13)	−309(8)	1749(5)	−2835(4)
C(14)	−1370(7)	865(6)	−2914(4)
C(15)	−936(7)	174(6)	−2132(5)
C(16)	545(7)	393(5)	−1268(4)

synthesis, and hydrogens were therefore placed at their calculated positions but were not refined in the final cycles. In all cases the reflections were assigned unit weights. Refined fractional coordinates of the non-hydrogen atoms are listed for the three

Table 5

Fractional coordinates ($\times 10^4$) for [pyH]$_2$[PhSbCl$_4$] with e.s.d.'s in parentheses

Atom	x/a	y/b	z/c
Sb(1)	2401.5(6)	4144.5(6)	2286.1(3)
Cl(1)	2815(3)	3396(3)	442(1)
Cl(2)	2231(3)	4749(3)	4088(1)
Cl(3)	1773(3)	1117(2)	2346(2)
Cl(4)	3411(3)	7554(3)	2357(2)
C(11)	5124(9)	4832(8)	2504(4)
C(12)	6281(10)	5823(10)	1935(5)
C(13)	8031(10)	6209(11)	2052(6)
C(14)	8652(11)	5635(13)	2705(7)
C(15)	7542(13)	4699(13)	3289(7)
C(16)	5762(11)	4298(10)	3188(5)
N(21)	5664(10)	2072(11)	766(6)
C(22)	5706(13)	1058(13)	1301(7)
C(23)	6965(15)	574(13)	1287(7)
C(24)	8255(13)	1129(14)	708(8)
C(25)	8227(14)	2184(15)	140(8)
C(26)	6895(17)	2661(13)	188(7)
N(31)	2396(10)	8835(10)	4322(5)
C(32)	3508(16)	511(13)	4407(8)
C(33)	6466(16)	8391(13)	4801(8)
C(34)	7517(16)	8981(14)	4118(8)
C(35)	8660(14)	753(14)	4232(7)
C(36)	1378(13)	8202(12)	4960(8)

Table 6

Fractional coordinates ($\times 10^4$) for $Me_4N[Ph_2SbCl_2]$ with e.s.d.'s in parentheses

Atom	x/a	y/b	z/c
Sb(1)	4204.9(5)	825.4(5)	1650.0(4)
Cl(1)	4121(2)	2775(2)	567(2)
Cl(2)	4529(2)	−1042(2)	2842(2)
C(1)	5979(7)	633(7)	1751(6)
C(2)	6821(7)	1502(8)	2224(6)
C(3)	7971(8)	1345(10)	2278(7)
C(4)	8273(9)	344(11)	1834(8)
C(5)	7440(9)	−501(9)	1378(7)
C(6)	6311(8)	−341(8)	1333(7)
C(7)	4532(7)	1990(7)	2935(7)
C(8)	5383(8)	1759(9)	3838(7)
C(9)	5551(10)	2475(10)	4658(7)
C(10)	4840(11)	3470(10)	4582(9)
C(11)	3981(11)	3720(9)	3680(9)
C(12)	3809(8)	3003(9)	2848(7)
N(1)	1940(6)	1234(6)	4735(5)
C(21)	1991(8)	697(9)	5700(7)
C(22)	2849(9)	708(9)	4398(8)
C(23)	769(8)	1040(9)	3969(7)
C(24)	2105(10)	2569(9)	4876(8)

compounds in Tables 4–6. Tables of thermal parameters and lists of calculated and observed structure factors are available from the authors.

Results and discussion

Chloroanions based on both $PhSbCl_2$ and Ph_2SbCl can be readily produced by simple methods such as co-crystallisation from EtOH of a mixture of an ionic chloride, e.g. Me_4NCl and [Hpy]Cl, and the phenylantimony(III) chloride.

