

reference to the amide carbonyl group. Unlike the free ligand, the hydroxyimino group in the complex is in a *cis* position with reference to the amide carbonyl, which is dictated by the chelate formation. The dihedral angle between the carboxyl group and the nearly planar anion framework is $\approx 22^\circ$, whereas in the free H₃Mt it is $\approx 47^\circ$.

In the coordinated pyridine rings the average distances are N—C = 1.345 and C—C = 1.368 Å; the bond angles near N are $\approx 116.5^\circ$ and near C are $\approx 120.7^\circ$. The dihedral angles between pyridine molecules and the chelate ring are: *A, B* = 101.7; *A, C* = 122.1; *A, M* = 93.5; *B, C* = 94.8; *B, M* = 14.6; *C, M* = 89.1° (*A, B, C* = pyridine molecules; *M* = chelate).

The ethanol molecule is linked to the complex cation by the hydrogen bond N1—H(N1)···O(8) = 3.01 Å [H(N1)—O(8) = 2.25, N1—H(N1) = 1.08 Å; N1—H(N1)···O(8) = 126°]. The nitrate ions have normal N—O distances (1.23–1.28 Å) and bond angles (117.8–121.3°). The short contacts O(8)···O(7)

= 2.70 Å and O(8)···O(6)* = 2.83 Å can be interpreted as hydrogen bonds.

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Structures of Triphenylantimony(V) Dibromide and Dichloride

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Abstract. (1) Dibromotriphenylantimony(V), [SbBr₂(C₆H₅)₃], *M_r* = 513.0, orthorhombic, *Fdd*2, *a* = 24.179 (8), *b* = 10.282 (3), *c* = 14.234 (5) Å, *V* = 3538.7 Å³, *Z* = 8, *D_x* = 1.93 g cm⁻³, Mo *Kα* radiation (graphite monochromator), λ = 0.7107 Å, μ = 63.6 cm⁻¹, *F*(000) = 1952, *T* = 294 K, *R* = 0.0428, *wR* = 0.0451, for 96 least-squares parameters and 739 unique observed reflections with *I* > 3σ(*I*). The Sb atom and one of the phenyl groups lie on a twofold axis. (2) Dichlorotriphenylantimony(V), [SbCl₂(C₆H₅)₃], *M_r* = 423.9, orthorhombic, *P2₁2₁2₁*, *a* = 10.882 (4), *b* = 12.127 (4), *c* = 12.986 (4) Å, *V* = 1713.7 Å³, *Z* = 4, *D_x* = 1.64 g cm⁻³, Mo *Kα* radiation (graphite monochromator), λ = 0.7107 Å, μ = 19.3 cm⁻¹, *F*(000) = 832, *T* = 294 K, *R* = 0.0272, *wR* = 0.0274, for 190 least-squares parameters and 1555 unique observed reflections with *I* > 3σ(*I*). In both compounds, the Sb atom is in trigonal bipyramidal coordination with two axial halogen atoms [Sb—Br 2.632 (1); Sb—Cl 2.468 (2), 2.458 (2) Å] and three equatorial phenyl groups [Sb—C 2.11 (1) and

2.12 (1) Å for the bromide and 2.084 (2), 2.100 (2) and 2.106 (2) Å for the chloride].

Introduction. There is current interest in the structures of Group 15 compounds with the stoichiometry Ph₃MX₂ (*X* = halogen) as, contrary to most expectations, both triphenylphosphorus diiodide (Godfrey, Kelley, McAuliffe, Mackie, Pritchard & Watson, 1991) and triphenylarsenic diiodide (McAuliffe, Beagley, Gott, Mackie, MacRory & Pritchard, 1987; Beagley, Colburn, El-Sayrafi, Gott, Kelley, Mackie, McAuliffe, MacRory & Pritchard, 1988) have an unusual four-coordinate structure in which the iodine–iodine bond remains intact. This contrasts with the five-coordinate trigonal bipyramidal arrangement with axial halogen atoms and equatorial phenyl groups about the Group 15 atom in Ph₃AsF₂ (Augustine, Ferguson & March, 1975), Ph₃SbCl₂ (Polynova & Porai-Koshits, 1966) and Ph₃BiCl₂ (Hawley & Ferguson, 1968). The triphenylantimony dichloride structure was solved from film data, and refined to a final *R* value of 0.17. The structure of triphenylantimony dichloride as a weak

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Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for Ph_3SbBr_2

$U_{\text{eq}} = (ax_1, ax_2, ax_3)^{1/3}$, where ax_n are the magnitudes of the principal axes of the thermal ellipsoid.

	x	y	z	U_{eq}
Sb(1)	0.0000	0.0000	0.0000	0.0503
Br(1)	-0.04694 (5)	0.2310 (1)	0.0015 (1)	0.0726
C(1)	0.0681 (5)	0.074 (1)	-0.0765 (8)	0.0616
C(2)	0.1200 (7)	0.049 (2)	-0.046 (1)	0.0998
C(3)	0.1635 (8)	0.099 (3)	-0.099 (2)	0.1326
C(4)	0.1558 (9)	0.161 (2)	-0.180 (2)	0.1083
C(5)	0.105 (2)	0.175 (3)	-0.212 (2)	0.1419
C(6)	0.0569 (7)	0.134 (2)	-0.158 (1)	0.0973
C(11)	0.0000	0.0000	0.1490 (9)	0.0469
C(12)	0.0481 (8)	0.006 (3)	0.197 (1)	0.0966
C(13)	0.0467 (7)	0.002 (3)	0.294 (1)	0.0932
C(14)	0.0000	0.0000	0.342 (1)	0.0811

Table 2. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for Ph_3SbCl_2

$U_{\text{eq}} = (ax_1, ax_2, ax_3)^{1/3}$, where ax_n are the magnitudes of the principal axes of the thermal ellipsoid.

	x	y	z	U_{eq}
Sb(1)	0.13118 (4)	0.23007 (4)	0.22937 (4)	0.0550
Cl(1)	0.3387 (1)	0.3115 (2)	0.2194 (2)	0.0652
Cl(2)	-0.0732 (2)	0.1439 (2)	0.2274 (2)	0.0760
C(1)	0.0853 (7)	0.3141 (6)	0.0947 (6)	0.0560
C(2)	-0.0213 (7)	0.3741 (7)	0.0906 (6)	0.0647
C(3)	-0.0522 (8)	0.4328 (8)	0.0022 (7)	0.0767
C(4)	0.0238 (9)	0.4292 (8)	-0.0825 (6)	0.0770
C(5)	0.1313 (9)	0.3674 (7)	-0.0791 (6)	0.0201
C(6)	0.1630 (7)	0.3104 (6)	0.0096 (6)	0.0663
C(11)	0.2094 (7)	0.0718 (5)	0.2292 (6)	0.0547
C(12)	0.2910 (7)	0.0478 (6)	0.3072 (6)	0.0593
C(13)	0.3421 (7)	-0.0571 (6)	0.3116 (7)	0.0710
C(14)	0.3135 (7)	-0.1336 (6)	0.2384 (8)	0.0737
C(15)	0.2346 (8)	-0.1084 (7)	0.1607 (7)	0.0690
C(16)	0.1793 (7)	-0.0053 (7)	0.1560 (6)	0.0650
C(21)	0.1043 (7)	0.2940 (5)	0.3784 (5)	0.0530
C(22)	0.0288 (7)	0.2354 (7)	0.4449 (6)	0.0703
C(23)	0.0171 (8)	0.2725 (9)	0.5464 (7)	0.0817
C(24)	0.073 (1)	0.3658 (9)	0.5768 (7)	0.0883
C(25)	0.144 (1)	0.4248 (7)	0.5114 (7)	0.0950
C(26)	0.1621 (8)	0.3882 (7)	0.4092 (6)	0.0723

adduct with antimony trichloride is also available (Hall & Sowerby, 1983). We have redetermined the structure of the free chloride to obtain more accurate parameters and have also determined the structure of the related dibromide to confirm the expected trigonal bipyramidal structure.

Experimental. Both compounds were prepared by oxidizing triphenylantimony with the appropriate halogen in chloroform solution; the bromide was recrystallized from the same solvent and the chloride from a cyclohexane-methanol (3/2) mixture.

Triphenylantimony dibromide. Crystal size $0.2 \times 0.2 \times 0.2$ mm. The lattice parameters were refined using 12 reflections in the range $22 < 2\theta < 28^\circ$ on a Hilger & Watts Y290 diffractometer fitted with a graphite monochromator. Using Mo $K\alpha$ radiation and ω - 2θ scans, 1737 intensities were measured for $2\theta < 50^\circ$ and $-27 < h < 27$, $0 < k < 12$, $-15 < l < 0$. Three

Table 3. Selected bond distances (\AA) and angles ($^\circ$) for Ph_3SbBr_2

Sb(1)—Br(1)	2.632 (1)	Sb(1)—C(11)	2.12 (1)
Sb(1)—C(1)	2.11 (1)		
Br(1)—Sb(1)—Br(1')	179.06 (9)	C(1)—Sb(1)—C(1')	118.0 (7)
Br(1)—Sb(1)—C(1)	91.0 (3)	Sb(1)—C(1)—C(2)	119 (1)
Br(1)—Sb(1)—C(1')	89.5 (3)	Sb(1)—C(1)—C(6)	117 (1)
Br(1)—Sb(1)—C(11)	89.5 (4)	Sb(1)—C(11)—C(12)	120.5 (9)
C(1)—Sb(1)—C(11)	121.0 (3)		

Symmetry code: (') $-x, -y, z$.

Table 4. Selected bond distances (\AA) and angles ($^\circ$) for Ph_3SbCl_2

Sb(1)—Cl(1)	2.468 (2)	Sb(1)—C(11)	2.100 (6)
Sb(1)—Cl(2)	2.458 (2)	Sb(1)—C(21)	2.106 (7)
Sb(1)—C(1)	2.084 (7)		
Cl(1)—Sb(1)—Cl(2)	176.07 (8)	C(1)—Sb(1)—C(21)	123.9 (3)
Cl(1)—Sb(1)—C(1)	88.8 (2)	C(11)—Sb(1)—C(21)	113.2 (3)
Cl(1)—Sb(1)—C(11)	89.7 (2)	Sb(1)—C(1)—C(2)	119.7 (6)
Cl(1)—Sb(1)—C(21)	91.6 (2)	Sb(1)—C(1)—C(6)	120.3 (6)
Cl(2)—Sb(1)—C(1)	89.0 (2)	Sb(1)—C(11)—C(12)	117.0 (6)
Cl(2)—Sb(1)—C(11)	88.8 (1)	Sb(1)—C(11)—C(16)	121.8 (6)
Cl(2)—Sb(1)—C(21)	92.3 (2)	Sb(1)—C(21)—C(22)	117.7 (6)
C(1)—Sb(1)—C(11)	122.9 (3)	Sb(1)—C(21)—C(26)	120.9 (6)

standard reflections monitored every 100 reflections showed no significant loss of intensity over the period of data collection, Lp corrections were applied as well as an analytical absorption correction using *ABSORB* (Stewart & Hall, 1985) with minimum and maximum transmission factors of 0.23 and 0.48. 739 unique intensities with $I > 3\sigma(I)$ were obtained; merging $R = 5.06\%$. The structure was solved by Patterson methods and subsequent difference Fourier maps. The origin was fixed by placing the antimony atom at $z = 0$. Full-matrix least-squares refinement was performed with anisotropic thermal parameters for all non-H atoms and H atoms placed at calculated positions (C—H = 1.00 \AA). The absolute structure was confirmed, as the inverted structure gave a significantly larger R value. The weighting scheme was based on a four-coefficient Chebyshev polynomial. Final $R = 4.28$, $wR = 4.51\%$. Maximum shift to e.s.d. was 0.02, and maximum and minimum residual electron densities were 0.87 and -1.47 e \AA^{-3} , with all large peaks in the vicinity of the Sb and Br atoms. Scattering factors were those for neutral atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations used the *CRYSTALS* programs (Watkins, Carruthers & Betheridge, 1985).

Triphenylantimony dichloride. Crystal size $0.2 \times 0.3 \times 0.5$ mm. Lattice parameters were refined using 12 reflections in the range $22 < 2\theta < 28^\circ$ on a Hilger & Watts Y290 diffractometer with graphite monochromator. Using Mo $K\alpha$ radiation and ω - 2θ scans, 2075 intensities were measured for $2\theta < 56^\circ$ and $0 < h < 12$, $0 < k < 14$, $0 < l < 15$. Three standard reflections monitored every 100 reflections showed no

significant loss of intensity over the period of data collection, L_p corrections were applied but no absorption correction. 1555 unique intensities with $I > 3\sigma(I)$ were obtained. The structure was solved as described above, including the absolute structure. Final $R = 2.72$, $wR = 2.74\%$. Maximum shift to e.s.d. was 0.02, and maximum and minimum residual electron densities were 0.14 and -0.11 e \AA^{-3} .

Discussion. Tables 1 and 2 list atomic coordinates for the dibromide and dichloride respectively, while important bond distances and angles are collected in Tables 3 and 4.* Diagrams of the two structures showing the atom-numbering schemes are presented in Figs. 1 and 2. Both compounds are simple molecular species with conventional trigonal bipyramidal geometry about the Sb atom; halogen atoms occupy axial sites and the phenyl groups are in equatorial positions. In the case of the dibromide, there is a twofold axis passing through the Sb atom and the C(11) and C(14) atoms of one of the phenyl groups.

Deviations from ideal geometry are small for the bromide but for the chloride, the angle between the axial halogens is reduced to $176.07(8)^\circ$ and the equatorial angles are $113.2(3)$, $122.9(3)$ and $123.9(3)^\circ$. For both compounds, however, the equatorial angles sum to exactly 360° . Substantial deviations of the equatorial angles from the 120° ideal,

* Lists of structure factors, anisotropic thermal parameters, calculated H-atom positions and bond distances and angles within the phenyl groups have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55852 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1016]

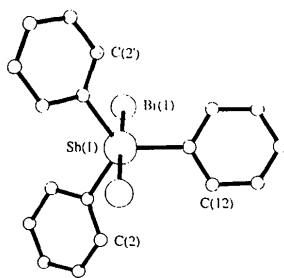


Fig. 1. Molecular structure of Ph_3SbBr_2 .

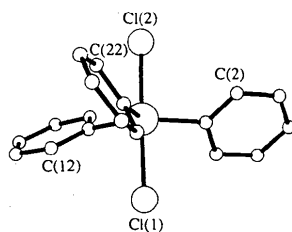


Fig. 2. Molecular structure of Ph_3SbCl_2 .

coupled with a slight reduction of the axial angle, have been noted previously in the basically trigonal bipyramidal structure of, for example, triphenylantimony diacetate (Sowerby, 1979) as a result of strong $\text{Sb}\cdots\text{O}$ intramolecular interactions. Similar intramolecular interactions are not possible for the dichloride as the closest intermolecular $\text{Sb}\cdots\text{Cl}$ contact is $>6.5 \text{ \AA}$.

Although the two structures are very similar, they are differentiated by the orientations of the phenyl groups about the Sb atom. In the chloride, the $\text{Sb}-\text{C}$ torsion angles with respect to Cl(1) are 48.3 , 58.6 and 28.2° , respectively, for the C(1), C(11) and C(21) groups, describing a propeller arrangement. This same arrangement [torsion angles of 46.7 , 74.8 and 36.7° with respect to Cl(2) for, respectively, the C(21), C(11) and C(1) groups] is also observed for the phenyl groups in the weak addition compound between triphenylantimony dichloride and antimony trichloride (Hall & Sowerby, 1983).

In the corresponding bromide, one of the phenyl groups has a reversed orientation [torsion angles with respect to Br(1) of 55.8 , 55.8 and -67.7°], an arrangement similar to that in both Ph_3AsF_2 (Augustine *et al.*, 1975) and Ph_3BiCl_2 (Hawley & Ferguson, 1968).

It is difficult to offer any rationalization for these changes, but in triphenylantimony dichloride the very small $\text{Cl}-\text{Sb}-\text{C}$ torsion angle of 28.2° causes short intermolecular contacts between the Cl atoms and the *ortho* H atoms, *i.e.* $\text{Cl}(1)\cdots\text{H}(26)$ 2.68 and $\text{Cl}(2)\cdots\text{H}(22)$ 2.58 \AA . This is also responsible for the distorted $\text{Cl}-\text{Sb}-\text{Cl}$ bond angle (176.07°) and is reflected in the larger $\text{Cl}-\text{Sb}-\text{C}$ angles of 92.3 and 91.6° .

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