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Trichlorobis(triphenylphosphine oxide)antimony(III)

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Abstract. $SbCl_3[(C_6H_5)_3PO]_2$, monoclinic, $C2/c$ (No. 15); $a = 17 \cdot 296$ (2), $b = 12 \cdot 212$ (2), $c = 17 \cdot 140$ (3) Å, $\beta = 104 \cdot 84$ (2)°; $D_o = 1 \cdot 47$ (1), $D_c = 1 \cdot 488$ g cm^{-3}, $Z = 4$, $R = 0 \cdot 027$ for 2713 reflections $[I > 3\sigma(I)]$. Coordination around Sb is a nearly regular square pyramid with the O-coordinated triphenylphosphine oxide ligands in the *cis* position. There is disorder of the apical Cl atoms [refined population parameters are $0 \cdot 503$ (4) for the apical and $0 \cdot 999$ (5) for the Cl atom in the base].

Introduction. A number of interesting configurations in the complexes of Sb^{III} or Bi^{III} halides with organic oxo-bases, $(C_6H_5)_3PO$ and $(C_6H_5)_3AsO$, have been determined by crystal structure analysis (Lazarini, Golič & Pelizzi, 1975, 1976; Lazarini & Milićev, 1976) or suggested by vibrational spectroscopy (Milićev & Hadži, 1977). The crystal structure determination of $SbCl_3[(C_6H_5)_3PO]_2$ is reported here. The complex $SbBr_3[(C_6H_5)_3PO]_2$ is isomorphous, as shown by powder diffraction data and vibrational spectra (Milićev & Hadži, 1977).

Crystals of $SbCl_3[(C_6H_5)_3PO]_2$ were obtained by the method of Milićev & Hadži (1977). The unit-cell parameters were determined by single crystal diffractometry. A unique set of 5032 reflections was measured in the range $1 \cdot 5 < \theta < 30°$ on an Enraf–Nonius CAD-4 diffractometer with ω–2θ scan and Mo $K\alpha_1$ radiation [graphite monochromator, $\lambda = 0 \cdot 7107$ Å, $t = 20$ (1)°C]. A crystal ground to a sphere ($r = 0 \cdot 2$ mm) was used for intensity measurements. 2713 reflections having $I > 3\sigma(I)$ were taken as observed. The

intensities were corrected for Lorentz, polarization and absorption ($\mu = 11 \cdot 5$ cm^{-1}) effects.

The structure was solved from a Patterson summation and successive Fourier syntheses. Because of the stoichiometry an Sb as well as a Cl atom should be expected in a special position. Just one peak on the twofold axis belonging to the Sb was observed and an additional peak of half the intensity expected for the Cl atom was found in the general position. Consequently the Cl atom with a population parameter of $0 \cdot 5$ was placed in this position. Population parameters of both Cl atoms, positional parameters and anisotropic temperature factors of all non-hydrogen atoms were included in the refinement of the structure. The H-atom parameters were calculated and included in the structure factor calculation (with an isotropic temperature factor $U = 0 \cdot 07$ Å^2) but not refined. The function minimized in the least-squares procedure was $\sum w(|F_o| - |F_c|)^2$. The weighting scheme applied was as follows:

$$|F_o| < 35: w_F = (|F_o|/35);$$

$$\sin \theta < 0 \cdot 22: w_S = (\sin \theta / 0 \cdot 22)$$

$$35 \le |F_o| < 64: w_F = 1 \cdot 0;$$

$$0 \cdot 22 \le \sin \theta < 0 \cdot 40: w_S = 1 \cdot 0$$

$$|F_o| \ge 64: w_F = (64/|F_o|);$$

$$\sin \theta \ge 0 \cdot 40: w_S = (0 \cdot 40 / \sin \theta)$$

$$w = w_F \, w_S.$$

Final R values are $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0 \cdot 027$ and $R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2} = 0 \cdot 031$ for

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Table 1. *Final positional parameters* $(\times 10^5)$ *with standard deviations in parentheses*