Hydrochlorination of Ph_3Sb in the presence of pyridine offered a possible alternative route since triphenylantimony is known to react with refluxing methanolic hydrogen chloride to give diphenylantimony chloride [9]. We confirmed that this reaction does occur, but is difficult to control and leads to a non-reproducible mixture of inorganic and monophenylated antimony anions. This approach was therefore not continued.

It is significant that one or two chloride ions can be added to $PhSbCl_2$ giving $[PhSbCl_3]^-$ and $[PhSbCl_4]^{2-}$ species, but even in the presence of a large excess of an ionic chloride the potential third member of the series $[PhSbCl_5]^{3-}$, the analogue of $[SbCl_6]^{3-}$, could not be produced in ethanol solution. Similarly, Ph_2SbCl would apparently add only one chloride ion, to give $[Ph_2SbCl_2]^-$ salts irrespective of the amount of excess added ionic chloride, and with triphenylantimony itself there was no evidence for anion formation of any kind.

These observations are in keeping with the expected reduction in antimony Lewis acidity with increasing phenyl substitution, but the fact that the maximum coordination numbers for antimony in the anions derived from $PhSbCl_2$ and Ph_2SbCl are five and four, respectively, and the observed non-formation of anions with Ph_3Sb can be interpreted to give potential structural information.

We have previously noted that purely inorganic chloroantimonate anions can be considered to arise by successive additions of chloride ions *trans* to the chlorine atoms in $SbCl_3$ [1]. The original $SbCl_3$ molecule, in keeping with its ca. 90° bond angles, is considered to be bonded via *p*-orbitals, rather than some form of *sp* hybrids. The electron densities in both the Sb–Cl and the initially formed Sb $\cdots$ Cl^- bonds may then undergo reorganisation until in the limit they are equal and the charge is equally shared between the two *trans* chlorides. This is equivalent to treating each Cl–Sb $\cdots$ Cl^- system as a three-centre four-electron unit, and there will be an inverse relationship between the length of Sb–Cl bonds *trans* to each other. The simplest application of this approach presupposes the formation of monomeric anions, but it is readily extended [10] to the polymeric structures often found for compounds with the stoichiometries $M[SbCl_4]$ [11], $M_3[Sb_2Cl_9]$ [1,12], and $M_2[SbCl_5]$ [13], where the interrelationship between the lengths and strengths of *trans* Sb–Cl bonds is maintained.

Structural data are not available for either Ph_2SbCl or $PhSbCl_2$ but their bond angles are likely to be close to 90° (angles in (p-tolyl)$SbCl_2$, for example, average 93.6° [14]), and each can be treated in the same way as $SbCl_3$ above as the starting point for anion formation.

If it is assumed in the first instance that monomeric units will be formed, chloride ions can approach *trans* to chlorines already present with consequent delocalisation of the ionic charge and stabilisation of the system. Approach of a chloride ion *trans* to a phenyl group, on the other hand, will not allow bond reorganisation and charge delocalisation via a three centre system, and so does not take place. If this is correct then, as shown in Fig. 1, $PhSbCl_2$ will be the basis for $[PhSbCl_3]^-$ (see-saw structure) and $[PhSbCl_4]^{2-}$ (square pyramidal with an apical phenyl group) while Ph_2SbCl will give only $[Ph_2SbCl_2]^-$ (see-saw structure). If more complex structures arise through chlorine-bridging, as for inorganic chloroantimonates, the coordination position *trans* to the organic group would still remain vacant, effectively limiting chlorine bridge formation to the $[PhSbCl_3]^-$ anion.

Vibrational spectra

Complications arise when the chlorine atoms on antimony trichloride are substituted successively by phenyl groups, owing to the multiplicity of modes associated with the organic group. Following Whiffen's notation [15], the *y*, *t* and *u* modes occur in the region below 500 cm^{-1}, but it is the *t* mode which shows the greatest change upon phenyl substitution (see Table 1). The mean energy, however, remains essentially constant, implying that the antimony–carbon bond strengths in the neutral compounds are also approximately constant. There are, however, substantial
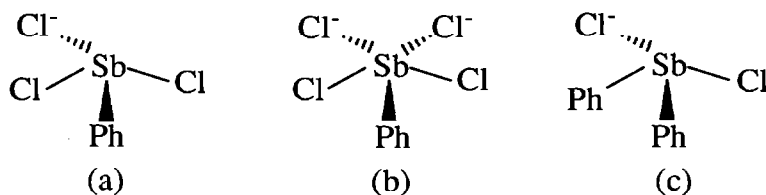
Fig. 1. Formation of (a) $[PhSbCl_3]^-$ and (b) $[PhSbCl_4]^{2-}$ ions from $PhSbCl_2$ and (c) $[Ph_2SbCl_2]^-$ from Ph_2SbCl by addition of chloride ions *trans* to chlorine atoms in $PhSbCl_2$ and Ph_2SbCl.

decreases in the mean energy of the antimony–chlorine stretching vibration, suggesting a progressive weakening of Sb–Cl interaction with increased phenyl group substitution. There are no crystallographic data for either of the phenylantimony(III) chlorides, but this conclusion is supported by the larger Sb–Cl distance in (p-tolyl)SbCl$_2$ (2.38 Å) [14] compared with that in SbCl$_3$ (2.36 Å) [16]; this is paralleled in the corresponding fluorine series, where the mean Sb–F bond length is SbF$_3$ (1.93 Å) [17] increases to 2.17 Å in Ph$_2$SbF [18].

The data in Table 2 show that spectra in the region below 500 cm^{-1} are little affected by cation change, though there appears to be a larger splitting in the y mode for the [Ph$_2$SbCl$_2$]$^-$ anion when the counterion is tetraethylammonium. As with the neutral phenylantimony chlorides, Sb–Cl stretching vibrations are of most interest and immediately obvious are the decrease in the energy of this mode with increase in the charge on the anion and with increase in the number of phenyl groups, implying a weakening and consequent lengthening of the Sb–Cl bonds in each case. It is difficult to draw any further clear structural conclusions, but data for [Ph$_2$SbCl$_2$]$^-$ that show two components for both the phenyl t mode and Sb–Cl stretching could indicate a monomeric structure, while complexity in the Sb–Cl stretching region for [PhSbCl$_3$]$^-$ could indicate a more highly polymerised solid state structure. These problems have been resolved by determining crystal structures for Me$_4$N[PhSbCl$_3$], [Hpy]$_2$[PhSbCl$_4$] and Me$_4$N[Ph$_2$SbCl$_2$].

Structural studies

Important bond distances and angles are listed in Tables 7–9 for Me$_4$N[PhSbCl$_3$], [Hpy]$_2$[PhSbCl$_4$] and Me$_4$N[Ph$_2$SbCl$_2$] respectively, and diagrams showing the structures and atom numbering schemes are in Figs. 2–4, respectively. It is clear from these that predictions of monomeric structures for both [PhSbCl$_4$]$^-$ and [Ph$_2$SbCl$_2$]$^-$, with chlorine atoms absent from positions *trans* to phenyl groups, are

Table 7

Bond distances (Å) and angles (°) for Me$_4$N[PhSbCl$_3$], with e.s.d.'s in parentheses

Sb(1)–C(11)	2.12(1)
Sb(1)–Cl(1)	2.423(3)
Sb(1)–Cl(2)	2.657(3)
Sb(1)–Cl(2′) [a]	3.121(4)
Sb(1)–Cl(3)	2.540(4)
C(11)–Sb(1)–Cl(1)	94.0(3)
C(11)–Sb(1)–Cl(2)	88.7(3)
C(11)–Sb(1)–Cl(2′)	89.8(3)
C(11)–Sb(1)–Cl(3)	86.9(3)
Cl(1)–Sb(1)–Cl(2)	89.6(1)
Cl(1)–Sb(1)–Cl(2′)	169.9(1)
Cl(1)–Sb(1)–Cl(3)	89.1(1)
Cl(2)–Sb(1)–Cl(2′)	80.9(1)
Cl(2)–Sb(1)–Cl(3)	175.4(1)
Cl(2′)–Sb(1)–Cl(3)	100.4(1)
Sb(1)–Cl(2)–Sb(2′)	99.1(1)

[a] Cl(2′) is related to Cl(2) by the symmetry operation 1 − x, − y, − z.

Table 8

Bond distances (Å) and angles (°) for $(pyH)_2[PhSbCl_4]$ with e.s.d.'s in parentheses

Sb(1)–C(11)	2.157(9)
Sb(1)–Cl(1)	2.702(3)
Sb(1)–Cl(2)	2.591(3)
Sb(1)–Cl(3)	2.537(3)
Sb(1)–Cl(4)	2.770(3)
Cl(1)···N(21)	3.17(1)
Cl(4)···N(31)	3.12(1)
C(11)–Sb(1)–Cl(1)	85.4(2)
C(11)–Sb(1)–Cl(2)	89.9(2)
C(11)–Sb(1)–Cl(3)	89.4(3)
C(11)–Sb(1)–Cl(4)	85.0(3)
Cl(1)–Sb(1)–Cl(2)	174.1(1)
Cl(1)–Sb(1)–Cl(3)	86.9(1)
Cl(1)–Sb(1)–Cl(4)	99.9(1)
Cl(2)–Sb(1)–Cl(3)	89.6(1)
Cl(2)–Sb(1)–Cl(4)	87.2(1)
Cl(3)–Sb(1)–Cl(4)	173.6(1)
Sb(1)–Cl(1)···N(21)	95.3(3)
Sb(1)–Cl(4)···N(31)	104.5(3)

Table 9

Bond distances (Å) and angles (°) for $Me_4N[Ph_2SbCl_2]$ with e.s.d.'s in parentheses

Sb(1)–C(1)	2.137(8)
Sb(1)–C(7)	2.150(8)
Sb(1)–Cl(1)	2.631(2)
Sb(1)–Cl(2)	2.611(2)
C(1)–Sb(1)–C(7)	97.5(3)
C(1)–Sb(1)–Cl(1)	86.8(2)
C(1)–Sb(1)–Cl(2)	88.0(2)
C(7)–Sb(1)–Cl(1)	87.6(2)
C(7)–Sb(1)–Cl(2)	89.3(2)
Cl(1)–Sb(1)–Cl(2)	173.6(1)
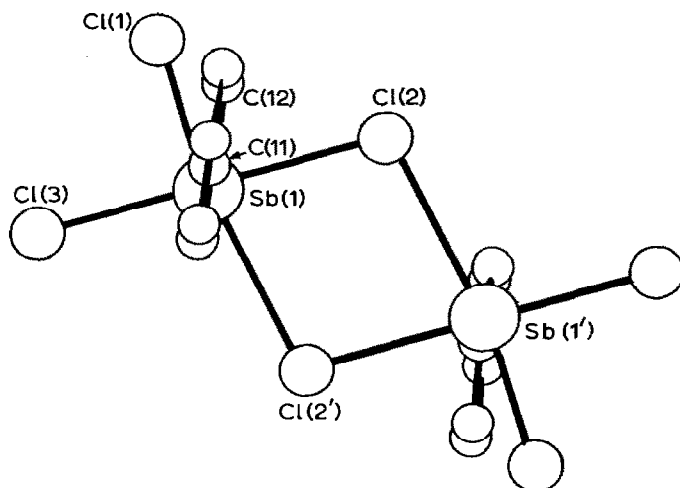
Fig. 2. Structure of the $[PhSbCl_3]^-$ anion.
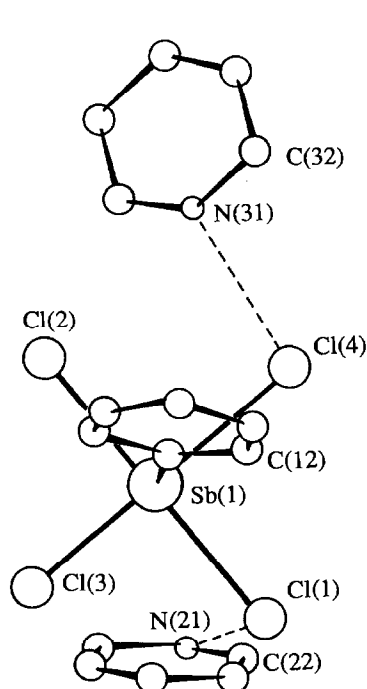
Fig. 3. Structure of [Hpy]₂[PhSbCl₄].
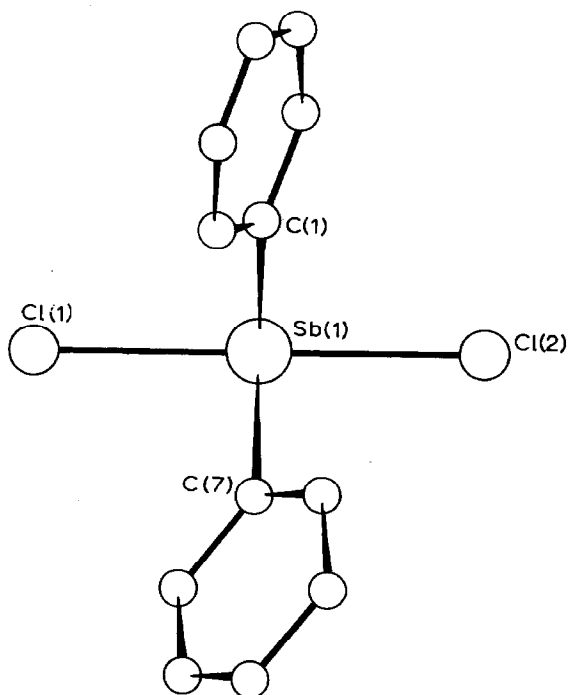
Fig. 4. Structure of the [Ph₂SbCl₂]⁻ anion.

borne out. The possibility of chlorine-bridge formation, suggested by the more complex vibrational spectra of [PhSbCl₃]⁻, is also realised in the observed dimeric structure. There are, however, instances where the structure adopted by a specific chloroantimonate stoichiometry varies with cation [11,13], and this possibility should be borne in mind in the present cases.

Me₄N[PhSbCl₃]

The anion here is a centrosymmetric dimer (see Fig. 2), with antimony in square pyramidal coordination to an apical phenyl group and a basal system of four chlorine atoms, similar to that in Pr₄N[SbCl₄] [19]. There are no interactions of the anion with the tetrahedral cation, which has angles in the 107.0(7)–111.0(7)° range and a mean C–N distance of 1.48 Å. There are no unusual features associated with the phenyl group. The Sb–Cl distances range between 2.423(3) and 3.121(4) Å, (cf. 2.32 Å for a single bond and ca. 4.0 Å for the sum of the Van der Waals radii), clearly all greater than 2.32 Å, the 'statistically determined' single bond distance [1,10]. The relationship between the lengths of *trans* related Sb–Cl contacts, i.e. 2.423(3), 3.121(4) and 2.540(4), 2.657(3) Å, however, points to the validity of the approach used above in that *trans* related contacts can range between a single bond–Van der Waals contact in one limit to two bonds of 0.5 order in the other limit as electron density in the Cl–Sb · · · Cl⁻ system is reorganised.

