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Preparation and crystal structures of five organoantimony halides; (*p*-tolyl)antimony(III) dichloride and dibromide, diphenylantimony(III) bromide, (biphenyl-2,2′-diyl)antimony(III) chloride and bis-(2′-chlorobiphenyl-2-yl)antimony(V) trichloride

Peter L. Millington and D. Bryan Sowerby

Department of Chemistry, University of Nottingham, Nottingham NG7 2RD (UK)

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Abstract

Crystal structures are reported for four organoantimony(III) halides, *i.e.* (*p*-tolyl)antimony dichloride (1) and dibromide (2), diphenylantimony bromide (3), (biphenyl-2,2′-diyl)antimony chloride (4) and a new antimony(V) compound, bis(2′-chlorobiphenyl-2-yl)antimony(V) trichloride (5), obtained by oxidising (4) with an excess of chlorine. The two tolyl compounds (1) and (2), which are isostructural and also isostructural with the corresponding phenyl derivatives, contain pyramidal $CSbX_2$ units. These are interlinked by (a) two weak intermolecular Sb ··· halogen interactions (mean 3.54 and 3.69 Å for the chloride and bromide, respectively), raising the antimony coordination number to five giving infinite chains, and (b) weak contacts between antimony and three of the carbon atoms of a symmetry-related tolyl group (mean 3.41 and 3.42 Å for the chloride and bromide, respectively).

There are no intermolecular Sb ··· Br contacts in 3 but two Sb ··· C interactions (mean 3.64 Å) interconnect the pyramidal monomers. Such Sb ··· C interactions (mean 3.43 Å) are also present in the biphenylyl derivative 4, in which the C–Sb–C angle in the pyramidal monomer is constrained to 81.0° by the short bite of the biphenylyl group. Loose dimers are formed in the solid state by Sb ··· Cl contacts at 3.71 Å.

In contrast to the chlorine bridged dimeric structure of Ph_2SbCl_3, compound 5 is a distorted trigonal bipyramidal monomer in the solid state, providing the first example of an antimony(V) compound with chlorine atoms in both axial and equatorial sites. As expected, distances to the two axial chlorines are substantially longer (2.420(3), 2.421(3) Å) than that to the equatorial atom (2.280(3) Å). The greatest distortion is shown by the equatorial C–Sb–C angle, which is increased to 137.1°, probably as a consequence of the steric requirements of the bulky chlorobiphenylyl groups.

Key words: Antimony; Crystal structure; Halide; Group 15; Biphenyl

1. Introduction

Secondary bonding plays an important role in the solid state structures of antimony(III) halides, effectively raising the antimony coordination number in the trichloride to eight, with three short contacts (2.340(2)–2.368(1) Å) and five longer ones (3.457(1)–3.736(1) Å) [1]. In the corresponding bromide [2] and iodide [3], in which the heavier halogens are either close packed or nearly so, antimony forms distorted octahedral units with three short (*ca.* 2.49 Å for the bromide and *ca.* 2.76 Å for the iodide) and three longer contacts (*ca.* 3.60 and 3.70 Å for the bromide and iodide, respectively). In all three compounds, successive substitution of halogen atoms by organic groups will reduce the Lewis acidity of the antimony centre and consequently weaken such secondary interactions. Clearly, no secondary interactions are to be expected in triorganostibines.

Recently reported structures for $PhSbX_2$, where X = Cl, Br or I, show that in addition to two secondary Sb ··· X contacts, there is further interaction between antimony and a symmetry-related phenyl group [4]. This is probably similar to that in the well-known Menshutkin complexes but here there are shorter con-

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Correspondence to: Dr. D.B. Sowerby.

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tacts to three of the ring carbon atoms. Similar problems of secondary bonding with halogen [5] and phenyl [6] groups are encountered in derivatives of neighbouring elements, in particular, tin and tellurium.

We have synthesised and determined the structures of two *p*-tolyl derivatives, $MeC_6H_4SbX_2$, where X = Cl (**1**) or Br (**2**), for comparison with those of the corresponding phenyl compounds and to assess the effect of introducing an electron donating methyl group into the phenyl ring. The effects of diorganosubstitution are assessed by an investigation of the structures of both Ph_2SbBr (**3**) and the constrained analogue, (biphenyl-2,2′-diyl)antimony chloride (**4**). Oxidation of the latter with elemental chlorine yields the related trichloride [7], an analogue of the previously investigated biphenyl-2,2′-diyltriphenylantimony [8], but the trichloride is unstable and crystals suitable for X-ray investigation could not be obtained. Reaction with an excess of chlorine, on the other hand, gave a rearrangement product, bis(2′-chlorobiphenyl-2-yl)antimony(V) trichloride (**5**), and the crystal structure of this compound has also been determined.

2. Experimental section

2.1. Preparations

Tri-*p*-tolylantimony was prepared as previously described from anhydrous *p*-bromotoluene, lithium metal and antimony trichloride in ether [9].