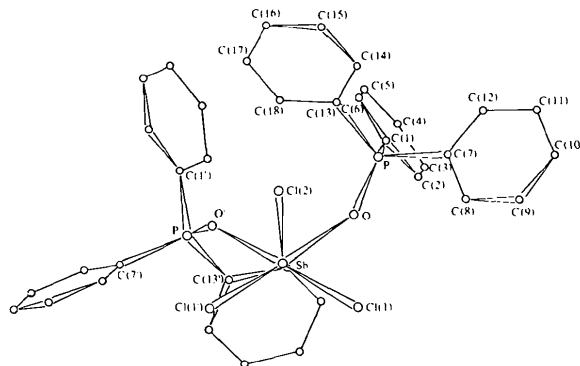|	x	y	z
Sb	$\frac{1}{2}$	66677 (2)	$\frac{1}{4}$
Cl(1)	40590 (7)	80620 (8)	17656 (8)
Cl(2)	44266 (10)	67205 (14)	35133 (9)
P	34679 (4)	44301 (6)	20727 (5)
O	40688 (12)	52060 (17)	18823 (13)
C(1)	35793 (16)	30928 (22)	16777 (17)
C(2)	34986 (26)	30177 (31)	8508 (20)
C(3)	36141 (29)	20146 (39)	5181 (24)
C(4)	38165 (23)	10975 (32)	9923 (28)
C(5)	39053 (27)	11751 (31)	18017 (28)
C(6)	37809 (24)	21612 (30)	21469 (21)
C(7)	24678 (17)	48774 (25)	15998 (17)
C(8)	23659 (20)	58959 (28)	12297 (21)
C(9)	16006 (25)	62558 (33)	8410 (25)
C(10)	9478 (21)	56159 (37)	8395 (23)
C(11)	10423 (20)	46099 (34)	12092 (23)
C(12)	18037 (19)	42273 (29)	15834 (19)
C(13)	35767 (17)	42869 (26)	31403 (18)
C(14)	29500 (21)	44676 (34)	34944 (21)
C(15)	30856 (24)	43892 (40)	43270 (22)
C(16)	38289 (24)	41355 (35)	48019 (20)
C(17)	44489 (21)	39509 (36)	44493 (21)
C(18)	43285 (18)	40261 (33)	36228 (19)

Fig. 1. A molecule of the complex viewed perpendicular to the plane of the chlorine atoms. A twofold crystallographic axis bisects the angle Cl(1)—Sb—Cl(1) and only one of the two equivalent positions of Cl(2), which is in statistical disorder, is shown as occupied. The atom-numbering system is shown.
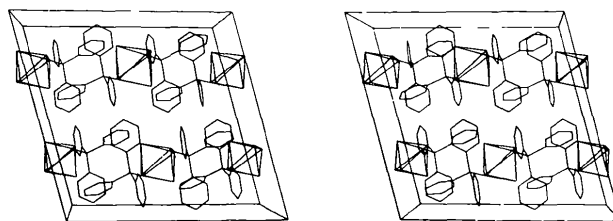

Fig. 2. Stereoscopic view of the unit cell along the *b* axis.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with standard deviations in parentheses*

Sb—Cl(1)	2·466 (1)	P—C(1)	1·797 (3)
Sb—Cl(2)	2·211 (2)	P—C(7)	1·797 (3)
Sb—O	2·455 (2)	P—C(13)	1·799 (3)
O—P	1·503 (2)		

	C—C(mean)	1·382 (5)	
	C—C(max)	1·391 (5)	
	C—C(min)	1·359 (7)	

Cl(1)—Sb—Cl(2)	90·6 (1)	Sb—O—P	141·1 (1)
Cl(1)—Sb—Cl(1^i)	92·7 (1)	O—P—C(1)	110·1 (1)
Cl(1)—Sb—O	90·4 (1)	O—P—C(7)	110·5 (1)
Cl(2)—Sb—O	89·0 (1)	O—P—C(13)	112·6 (1)
O—Sb—O^i	86·7 (1)		

	C—C—C(mean)	120·0 (3)	
	C—C—C(max)	121·2 (4)	
	C—C—C(min)	118·8 (3)	

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

2713 reflections and 206 parameters. The average parameter shift to error ratio was 0·01 in the final cycle.