[Hpy] ₂[PhSbCl₄]

With the addition of a second chloride ion to $PhSbCl_2$, the structure reverts to monomeric, with again a square pyramidal arrangement of atoms about antimony. The phenyl group is again axial (see Fig. 3), but the spread of Sb–Cl contacts, 2.537(3)–2.770(3) Å, is as expected lower than in the previous case since none of the chlorine atoms is bridging. This system is slightly more complicated because owing to difficulties in growing crystallographic quality crystals of $[Me_4N]_2[PhSbCl_4]$ the structure determined was that of the pyridinium salt, in which the cation is potentially hydrogen bonding. Although the hydrogen atoms were not located, the close separation between Cl(1) and N(21) and Cl(4) and N(31) implies a measure of hydrogen bonding and this added interaction with two of the chlorine atoms will slightly modify the *trans* related Sb–Cl distances.

These distances do, however, fall into the expected pattern, the shortest, Sb(1)–Cl(3) 2.537(3) Å, being *trans* to the longest, Sb(1)–Cl(4) 2.770(3) Å, while the Sb(1)–Cl(1) and Sb(1)–Cl(2) distances fall between these limits and are more nearly equal. As expected, hydrogen bonding involves Cl(1) and Cl(4), i.e. those atoms involved in the longest Sb–Cl distances and thus carrying a greater proportion of the anion charge.

Me₄N[Ph₂SbCl₂]

This monomeric anion (see Fig. 4) has a see-saw structure (pseudo-trigonal bipyramidal) with phenyl groups in equatorial positions and axially placed chlorines. The latter differ slightly in length, but the mean distance, 2.62 Å, is exactly that calculated by Hall [1,10] for the half bond distance achieved when electron density in the two parts of an initial Cl–Sb · · · Cl⁻ system becomes equal. It is significant that again there are no chlorine interactions *trans* to the phenyl groups. As in the first compound, there are no close intermolecular contacts and the dimensions of the cation and the phenyl groups present no unusual features.

Conclusions

One of the major reasons for investigating the chemistry and, in particular, the structures of compounds of this type is to obtain evidence on whether or not the antimony lone pair is stereochemically active. A major factor in any discussion of this topic is the regular octahedral geometry of the anion in $[Co(NH_3)_6][SbCl_6]$ [20]. Few structures containing the $[SbCl_6]^{3-}$ ion are known; that with the diethylene-triammonium cation [21] is distorted octahedral but the distortion is ascribed directly to hydrogen bonding effects. Bromide systems have been more extensively investigated, and $[SbBr_6]^{3-}$ ions with close to regular octahedral geometry are found in the mixed oxidation state compounds $[NH_4]_4[Sb^{III}Br_6][Sb^VBr_6]$ [22] and $[Hpy]_6[Sb^{III}Br_6][Sb^VBr_6]_3$ [23], and in $[Pr_2NH_2]_3[SbBr_6]$ [24]. Hydrogen bonding in the latter involves each of the bromine atoms and gives rise to no distortion, while anion distortion in the corresponding diethylammonium salt [24] is produced by less symmetrical hydrogen bonding.

In $[SbX_6]^{3-}$ systems, therefore, the lone pair is not stereochemically active, and this throws doubts on the conventional (VSEPR) approach to bonding in $[SbCl_4]^-$ and $[SbCl_5]^{2-}$. Certainly the structures can be rationalised on this basis, but there is no certainty that the electron pair actually occupies the available position in the coordination polyhedron.

The overall structures of the $[PhSbCl_3]^-$, $[PhSbCl_4]^{2-}$ and $[Ph_2SbCl_2]^-$ ions determined during this work can similarly be rationalised on VSEPR arguments, but not all the expected details are observed. For example, a stereochemically active lone pair would lead to the antimony atom lying below the basal plane of chlorines in both $[PhSbCl_3]^-$ and $[PhSbCl_4]^{2-}$, but in the former antimony actually lies in the best plane through the four chlorine atoms, although they themselves deviate in pairs by ca. 0.1 Å above [Cl(2) and Cl(3)] and below [Cl(1) and Cl(2')] the mean plane. In $[PhSbCl_4]^{2-}$ antimony does lie ca. 0.1 Å below the mean plane through the chlorine atoms (mean deviation ca. 0.01 Å), and in $[Ph_2SbCl_2]^-$ the angles between the phenyl groups (97.5°) and the *trans* chlorines (173.6°) are reduced from trigonal bipyramidal ideal, as expected as a result of lone pair repulsion.