2.1.1. p-Tolylantimony dichloride (1)

A mixture of tri-*p*-tolylantimony (4.00 g, 10.1 mmol) and freshly sublimed antimony trichloride (4.63 g, 20.3 mmol) in a stoppered flask was warmed gently to give a viscous liquid [10]. The mixture was shaken overnight to complete the reorganisation and then recrystallised from anhydrous dichloromethane to give white crystals. Yield, 5.1 g, 59%. M.p. 93°C. (Found: C, 29.4; H, 2.4. $C_7H_7Cl_2Sb$: calc.: C, 29.6, H, 2.5%).

2.1.2. p-Tolylantimony dibromide (2)

The method described above was used but starting from tri-*p*-tolylantimony (4.0 g, 10.1 mmol) and freshly sublimed antimony tribromide (7.33 g, 20.3 mmol). Recrystallisation from anhydrous dichloromethane gave white crystals, which turned brown on exposure to the atmosphere. Yield, 6.3 g, 56%. M.p. 83–84°C. (Found: C, 22.4; H, 1.8. $C_7H_7Br_2Sb$: calc.: C, 22.8, H, 1.9%).

2.1.3. Diphenylantimony bromide (3)

This was also prepared as described above but from triphenylantimony (6.61 g, 18.7 mmol) and freshly sublimed antimony tribromide (3.39 g, 9.38 mmol). Crystallisation from dichloromethane gave material suitable for X-ray analysis. (Found: C, 39.8; H, 2.8. $C_{12}H_{10}BrSb$: calc.: C, 40.5, H, 2.8%).

2.1.4. (Biphenyl-2,2′-diyl)antimony chloride (4)

This was prepared as described previously [7] from biphenyl-2,2′-diylcadmium. The cadmium salt (5.2 g, 20

TABLE 1. Crystal data

Compound	1	2	3	4	5
Formula	$C_7H_7Cl_2Sb$	$C_7H_7Br_2Sb$	$C_{12}H_{10}BrSb$	$C_{12}H_8ClSb$	$C_{24}H_{16}Cl_5Sb$
M	283.7	372.6	355.7	309.2	603.1
Crystal system	triclinic	triclinic	monoclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	*Pbcn*	$P2_1/c$
a (Å)	7.551(4)	7.640(4)	11.997(5)	13.595(5)	7.570(4)
b (Å)	7.636(4)	7.906(4)	8.776(4)	11.170(5)	17.723(6)
c (Å)	8.899(5)	9.123(5)	11.164(5)	13.853(6)	16.977(6)
α (°)	108.62(3)	109.98(3)			
β (°)	87.16(3)	85.53(3)	92.08(3)		98.01
γ (°)	110.37(3)	110.58(3)			
V (Å^3)	454.8	484.3	1174.6	2103.7	2255.5
Z	2	2	4	8	4
D_c (g cm^{-3})	2.07	2.55	2.01	1.95	1.78
F (000)	268	340	672	1184	1184
μ (Mo Kα) (cm^{-1})	35.7	115.5	59.4	28.5	18.3
Crystal size (mm)	0.45 × 0.3 × 0.15	0.5 × 0.3 × 0.2	–	–	–
Observed reflections	1522	1512	1599	1743	2829
Final R (%)	3.01	6.04	4.55	4.28	6.21
Final R_w (%)	3.83	8.38	5.17	4.37	7.34

TABLE 2. Atomic coordinates, with estimated standard deviations in parentheses, for (*p*-tolyl)$SbCl_2$ (**1**)

Atom	x	y	z	U_{eq}
Sb(1)	0.19062(6)	0.33196(6)	0.02333(5)	0.0346
Cl(1)	0.2115(3)	0.1156(3)	0.1570(2)	0.0488
Cl(2)	−0.0570(2)	0.4119(3)	0.1766(2)	0.0461
C(1)	0.4062(9)	0.5860(9)	0.1773(8)	0.0345
C(2)	0.440(1)	0.764(1)	0.1504(8)	0.0400
C(3)	0.576(1)	0.938(1)	0.2490(9)	0.0422
C(4)	0.6759(9)	0.935(1)	0.3733(8)	0.0400
C(5)	0.643(1)	0.755(1)	0.3968(9)	0.0475
C(6)	0.509(1)	0.582(1)	0.2998(9)	0.0450
C(7)	0.818(1)	1.123(1)	0.479(1)	0.0568

mmol) was stirred with resublimed antimony trichloride (4.48 g, 20 mmol) at −70°C in ether and the solution allowed to warm to room temperature. After 48 h water was added and the insoluble material filtered off and extracted with ether. The ether solutions were combined, dried over anhydrous sodium sulfate and reduced in volume, to yield on cooling pale yellow crystals of the compound. Yield, 2.6 g, 42%. M.p. 204–205°C. (Found: C, 46.3; H, 2.9; Cl, 11.3. $C_{12}H_8ClSb$ calc.: C, 46.5; H, 2.6; Cl, 11.5%).

TABLE 3. Atomic coordinates, with estimated standard deviations in parentheses, for (*p*-tolyl)$SbBr_2$ (**2**)

Atom	x	y	z	U_{eq}
Sb(1)	0.1948(1)	0.3371(1)	0.03036(8)	0.0370
Br(1)	0.2169(2)	0.1101(2)	0.1596(1)	0.0491
Br(2)	−0.0689(2)	0.4220(2)	0.1925(1)	0.0483
C(1)	0.408(2)	0.585(2)	0.181(1)	0.0364
C(2)	0.441(2)	0.758(2)	0.156(1)	0.0393
C(3)	0.574(2)	0.922(2)	0.251(1)	0.0412
C(4)	0.673(2)	0.926(2)	0.373(1)	0.0417
C(5)	0.640(2)	0.752(2)	0.393(1)	0.0513
C(6)	0.509(2)	0.584(2)	0.298(1)	0.0465
C(7)	0.809(2)	1.109(2)	0.478(2)	0.0499

TABLE 4. Atomic coordinates, with estimated standard deviations in parentheses, for Ph_2SbBr (**3**)

Atom	x	y	z	U_{eq}
Sb(1)	0.22906(4)	0.16609(7)	0.53194(4)	0.0560
Br(1)	0.29704(7)	0.4047(1)	0.42619(9)	0.0658
C(11)	0.3200(6)	0.0094(8)	0.4254(7)	0.0480
C(12)	0.3319(6)	0.0284(9)	0.3048(7)	0.0531
C(13)	0.3964(7)	−0.074(1)	0.2420(8)	0.0630
C(14)	0.4487(7)	−0.193(1)	0.2993(9)	0.0660
C(15)	0.4356(7)	−0.2128(9)	0.419(1)	0.0692
C(16)	0.3726(6)	−0.110(1)	0.4842(7)	0.0576
C(21)	0.0730(6)	0.1613(9)	0.4311(7)	0.0513
C(22)	0.0506(6)	0.060(1)	0.3392(7)	0.0557
C(23)	−0.0532(7)	0.063(1)	0.2786(8)	0.0645
C(24)	−0.1329(7)	0.167(1)	0.3099(8)	0.0671
C(25)	−0.1110(7)	0.267(1)	0.403(1)	0.0736
C(26)	−0.0067(7)	0.264(1)	0.4642(8)	0.0678

TABLE 5. Atomic coordinates, with estimated standard deviations in parentheses, for (biphenyl-2,2′-diyl) antimony chloride (**4**)

Atom	x	y	z	U_{eq}
Sb(1)	0.01622(2)	0.21980(3)	0.00928(2)	0.0457
Cl(1)	−0.05586(9)	0.0849(1)	−0.10797(9)	0.0519
C(1)	−0.0672(3)	0.3715(4)	−0.0456(3)	0.0430
C(2)	−0.0350(4)	0.4430(4)	−0.1214(3)	0.0487
C(3)	−0.0933(4)	0.5420(4)	−0.1458(3)	0.0530
C(4)	−0.1760(4)	0.5671(4)	−0.0922(4)	0.0537
C(5)	−0.2034(4)	0.4959(4)	−0.0156(3)	0.0493
C(6)	−0.1473(3)	0.3958(4)	0.0089(3)	0.0417
C(7)	−0.1718(3)	0.3137(4)	0.0888(3)	0.0390
C(8)	−0.1049(3)	0.2194(4)	0.1073(3)	0.0417
C(9)	−0.1221(4)	0.1404(4)	0.1818(3)	0.0493
C(10)	−0.2059(4)	0.1514(5)	0.2387(3)	0.0587
C(11)	−0.2723(4)	0.2431(5)	0.2197(4)	0.0557
C(12)	−0.2550(3)	0.3234(4)	0.1464(3)	0.0483

2.1.5. *Bis(2′-chlorobiphenyl-2-yl)antimony trichloride (5)*

A solution of (biphenyl-2,2′-diyl)antimony chloride (1.95 g, 6.3 mmol) in carbon tetrachloride was cooled

TABLE 6. Atomic coordinates, with estimated standard deviaitons in parentheses, for bis(2′-chloro-biphenyl-2-yl) antimony trichloride (**5**)

Atom	x	y	z	U_{eq}
Sb(1)	0.38178(9)	0.14056(3)	0.15271(3)	0.0448
Cl(1)	0.5673(4)	0.0658(1)	0.2509(2)	0.0630
Cl(2)	0.1975(4)	0.2109(2)	0.0500(1)	0.0613
Cl(3)	0.5820(5)	0.1157(2)	0.0674(2)	0.0776
Cl(4)	0.2175(6)	0.4180(2)	0.1001(2)	0.0938
Cl(5)	0.1433(9)	−0.0142(3)	0.3579(3)	0.1364
C(1)	0.428(1)	0.2370(5)	0.2276(5)	0.0441
C(2)	0.409(1)	0.2214(6)	0.3056(5)	0.0539
C(3)	0.426(2)	0.2799(7)	0.3588(6)	0.0619
C(4)	0.466(2)	0.3506(7)	0.3356(7)	0.0648
C(5)	0.489(2)	0.3649(6)	0.2588(7)	0.0618
C(6)	0.474(1)	0.3085(5)	0.2025(5)	0.0425
C(7)	0.517(1)	0.3284(5)	0.1254(6)	0.0495
C(8)	0.419(2)	0.3792(6)	0.0755(7)	0.0605
C(9)	0.470(2)	0.4004(8)	0.0048(8)	0.0806
C(10)	0.623(2)	0.3702(9)	−0.0173(9)	0.0866
C(11)	0.721(2)	0.3213(9)	0.0313(8)	0.0833
C(12)	0.667(2)	0.3004(7)	0.0999(7)	0.0644
C(13)	0.200(1)	0.0498(5)	0.1378(5)	0.0418
C(14)	0.217(2)	−0.0008(6)	0.0774(6)	0.0562
C(15)	0.106(2)	−0.0647(6)	0.0681(7)	0.0614
C(16)	−0.015(2)	−0.0771(6)	0.1175(7)	0.0675
C(17)	−0.034(2)	−0.0257(6)	0.1775(7)	0.0630
C(18)	0.072(1)	0.0392(5)	0.1873(6)	0.0486
C(19)	0.043(1)	0.0957(6)	0.2488(6)	0.0495
C(20)	0.059(2)	0.0768(7)	0.3267(6)	0.0620
C(21)	0.027(2)	0.1309(8)	0.3817(6)	0.0702
C(22)	−0.026(2)	0.2018(8)	0.3591(7)	0.0681
C(23)	−0.045(2)	0.2214(6)	0.2811(7)	0.0620
C(24)	−0.012(2)	0.1688(6)	0.2267(6)	0.0521

to 0°C. Dry chlorine gas was passed through the solution until it acquired a permanent pale green colour. Reduction of the volume to *ca.* 5 ml and cooling to −20°C gave white needles of the trichloride. Yield 0.7 g, 36%. M.p. 190–192°C. Found: C, 46.9; H, 2.6; Cl, 27.2. $C_{24}H_{16}Cl_5Sb$ calc.: C, 47.8; H, 2.7; Cl, 29.4%).

2.2. Crystal structure determinations

Crystal data are summarised in Table 1. Intensity data were collected on a Hilger and Watts four-circle diffractometer, with graphite monochromatised Mo Kα radiation in the range $0° < \theta < 25°$. The data were corrected for Lorentz and polarisation effects and for **2** an empirical absorption correction was also applied using the ABSORB program [11]. Crystallographic calculations used the CRYSTALS [12] programs and scattering factors, including the imaginary part for non-hydrogen atoms, were those for neutral atoms [13]. Except for **3**, the position of the antimony atom was obtained from a three dimensional Patterson synthesis and the other heavy atom positions were obtained following a series of full matrix least squares refinements and difference Fourier syntheses. For diphenylantimony bromide **3**, the antimony and bromine positions were obtained using MULTAN [14]. All non-hydrogen atoms were assigned anisotropic thermal parameters after refinement had converged with isotropic parameters. Hydrogen atoms were placed at their calculated positions but not refined in the final cycles of refinement. The data were weighted using a four coefficient Chebyshev scheme. In all cases, except in the vicinity of the heavy atoms, there were no peaks in a final difference map with intensities greater than 0.5 e$Å^{-3}$.

Final atomic coordinates are listed in Tables 2–6. Tables of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom positions have been deposited at the Cambridge Crystallographic Data Centre.

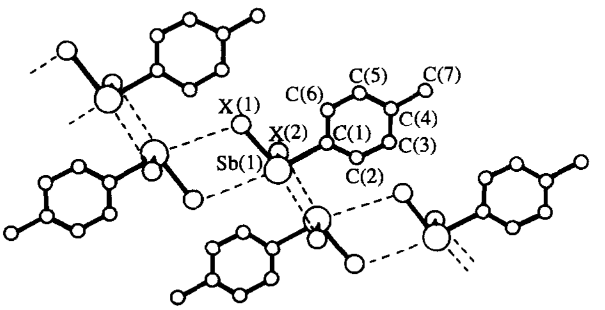

Fig. 1. Structure of (*p*-tolyl)antimony dichloride (**1**) and dibromide (**2**) (X = Cl or Br).

TABLE 7. Important bond distances (Å) and angles (deg) for *p*-tolyl antimony(III) dihalides, with estimated standard deviations in parentheses

	X = Cl (**1**)	X = Br (**2**)
Sb(1)–X(1)	2.372(2)	2.516(1)
Sb(1)–X(2)	2.396(2)	2.551(1)
Sb(1) ··· X(1′)	3.638(2)	3.774(1)
Sb(1) ··· X(2″)	3.433(2)	3.596(1)
Sb(1)–C(1)	2.148(6)	2.16(1)
Sb(1) ··· C(1‴)	3.420(6)	3.45(1)
Sb(1) ··· C(2‴)	3.312(6)	3.32(1)
Sb(1) ··· C(3‴)	3.486(6)	3.49(1)
Sb(1) ··· C(4‴)	3.756(6)	3.81(1)
Sb(1) ··· C(5‴)	3.812(6)	3.88(1)
Sb(1) ··· C(6‴)	3.657(6)	3.71(1)
X(1)–Sb(1) ··· X(2)	94.0(1)	95.7(1)
X(1)–Sb(1) ··· X(1′)	76.9(1)	77.6(1)
X(1)–Sb(1) ··· X(2″)	167.6(1)	167.4(1)
X(1)–Sb(1)–C(1)	94.5(2)	95.2(3)
X(1)–Sb(1) ··· C(1‴)	104.1(2)	104.5(3)
X(1)–Sb(1) ··· C(2‴)	82.1(2)	82.5(3)
X(1)–Sb(1) ··· C(3‴)	79.1(2)	79.7(3)
X(2)–Sb(1) ··· X(1′)	79.6(1)	79.6(1)
X(2)–Sb(1) ··· X(2″)	77.9(1)	80.6(1)
X(2)–Sb(1)–C(1)	92.3(2)	92.8(3)
X(2)–Sb(1) ··· C(1‴)	156.9(2)	156.2(3)
X(2)–Sb(1) ··· C(2‴)	173.6(2)	175.7(3)
X(2)–Sb(1) ··· C(3‴)	160.4(2)	160.3(3)
X(1′) ··· Sb(1) ··· X(2″)	92.3(1)	89.9(3)
X(1′) ··· Sb(1)–C(1)	167.6(2)	168.8(3)
X(2″) ··· Sb(1)–C(1)	95.3(2)	97.1(3)
Sb(1)–C(1)–C(2)	116.6(5)	116.2(8)
Sb(1)–C(1)–C(6)	124.1(5)	124.9(9)

Atoms designated by single, double and triple primes are related by the symmetry operations −x, −y, −z, −x, 1−y, −z and 1−x, 1−y, −z, respectively.

3. Results and discussion

3.1. p-Tolylantimony dichloride (1) and dibromide (2)

These two compounds were successfully prepared by reorganisation of mixtures of one mol of triphenylantimony and two mols of either antimony trichloride or tribromide and crystallised from dichloromethane. They are stable at room temperature but must be protected from the atmosphere.

Bond distances and angles for the two compounds are collected in Table 7 and the structure and atom numbering scheme are shown in Fig. 1. The two compounds are isostructural and also isostructural with the corresponding phenyl compounds [4]. Each antimony atom is pyramidally coordinated to two halogen atoms and the aromatic group with normal bond distances. The bond angles, which fall between 92.3° and 94.5° for the chloride are, for steric reasons, somewhat larger (92.8° to 95.7°) in the bromide, and suggest that the primary bonding uses almost pure p orbitals.

Each antimony also makes short secondary, intermolecular contacts to two different symmetry related halogen atoms, which, as shown in Fig. 1, lead to infinite chains in the solid. These contacts raise the coordination number to five, compared with eight in $SbCl_3$ [15] and six in $SbBr_3$ [16], giving square pyramidal geometry about antimony. The halogen atom X(2) occupies the apical position and C(1), X(1) and the two symmetry related halogen atoms form the basal plane. This arrangement differs from the square pyramidal arrangement about antimony in $[PhSbCl_4]^-$ (obtained by adding two chloride ions to $PhSbCl_2$), in which the apical position is occupied by phenyl and the halogen atoms form the basal plane [17]. This arrangement, with chlorine atoms *trans* to each other, is more stable than the alternative above as it allows delocalisation of the negative charge of the incoming chloride ions. This is not possible if an incoming chloride approaches *trans* to a phenyl group.

It is noteworthy that, while there is a slight shortening of the primary antimony–halogen distances in the *p*-tolyl compared with the phenyl derivatives (2.372(2), 2.396(2) *vs.* 2.376(2), 2.411(2) Å for the chloride and 2.516(1), 2.551(1) *vs.* 2.526(1), 2.563(1) Å for the bromide), the shortening is more significant in the secondary Sb ··· halogen contacts (3.638(2), 3.433(2) *vs.* 3.865(3), 3.443(2) Å for the chloride and 3.774(1), 3.596(1) *vs.* 4.058(1), 3.620(1) Å for the bromide).

There are also weak contacts between antimony and the carbon atoms of a symmetry related tolyl group, as found for the phenyl analogues. Contacts to C(1), C(2) and C(3) are the most significant and fall between 3.312 and 3.486 Å for the chloride (3.32 and 3.49 Å for the bromide). Contacts to C(4) to C(6) are less significant (3.657–3.812 Å and 3.71–3.88 Å for the chloride and bromide respectively). Mean values for the three closer Sb ··· C separations in the *p*-tolyl derivatives are, surprisingly in view of the presence of the methyl substituent, slightly longer (3.57 and 3.61 Å, respectively, for the chloride and bromide) than in the unsubstituted phenyl analogues (3.52 and 3.56 Å, respectively).

TABLE 8. Important bond distances (Å) and angles (°), with estimated standard deviations in parentheses for Ph_2SbBr (3)

Sb(1)–Br(1)	2.553(1)
Sb(1)–C(11)	2.143(8)
Sb(1)–C(21)	2.150(7)
Sb(1) ··· C(23')	3.646(8)
Sb(1) ··· C(24')	3.624(7)
Br(1)–Sb(1)–C(11)	95.3(2)
Br(1)–Sb(1)–C(21)	93.5(2)
C(11)–Sb(1)–C(21)	98.5(3)
Sb(1)–C(11)–C(12)	122.8(6)
Sb(1)–C(11)–C(16)	117.2(6)
Sb(1)–C(21)–C(22)	123.1(6)
Sb(1)–C(21)–C(26)	116.6(6)

Atoms carrying primes are related by the symmetry operation −x, −y, 1−z.

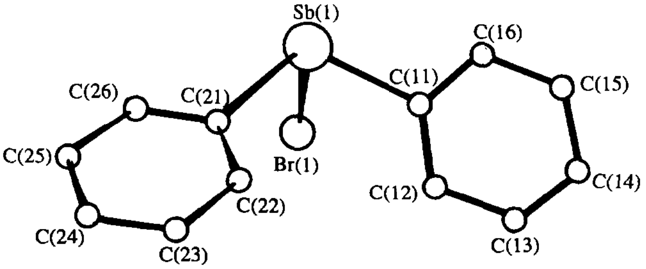

Fig. 2. Structure of diphenylantimony bromide (3).

3.2. *Diphenylantimony bromide (3)*

Reorganisation of a 2:1 mixture of triphenylantimony and antimony tribromide leads to diphenylantimony bromide, which can be recrystallised from dichloromethane or other chlorinated solvents. Important bond distances and angles are listed in Table 8, and the structure and numbering scheme are shown in Fig. 2. The monomeric unit is pyramidal with bond angles falling between 93.5 and 98.5°; Sb–C and Sb–Br bond distances are unremarkable. In contrast to the two structures above, there are no intermolecular antimony-halogen interactions of less than 4.2 Å, the sum of the antimony and bromine van der Waals radii. This continues the trend established above in the reduction in antimony coordination number with increasing phenyl substitution. Structural data are not available for the related chloride, Ph_2SbCl, for which the Lewis acidity would be greater but, as shown below, one weak secondary bond is found for the biphenylyl analogue (**4**).

The structure does, on the other hand, include weak intermolecular contacts (at 3.65 and 3.62 Å respectively) between antimony and the C(23) and C(24) atoms of a symmetry related (−x, y, 1 − z) phenyl group. Contacts to C(22) and C(25) of the same group at 4.20 and 4.13 Å, respectively and to C(15) of a phenyl group related by the operation 1 − x, −y, 1 − z at 4.06 Å are not significant. Thus here there are both weaker and more localised antimony-carbon interactions than in the *p*-tolyl compounds above.

3.3. *(Biphenyl-2,2'-diyl)antimony chloride (4)*

This compound has been characterised by IR and EI mass spectrometry. The three most intense (monoisotopic) mass spectral peaks are assigned to the molecular ion (*m*/*z* 308 carrying 23.4% of the total ion current), the (M–Cl) ion (*m*/*z* 273, 19.8%) and the biphenyl ion (*m*/*z* 152, 24.0%).

Selected bond distances and angles are listed in Table 9 and the molecular structure is shown in Fig. 3. Again, the antimony is pyramidal, but a major feature is the effect of the small bite of the biphenylyl group, which reduces the C–Sb–C angle to 81.0(3)°, compared with 98.5(3)° in Ph_2SbBr. The Sb–C distances are, however, not markedly affected by the constraint. The biphenylyl group is almost planar (torsion angle about the central C(6)–C(7) bond is 2.5°) and, indeed, the maximum deviations from the best plane through the seven atoms in the Sb-biphenylyl unit are +/– 0.03 Å. The torsion angle in the related five coordinate (biphenyl-2,2′-diyl)triphenylantimony is 3.1° [8] and it appears that coordination to antimony imposes planarity in the system. Torsion angles in systems in which biphenyl groups are attached via a single carbon are very much larger, *e.g. ca.* 58° in bis(biphenyl-2-yl)tin dichloride [18] and *ca.* 64° in compound **5**.

The presence of a chlorine atom in this compound obviously enhances the Lewis acidity and one secondary Sb · · · Cl bond (3.707(2) Å) is formed, leading to loose dimers in the solid state. As in compound **4**, antimony makes contacts to carbon atoms C(3) and C(4) of a symmetry related (–x, 1 – y, –z) biphenylyl group at 3.43 and 3.42 Å, respectively, shorter than those in **4**. Contacts to C(2) and C(5) at 4.08 and 4.07 Å are not significant.

3.4. *Bis(2′-chlorobiphenyl-2-yl)antimony(V) trichloride (5)*

Oxidation of compound **4** with a stoichiometric amount of chlorine gives biphenylylantimony trichloride [7], which is hygroscopic and difficult to crystallise. It also decomposes on standing, and crystals suitable for X-ray analysis could not be obtained. Oxidation with an excess of chlorine, on the other hand, gives a new compound **5**, which in contrast is stable at room temperature and can be readily recrystallised from carbon tetrachloride solution. Preliminary identification of **5** as a bis(chlorobiphenylyl)antimony trichloride came from its EI mass spectrum, which showed a weak peak at *m/z* 600 (monoisotopic), assigned to the molecular ion, followed by peaks at *m/z* 565 (carrying 0.7% of the total ion current), 530 (3.5%) and 495 (12.6%) assigned to ions resulting from the successive loss of the three chlorines from the molecular ion. Substantial intensity was also observed for peaks at *m/z* 460 (6.5%, $[(C_{12}H_8Cl)(C_{12}H_8)Sb]$), 425 (4.8%, $[(C_{12}H_8)_2Sb]$), 378 (2.2%, $[(C_{12}H_8Cl)SbCl_2]$), 343 (4.2%, $[(C_{12}H_8Cl)SbCl]$), 273 (8.0%, $[(C_{12}H_8)Sb]$), 187 (8.0%, $[C_{12}H_8Cl]$ and 152 (16.4%, $[C_{12}H_8]$). To confirm this identification, a full X-ray structural determination was carried out.

TABLE 9. Important bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for (biphenyl-2,2′-diyl) antimony chloride (**4**)

Sb(1)–Cl(1)	2.423(2)
Sb(1) · · · Cl(1′)	3.707(2)
Sb(1)–C(1)	2.152(8)
Sb(1)–C(8)	2.136(8)
Sb(1) · · · C(3″)	3.427(8)
Sb(1) · · · C(4″)	3.421(8)
Cl(1)–Sb(1)–C(1)	92.9(2)
Cl(1)–Sb(1)–C(8)	96.6(2)
C(1)–Sb(1)–C(8)	81.0(3)
Sb(1)–C(1)–C(2)	126.5(6)
Sb(1)–C(1)–C(6)	111.5(5)

Atoms carrying primes and double primes are related by the symmetry operations –x, –y, –z and –x, 1–y, –z, respectively.

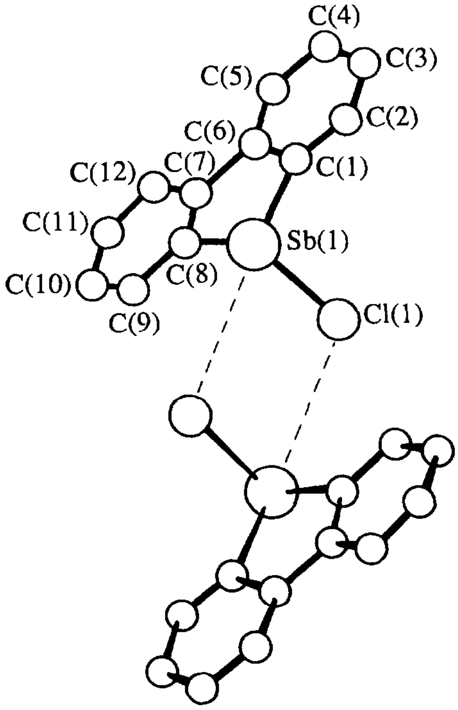

Fig. 3. Structure of (biphenyl-2,2′-diyl)antimony chloride (**4**).

Selected bond distances and angles are listed in Table 10 and the molecular structure illustrated in Fig. 4. The determination clearly shows that the compound is a trigonal bipyramidal monomer, with two chlorobiphenylyl groups in equatorial positions and the three chlorine atoms occupying the two axial sites and the third equatorial position. As expected, the Sb–Cl separation (2.282(4) Å) for the equatorial chlorine atom is substantially shorter than those in the axial positions (2.421(4) and 2.422(4) Å, respectively). The angle between the latter is 177.2(1)° and the axial Sb–Cl distances are somewhat shorter than those in trigonal bipyramidal Ph_3SbCl_2 (2.468(2) and 2.458(3) Å) [19], probably as a result of the higher Lewis acidity of the antimony centre in the present compound. The Sb–C distances are slightly longer (mean 2.13 Å) than those (mean 2.10 Å) in Ph_3SbCl_2, probably for steric reasons.

The monomeric structure is unusual and is the first example of an antimony(V) compound with chlorine atoms in both axial and equatorial sites. The related trichlorides, Ph_2SbCl_3 [20] and Me_2SbCl_3 [21], for example, are dimeric in the solid state with two chlorine bridges and six fold coordination about antimony. Bromine atoms in both equatorial and axial positions are, however, observed for Ph_2SbBr_3, which has basically trigonal bipyramidal geometry [22], but here residual Lewis acidity at antimony leads to a weak intermolecular Sb ··· Br contact, which opens the C–Sb–C angle to 153.4(7)°.

The equatorial C(1)–Sb(1)–C(13) angle (137.1(5)°) in the present compound is also opened but, as the closest intermolecular Sb ··· Cl contact (to Cl(3)) is at *ca.* 6.0 Å, a similar explanation cannot be given in this case. In spite of the large increase in one of the equatorial angles, planarity is maintained in the equatorial system by reductions in the other two angles to 104.8(3) and 117.9(3)°, respectively. Widening of the C–Sb–C angle can probably be traced to repulsions between the two sterically demanding equatorial chlorobiphenylyl groups, and it is significant that in the related monomeric bis(biphenyl-2-yl)tin dichloride [6], the tetrahedral structure is also heavily distorted with an increase in the C–Sn–C angle to 130.8°.

The relative orientations of the two chlorobiphenylyl groups differ substantially as shown by Cl(3)–Sb(1)–C(1)–C(2) and Cl(3)–Sb(1)–C(13)–C(14) torsion angles of 41.4° and −7.0°, respectively, implying that the C(13)–C(18) ring lies almost in the C_2SbCl equatorial plane. As expected and in contrast to compound **4**, the two C_6H_4 groups of each biphenylyl group are no longer coplanar and torsion angles about the central C(6)–C(7) and C(18)–C(19) bonds are 66 and 62° respectively. The different orientations of the biphenylyl groups bring into play a number of short intra- and inter-molecular contacts of which those listed below are the most significant and are probably related to distortions of the trigonal bipyramidal structure. [intramolecular contacts: C(2) ··· C(23) 3.40, C(2) ··· C(24) 3.41, Sb(1) ··· C(12) 3.75, Sb(1) ··· C(24) 3.43 Å; intermolecular contacts: C(14) ··· C(15′) 3.34, C(15) ··· C(15′) 3.33, Cl(4) ··· Cl(5″) 3.16 Å (symmetry operations for atoms carrying primes and double primes are −x, −y, −z and −x, 0.5 + y, 0.5 − z, respectively)].

TABLE 10. Important bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for bis(2′-chlorobiphenyl-2-yl) antimony trichloride (**5**)

Sb(1)–Cl(1)	2.421(4)	Sb(1)–Cl(2)	2.422(4)
Sb(1)–Cl(3)	2.282(4)		
Sb(1)–C(1)	2.14(1)	Sb(1)–C(13)	2.11(1)
Cl(1)–Sb(1)–Cl(2)	177.2(1)	Cl(1)–Sb(1)–Cl(3)	87.3(2)
Cl(1)–Sb(1)–C(1)	89.7(4)	Cl(1)–Sb(1)–C(13)	88.3(3)
Cl(2)–Sb(1)–Cl(3)	90.8(2)	Cl(2)–Sb(1)–C(1)	93.0(4)
Cl(2)–Sb(1)–C(13)	90.3(3)	Cl(3)–Sb(1)–C(1)	117.9(4)
Cl(3)–Sb(1)–C(13)	104.8(3)	C(1)–Sb(1)–C(13)	137.1(5)
Sb(1)–C(1)–C(2)	111.9(9)	Sb(1)–C(13)–C(14)	118.8(9)
Sb(1)–C(1)–C(6)	124.4(9)	Sb(1)–C(13)–C(18)	122.1(9)

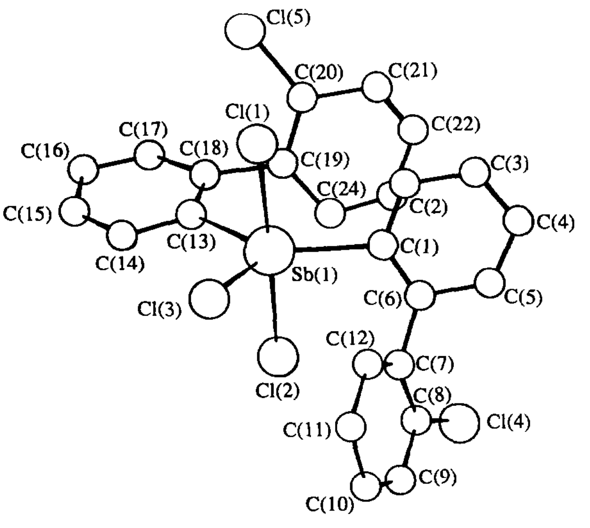

Fig. 4. Structure of bis(2′-chlorobiphenyl-2-yl)antimony trichloride (**5**).

It is clear that considerable reorganisation is necessary to obtain compound **5** by treating **4** with an excess of chlorine. One possible mechanism begins with formation of the expected, unstable oxidation product, $(C_{12}H_8)_2SbCl_3$, which with further chlorine could, by cleavage of one of the Sb–C bonds of the chelate structure, yield the chlorobiphenylyl compound, $(ClC_6H_4C_6H_4)SbCl_4$. Such antimony(V) tetrachlorides are known to be unstable and, for example, $PhSbCl_4$ is readily converted on standing into the more stable trichloride, Ph_2SbCl_3, with antimony pentachloride as the probable second product. Transfer of a phenyl group must involve a bridged species, similar to those involved in the reorganisation reactions between Ph_3Sb and either antimony trichloride or tribromide to give mono and diphenylantimony halides [10]. In the present case, formation of both chlorobiphenylyl and chlorine bridges between two molecules of $(ClC_6H_4C_6H_4)SbCl_4$ could give the observed compound with $SbCl_5$ as the other product.

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