All calculations were carried out on the CDC Cyber 72 computer of RRC Ljubljana using the XRAY 72 system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) adapted by one of us (LG). The atomic scattering factors tabulated by Cromer & Mann (1968) for heavy atoms and those tabulated by Stewart, Davidson & Simpson (1965) for H atoms were used. The values of f' and f'' for anomalous-dispersion correction tabulated by Cromer & Liberman (1970) were applied. Positional parameters are listed in Table 1. The structure of the

complex molecule and the atom-numbering system used are shown in Fig. 1 and a stereoscopic drawing (Johnson, 1965) of the structure is shown in Fig. 2. Important interatomic distances and angles are given in Table 2.*

Discussion. The molecular structure of the complex confirms expectations based on the Gillespie–Nyholm treatment (Gillespie, 1970) and vibrational spectra (Milićev & Hadži, 1977). The coordination around Sb is in fact a nearly regular square pyramid with the Sb atom in the basal plane. Triphenylphosphine oxide ligands are *cis*-coordinated through O. The chemical bonding may be rationalized by the VB method (Cotton & Wilkinson, 1972) with Sb using its vacant $5d$ orbitals in forming sp^3d^2 hybrids. In the trivalent state, a lone electron pair occupies one of the hybrid orbitals, three electrons are involved in bonding to three Cl atoms and the organic ligands coordinate by donating their O lone electron pair into the vacant Sb hybrid orbitals. The complex molecules are packed in alternating layers parallel to the *ab* plane. The phenyl

Table 3. *Mean values of some molecular parameters in antimony*(III) *and bismuth*(III) *halide complexes with* $(C_6H_5)_3PO$ *and* $(C_6H_5)_3AsO$

	Bond lengths in Å		Angle at oxygen	χ^a	Reference
	Sb—O	Sb—Cl (*trans* to O)			
$SbCl_3[(C_6H_5)_3PO]_2$	2·46	2·47	141·1°	2·45	(b)
$SbCl_3[(C_6H_5)_3AsO]_2$	2·26	2·59	139·0	2·45	(c)
$\{BiI_3[(C_6H_5)_3PO]_2\}_2$			154·4[d]	2·08	(e)
$[BiI_3]_2[(C_6H_5)_3AsO]_3$			147·0	2·08	(f)

(a) χ = electronegativity of the metal in its trihalides, calculated by the method of Huheey (1965). Ionization potentials and electron affinities of the metal are taken from Vedeneev, Gurvich, Kondrat'ev Medvedev & Frankevich (1962). (b) Present paper. (c) Lindqvist (1963). (d) $(C_6H_5)_3PO$ *trans* to a terminal I atom. (e) Lazarini & Milićev (1976). (f) Lazarini, Golič & Pelizzi (1976).

rings of one layer protude into the hollows of the next, isolating the inorganic parts of the molecules from one another. The basal plane of the complex molecule, including phenyl groups, has the C_2 point symmetry. Consequently, the apical positions on both sides of the basal plane are structurally and energetically equivalent. Statistical disorder of the apical Cl atoms and Sb lone electron pairs is feasible, and a twofold crystallographic axis through the Sb atom is generated. For this reason no displacement of the Sb atom out of the basal plane could be detected. As anticipated, the bond to the apical Cl atom is shorter than that to the *cis* Cl atoms in the base and the P—O distance is somewhat longer than in free triphenylphosphine oxide (1·46 Å, Bandoli, Bortolozzo, Clemente, Croatto & Panattoni, 1970).

Comparison of the molecular parameters with those of other known structures of triphenylphosphine oxide and triphenylarsine oxide complexes with Sb^{III} and Bi^{III} halides is interesting (Table 3). The Sb—O bonds are appreciably longer and the Sb—Cl bonds in the base appreciably shorter in $SbCl_3[(C_6H_5)_3PO]_2$ than in $SbCl_3[(C_6H_5)_3AsO]_2$. This is in agreement with the already established relative Lewis basicity of these oxobases (Hadži, Klofutar & Oblak, 1968; Milićev & