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Lewis acidity of Ph_2SbX_3, where X = Cl or Br. Crystal structures of $Ph_2SbCl_3 \cdot H_2O$ and $Ph_2SbBr_3 \cdot MeCN$

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Abstract

Diphenylantimony trichloride and tribromide are weak Lewis acids forming 1/1 addition compounds with acetonitrile which rapidly lose coordinated nitrile at room temperature. The structure of $Ph_2SbBr_3 \cdot MeCN$ has been determined; the acetonitrile, antimony, and one of the bromine atoms lie on a two-fold axis leading to distorted octahedral geometry about antimony, with phenyl groups in *trans* positions. The Sb–N distance, 2.53 Å, is long, in keeping with the instability of the compound. The hydrate $Ph_2SbCl_3 \cdot H_2O$ has a similar distorted octahedral structure with a two-fold axis passing through the antimony and oxygen atoms; the chlorine atom *trans* to the water molecule is, however, disordered about the two fold axis. There is a long Sb–O bond, 2.311 Å, but stability of this adduct is enhanced by a system of O–H...Cl hydrogen bonds, involving both of the water hydrogen atoms. Surprisingly, a hydrate of Ph_2SbBr_3 could not be obtained.

Introduction

The reduction in Lewis acidity of a non-metal or metalloid halide on replacement of halogen atoms by organic groups is well known and is illustrated by the transition from very high acidity for, say, antimony(V) chloride to virtually no acidity for Ph_3SbCl_2 [1]. Replacement of two halogens in $SbCl_5$ to give Ph_2SbCl_3, however, leaves sufficient acidity for this compound to have a doubly chlorine-bridged dimeric structure in the solid [2]; it will also accept a chloride ion to form $[Ph_2SbCl_4]^-$ salts [3], and gives a stable monohydrate on crystallisation from dilute hydrochloric acid [4].

Antimony(V) bromide, which is still unknown, would be a weaker acid than the chloride, and it follows that Ph_2SbBr_3 would be a weaker acid than Ph_2SbCl_3. Salts containing $[Ph_2SbBr_4]^-$ can, however, still be isolated, but in the solid state there are only weak intermolecular interactions between essentially Ph_2SbBr_3 monomers [5].

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Results and discussion

Our interest in the acidity of Ph_2SbX_3 compounds arose from the observation that $Ph_2SbCl_3 \cdot H_2O$ could be more readily obtained by crystallising the anhydrous chloride from acetonitrile containing ca. 5% water than by the conventional method. With Ph_2SbBr_3 under similar conditions the product was unexpectedly a weak 1/1 addition compound with acetonitrile. Although the compound lost acetonitrile rapidly at room temperature, and conventional analytical data were unsatisfactory, IR spectroscopy showed bands at 2270 and 2296 cm^{-1} consistent with coordinated acetonitrile. In addition with $CDCl_3$ solutions, there were ^1H NMR peaks at δ 1.71 and 1.99 which could be assigned to coordinated and free acetonitrile, respectively.

The analogous Ph_2SbCl_3 addition compound with acetonitrile resulted on crystallisation from the anhydrous solvent, but this too was unstable and rapidly decomposed at room temperature. As in the case of the bromide complex, there were IR peaks for coordinated nitrile (2276 and 2303 cm^{-1}). There were also changes in the 250–500 cm^{-1} region of the spectrum, resulting from the break up of the dimeric structure of $[Ph_2SbCl_3]_2$. In $CDCl_3$ ^1H NMR peaks at δ 1.57 and 2.00 were assigned as before to coordinated and free acetonitrile.

No hydrate of Ph_2SbBr_3 has been reported, and our attempts at synthesis were unsuccessful. The tribromide is insoluble in dilute hydrobromic acid and recrystallisation of the compound from ca. 5% aqueous acetonitrile gave the acetonitrile adduct. Increasing the water content was also unsuccessful, and only hydrolysis products could be obtained at higher water levels. The absence of $Ph_2SbBr_3 \cdot H_2O$ is a little surprising, since both $Ph_2SbBrCl_2 \cdot H_2O$ and $Ph_2SbBr_2Cl \cdot H_2O$ can be obtained by crystallisation of the appropriate mixed halide from 5 *M* hydrobromic acid [6].

There has been an earlier report on the crystal structure of $Ph_2SbCl_3 \cdot H_2O$ [4], but this was based on film data and refined only to $R = 0.16$. We have therefore repeated the determination and also carried out a structure determination on $Ph_2SbBr_3 \cdot MeCN$ to obtain insight into the nature of bonding in these adducts.

Diphenylantimony trichloride monohydrate

Bond distances and angles are listed in Table 1 for this compound and the structure and atom numbering scheme are shown in Fig. 1. As found in the earlier determination, the geometry about antimony is basically octahedral, with the phenyl groups in *trans* positions, but, in contrast to the earlier result, the refinement pointed to disordering of Cl(1) about the two fold axis passing through O(1) and Sb(1). This leads to a reduction in the Cl(1)–Sb(1)–O(1) angle from 180 to 172.8°. Further distortion of the octahedron about antimony is shown by values of 166.1 and 175.6° respectively for the angles at antimony for the *trans* related C(1)–C(1′) and Cl(2)–Cl(2′) atoms.

The inequality in the two independent Sb–Cl distances in the present determination is lower (2.361 and 2.462 Å) than in the earlier one (2.335 and 2.481 Å) [4], but in each case the chlorine *trans* to water shows the shorter contact. Our determination points to weaker bonding of water to antimony (2.311 Å). There are few Sb...O donor distances known for organoantimony(V) compounds, and comparison is thus difficult. The water molecule in $[Ph_3Sb(catechol)]_2 \cdot H_2O$ is particularly weakly held (Sb...O (water) 2.512 Å) compared with the normal Sb–O bonds to the

Table 1

Bond lengths (Å) and angles (°) for $Ph_2SbCl_3 \cdot H_2O$ (with estimated standard deviations in parentheses)

Sb(1)–Cl(1)	2.361(4)
Sb(1)–Cl(2)	2.462(2)
Sb(1)–O(1)	2.311(7)
Sb(1)–C(1)	2.121(8)
O(1)–H(1)	0.92(7)
H(1)–Cl(2″) [a]	2.25(7)
O(1)–Cl(2″)	3.166(8)
C(1)–C(2)	1.37(1)
C(1)–C(6)	1.38(1)
C(2)–C(3)	1.39(1)
C(3)–C(4)	1.39(1)
C(4)–C(5)	1.34(2)
C(5)–C(6)	1.38(2)
Cl(1)–Sb(1)–Cl(2)	92.1(1)
Cl(1)–Sb(1)–O(1)	172.8(2)
Cl(1)–Sb(1)–C(1)	90.9(4)
Cl(2)–Sb(1)–O(1)	87.8(2)
Cl(2)–Sb(1)–Cl(2′)	175.6(1)
Cl(2)–Sb(1)–C(1)	89.5(2)
Cl(2)–Sb(1)–C(1′)	90.0(2)
O(1)–Sb(1)–C(1)	83.1(2)
C(1)–Sb(1)–C(1′)	166.1(4)
Sb(1)–O(1)–H(1)	126 (5)
O(1)–H(1)–Cl(2″)	173 (6)
H(1)–O(1)–H(1′)	107 (9)
Sb(1)–C(1)–C(2)	120.6(5)
Sb(1)–C(1)–C(6)	117.4(7)
C(2)–C(1)–C(6)	122.1(8)
C(1)–C(2)–C(3)	118.6(8)
C(2)–C(3)–C(4)	120(1)
C(3)–C(4)–C(5)	120(1)
C(4)–C(5)–C(6)	123(1)
C(1)–C(6)–C(5)	117(1)

[a] Atoms carrying a prime or double prime are related to unprimed atoms by the symmetry operations $-x$, y, $0.5-z$ and $0.5+x$, $0.5-y$, $1-z$, respectively.

catechol residue (2.048 Å) [7]. In a range of $SbCl_5$ adducts with oxygen donors, Sb...O separations range between 1.94 Å for $SbCl_5 \cdot Me_3PO$ [8] and 2.428 Å for $2SbCl_4 \cdot$ succinyl chloride [9].

One consequence of the long Sb...O separation is an increase in the Cl(1)–Sb(1)–Cl(2) angles to 92.1° at the expense of the Cl(2)–Sb(1)–O(1) angles (87.8°), which contributes further to the distortion of the octahedral coordination about antimony.

$Ph_2SbCl_3 \cdot H_2O$ does have considerable stability, since removal of water occurs only on heating to 100°C in vacuum. It is probable that this arises from a supplementation of the modest Sb...O bond strength by intermolecular hydrogen bonding, involving both hydrogen atoms of the water molecule, with symmetry related Cl(2) atoms. It was possible to locate and refine the positions of the hydrogen atoms in this structure with some degree of confidence to give O–H and

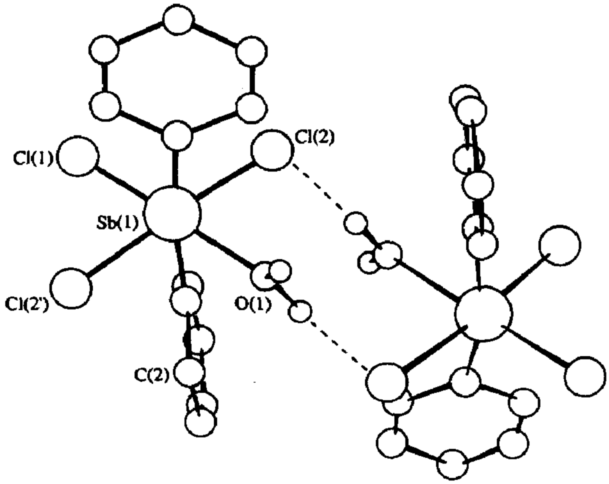

Fig. 1. Structure of $Ph_2SbCl_3 \cdot H_2O$, showing the atom numbering scheme and hydrogen bonding to an adjacent molecule.

H...Cl(2″) separations of 0.92(7) and 2.25(7) Å, respectively, and 173(6)° for the O–H...Cl(2″) angle. The overall distance between O(1) and Cl(2″) is 3.166(8) Å, within the 3.0–3.3 Å range usual for this type of interaction [10]. Hydrogen bonding between adjacent molecules is shown in Fig. 1, and the full extent of interaction, giving rise to two sets (for antimony atoms with *x* coordinates of 0 or 1/2) of double chains parallel to the *c* axis, is shown in Fig. 2.

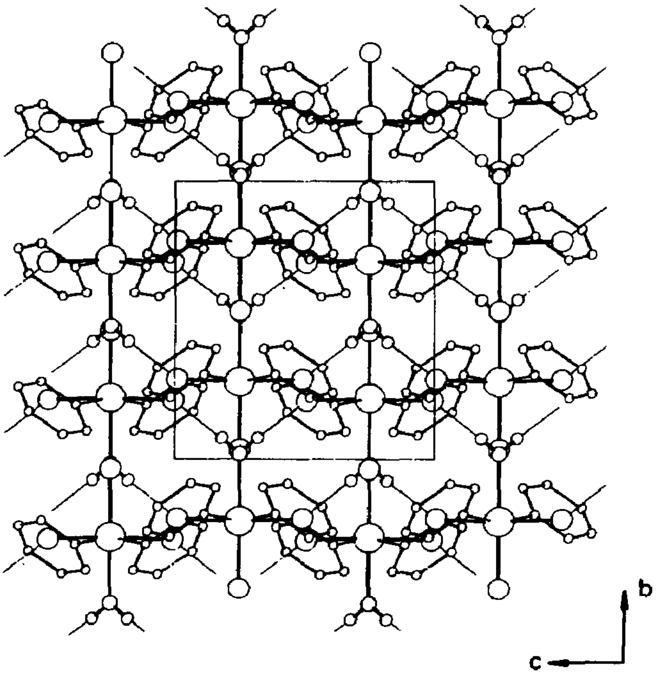

Fig. 2. Projection of the unit cell contents for $Ph_2SbCl_3 \cdot H_2O$ down the *a* axis; hydrogen bonds are shown as weak lines.

The diphenylantimony tribromide-acetonitrile adduct

Bond distances and angles for this compound are listed in Table 2, and the structure and atom numbering scheme are shown in Fig. 3. Although the compound is not isomorphous with the previous compound, there are strong structural similarities. The geometry is again basically octahedral with a two fold axis passing through Br(1) and Sb(1), but here the ligand is not disordered and the nitrogen and carbon atoms of the coordinated acetonitrile also lie on the axis. *trans* angles of 165.0 and 173.0° for C(1)–Sb(1)–C(1′) and Br(2)–Sb(1)–Br(2′), respectively, do, however, indicate distortion from octahedral geometry; there is again distortion in the plane containing the halogens and the ligand, with Br(1)–Sb(1)–Br(2) angles opened to 93.5° at the expense of the Br(2)–Sb(1)–N(1) angles (82.8°).

Again the antimony–halogen bond *trans* to the ligand (Sb(1)–Br(1), 2.519 Å) is substantially shorter than the Sb(1)–Br(2) bonds (2.605 Å) and the Sb(1)–N(1) distance (2.53 Å) is very long and presumably weak. For comparison, Sb–N separations in $SbCl_5$ addition compounds with acetonitrile, diisopropyl cyanamide,

Table 2

Bond lengths (Å) and angles (°) for $Ph_2SbBr_3 \cdot MeCN$ (with estimated standard deviations in parentheses)

Sb(1)–Br(1)	2.519(2)
Sb(1)–Br(2)	2.605(1)
Sb(1)–C(1)	2.13(1)
Sb(1)–N(1)	2.53(2)
C(1)–C(2)	1.41(1)
C(1)–C(6)	1.37(1)
C(2)–C(3)	1.36(1)
C(3)–C(4)	1.37(1)
C(4)–C(5)	1.38(1)
C(5)–C(6)	1.39(1)
N(1)–C(7)	1.09(3)
C(7)–C(8)	1.43(3)
Br(1)–Sb(1)–Br(2)	93.49(5)
Br(1)–Sb(1)–C(1)	97.5(3)
Br(1)–Sb(1)–N(1)	180.0
Br(2)–Sb(1)–Br(2′) [a]	173.0(1)
Br(2)–Sb(1)–C(1)	89.7(3)
Br(2)–Sb(1)–C(1′)	89.3(3)
Br(2)–Sb(1)–N(1)	86.5(1)
C(1)–Sb(1)–N(1)	82.5(3)
C(1)–Sb(1)–C(1′)	165.0(5)
Sb(1)–C(1)–C(2)	117.5(7)
Sb(1)–C(1)–C(6)	122.3(6)
C(2)–C(1)–C(6)	120.2(9)
C(1)–C(2)–C(3)	119.8(9)
C(2)–C(3)–C(4)	120 (1)
C(3)–C(4)–C(5)	120 (1)
C(4)–C(5)–C(6)	120.2(9)
C(1)–C(6)–C(5)	119.1(9)
Sb(1)–N(1)–C(7)	180.0
N(1)–C(7)–C(8)	180.0

[a] Atoms carrying a prime are related to unprimed atoms by the symmetry operation $-x, 1-y, z$.

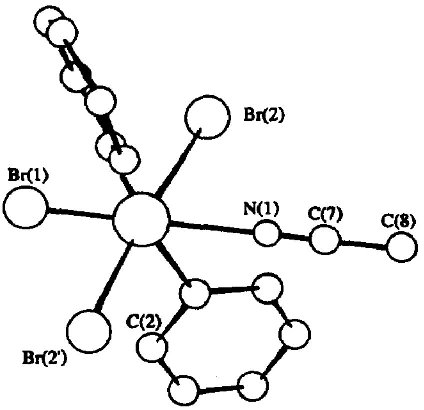

Fig. 3. Structure of $Ph_2SbBr_3 \cdot MeCN$, showing the atom numbering scheme.

and diisopropyl carbodiimide, are respectively 2.23 [11], 2.14 [12], and 2.154 Å [13]. A much weaker bond, 2.463 Å, occurs in tetramethyl(8-oxyquinolinato)antimony [14]. In view of the weakness of Sb–N interaction in the present compound and the absence of any added stabilisation via hydrogen bonding, it is perhaps not surprising that there is ready loss of acetonitrile at room temperature. It is a reasonable assumption that there is a similar situation in $Ph_2SbCl_3 \cdot MeCN$.

Experimental

Preparation of Ph_2SbX_3 (X = Cl or Br)

Redistribution at room temperature of a mixture of $2Ph_3Sb$ and SbX_3 gave Ph_2SbX [15], which was oxidised by the appropriate halogen in dichloromethane solution. The resulting solution was evaporated to dryness, and in each case the residue was recrystallised from anhydrous toluene.

Preparation of $Ph_2SbCl_3 \cdot H_2O$

Recrystallisation of the anhydrous chloride from acetonitrile containing 5% water gave the adduct as white crystals. Yield, 89%, m.p. 176 °C (Found: C, 36.3; H, 3.1; Cl, 26.7. $C_{12}H_{12}Cl_3OSb$ calcd.: C, 36.0; H, 3.0; Cl, 26.6%).

Preparation of $Ph_2SbX_3 \cdot MeCN$ (X = Cl or Br)

Crystallisation of the trihalides from hot anhydrous acetonitrile in each case gave colourless crystals on cooling to room temperature. On standing at room temperature, these crystals rapidly turned cloudy, and eventually became powders owing to loss of solvent.

Crystal structure determination

Crystals suitable for X-ray analysis were obtained by slow recrystallisation of $Ph_2SbCl_3 \cdot H_2O$ from dichloromethane and Ph_2SbBr_3 from anhydrous acetonitrile. The former was mounted on a glass fibre but the latter was sealed in a Lindemann capillary tube immediately after isolation. Crystal data for the two compounds are summarised in Table 3.

Table 3

Crystal data

	$Ph_2SbCl_3 \cdot H_2O$	$Ph_2SbBr_3 \cdot CH_3CN$
	$C_{12}H_{12}Cl_3OSb$	$C_{14}H_{13}Br_3NSb$
M	400.3	556.5
a (Å)	17.635(5)	8.926(3)
b (Å)	9.615(3)	27.970(8)
c (Å)	8.498(3)	13.868(5)
U (Å^3)	1440.9	3462.3
D_c (g cm^{-3})	1.85	2.13
Z	4	8
$F(000)$	776	2080
Space group	*Pbcn*	*Fdd*2
μ (cm^{-1})	24.7	89.3
θ max (°)	25	30
Observed reflections	821	1112
Crystal size (mm^3)	0.2×0.3×0.6	0.3×0.3×0.3

Data were collected using a Hilger and Watts Four Circle Diffractometer with Mo-K_α radiation and were corrected for Lorentz and polarisation effects. An absorption correction was applied in each case by use of ABSORB [16]. Crystallographic calculations used the CRYSTALS programs [17] and scattering factors including the anomalous dispersion contributions for non-hydrogen atoms were for neutral atoms [18]. The structures were solved by conventional Patterson methods and refined by full matrix least squares.

In the early stages of refinement of the $Ph_2SbCl_3 \cdot H_2O$ structure, Cl(1) was placed on the two fold axis together with Sb(1) and O(1), but this led to a very high U_{iso} parameter, probably indicating disorder of this atom about the axis. Moving the atom slightly off the axis solved the problem, and the refinement converged at $R = 0.134$ with isotropic thermal parameters. There were however, further problems in the anisotropic refinement stages owing to strong correlation between the x coordinate of Cl(1) and U_{11}, but these were solved by initially refining the positional

Table 4

Atomic coordinates for $Ph_2SbCl_3 \cdot H_2O$ (with estimated standard deviations in parenthesis)

Atom	x/a	y/b	z/c
Sb(1)	0.0000	0.22085(7)	0.2500
Cl(1)	0.0168(5)	0.4645(5)	0.2500
O(1)	0.0000	−0.0195(7)	0.2500
Cl(2)	−0.0766(1)	0.2111(2)	0.4920(2)
C(1)	0.0995(5)	0.1942(9)	0.3870(8)
C(2)	0.1539(5)	0.100(1)	0.3429(9)
C(3)	0.2185(5)	0.086(1)	0.436(1)
C(4)	0.2271(7)	0.170(2)	0.569(1)
C(5)	0.1719(7)	0.260(2)	0.608(1)
C(6)	0.1073(6)	0.276(1)	0.519(1)
H(1)	0.025(4)	−0.076(8)	0.319(9)

Table 5

Atomic coordinates for $Ph_2SbBr_3 \cdot MeCN$ (with estimated standard deviations in parentheses)

Atom	x/a	y/b	z/c
Sb(1)	0.0000	0.50000	0.5000
Br(1)	0.0000	0.50000	0.3184(1)
Br(2)	0.1845(1)	0.57197(4)	0.5114(2)
C(1)	0.182(1)	0.4520(3)	0.5201(7)
C(2)	0.190(2)	0.4119(4)	0.459(1)
C(3)	0.308(2)	0.3812(5)	0.466(1)
C(4)	0.417(1)	0.3884(5)	0.534(1)
C(5)	0.410(1)	0.4274(5)	0.5951(9)
C(6)	0.293(1)	0.4602(4)	0.5867(8)
N(1)	0.0000	0.5000	0.682(1)
C(7)	0.0000	0.5000	0.761(1)
C(8)	0.0000	0.5000	0.864(1)

coordinates with fixed U values. A difference Fourier synthesis revealed positions for all the hydrogen atoms, but the phenyl hydrogens were in fact placed at their calculated positions (C–H 1.0 Å) and not refined. The hydrogens of the water molecule were refined with isotropic thermal parameters and final convergence occurred at $R = 0.041$ after applying a four coefficient Chebyshev weighting scheme.

Refinement of the $Ph_2SbBr_3 \cdot MeCN$ structure converged at $R = 0.069$ with anisotropic thermal parameters for antimony and bromine, but strong correlation between the y coordinates of C(7) and C(8) and the U_{22} parameters suggested initially that the acetonitrile molecule was possibly disordered about the two fold axis. This was shown not to be the case, and the refinement was continued by initially fixing the y coordinates and refining the anisotropic parameters of C(7) and C(8). Hydrogen atoms were placed at the calculated positions but not refined. Convergence at $R = 0.055$ occurred after application of a four coefficient Chebyshev weighting scheme. The absolute structure was not determined.

Final values of the atomic coordinates are listed in Tables 4 and 5. Tables of anisotropic thermal parameters, calculated hydrogen atom positions, and observed and calculated structure factors for both compounds can be obtained from D.B.S.

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References

1 M. Hall and D.B. Sowerby, J. Chem. Soc. Dalton Trans., (1983) 1095.
2 J. Bordner, G.O. Doak and J.R. Peters, Jr., J. Am. Chem. Soc., 96 (1974) 6763.
3 R. Barbieri, N. Bertazzi and T.C. Gibb, J. Chem. Soc. Dalton Trans., (1979) 1925.
4 T.N. Polynova and M.A. Porai-Koshits, J. Struct. Chem., 8 (1967) 92.
5 S.P. Bone and D.B. Sowerby, J. Chem. Soc., Dalton Trans., (1979) 718.
6 S.P. Bone, PhD Thesis, University of Nottingham, 1979.
7 M. Hall and D.B. Sowerby, J. Am. Chem. Soc., 102 (1980) 628.
8 C.I. Branden and L. Lindqvist, Acta. Chem. Scand., 17 (1963) 353.

9 J.M. Le Carpentier and R. Weiss, Acta Crystallogr., B, 28 (1972) 1442.
10 G.C. Pimentel and A.L. McClellan, Ann. Rev. Phys. Chem., 22 (1971) 347.
11 H. Binas, Z. Anorg. Allg. Chem., 352 (1967) 271.
12 J.C. Jochins, R. Abu-el-Halawa, L. Zsolnai and G. Huttner, Chem. Ber., 117 (1984) 1161.
13 H.D. Hausen, W. Schwarz, G. Rajca and J. Weidlein, Z. Naturforsch. B, 41 (1986) 1223.
14 H. Schmidbaur, B. Milewski-Mahrla and F.E. Wagner, Z. Naturforsch. B, 38 (1983) 1477.
15 M. Nunn, D.B. Sowerby and D.M. Wesolek, J. Organomet. Chem., 251 (1983) C45.
16 The X-RAY system, version of June 1972, technical report TR-192, Computer Science Center, University of Maryland, June 1972.
17 J.R. Carruthers, CRYSTALS, the Oxford Crystallographic Programs, 1975.
18 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, vol. 4.