It is not easy to extend the VSEPR approach to rationalise the interrelationship between the lengths of *trans* Sb–Cl bonds, but this follows directly from the three-centre four-electron approach, where the antimony lone pair is localised. Although there is not direct proof of the validity of this assertion, it does lead to a more ready rationalisation of the major structural features of the chloroantimonates.

References

1 M. Hall, M. Nunn, M.J. Begley and D.B. Sowerby, J. Chem. Soc., Dalton Trans., (1986) 1231.
2 A.B. Bruker and N.M. Nikiforova, Zh. Obsh. Khim., 18 (1948) 1132.
3 D.A. Reutov, O.A. Ptitsyna, A.N. Lovtsova and V.F. Petrova, J. Gen. Chem. USSR, 29 (1959) 3848.
4 P. Pfeiffer and P. Schmidt, J. Prakt. Chem., 152 (1939) 27.
5 G. Alonzo, N. Bertazzi, F. Di Bianca and T.C. Gibb, J. Organomet. Chem., 210 (1981) 63.
6 M. Nunn, D.B. Sowerby and D.M. Wesolek, J. Organomet. Chem., 251 (1983) C45.
7 J.R. Caruthers, CRYSTALS, the Oxford Crystallographic Programs (1975).
8 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham (1974) Vol. 4.
9 G.O. Doak and L.D. Freedman, Organometallic Compounds of Arsenic, Antimony and Bismuth, Wiley-Interscience, New York, 1970.
10 M. Hall, PhD Thesis, University of Nottingham (1980).
11 See for example, A. Lipka, Z. Anorg. Allg. Chem., 469 (1980) 218; U. Ensinger, W. Schwarz and A. Schmidt, Z. Naturforsch. B, 37 (1982) 1584; S. Blösl, W. Schwarz and A. Schmidt, Z. Naturforsch. B, 38 (1983) 149; S.K. Porter and R.A. Jacobson, J. Chem. Soc. A, (1970) 1356; D. Brodalla and A. Lipka, Z. Naturforsch. B, 39 (1984) 1167.
12 K. Kihara and T. Sudo, Z. Kristallogr., 134 (1971) 142; K. Kihara and T. Sudo, Acta Crystallogr. Sect. B, 30 (1974) 1088.
13 B. Kruss and M.L. Ziegler, Z. Anorg. Allg. Chem., 388 (1972) 158; A. Lipka, Z. Anorg. Allg. Chem., 469 (1980) 229; A. Lipka, Z. Naturforsch. B, 38 (1983) 1615.
14 D.B. Sowerby and D.M. Wesolek, unpublished results.
15 D.H. Whiffen, J. Chem. Soc., (1956) 1350.
16 A. Lipka, Acta Crystallogr., Sect. B, 35 (1979) 3020.
17 A.J. Edwards, J. Chem. Soc. A, (1970) 2750.
18 S.P. Bone and D.B. Sowerby, J. Chem. Soc., Dalton Trans., (1979) 1430.
19 U. Ensinger, W. Schwarz and A. Schmidt, Z. Naturforsch. B, 37 (1982) 1584.
20 D.R. Schroeder and R.A. Jacobson, Inorg. Chem., 12 (1973) 210.
21 I.M. Vezzosi, L.P. Battaglia and A.M. Corradi, Inorg. Chim. Acta, 89 (1984) 151.
22 S.L. Lawton and R.A. Jacobson, Inorg. Chem., 5 (1966) 743.
23 S.L. Lawton, R.A. Jacobson and R.S. Frye, Inorg. Chem., 10 (1971) 701.
24 T. Okuda, M. Hiura, E. Koshimizu, H. Ishihara, T. Kushi and H. Negita, Chem. Lett., (1982) 1321.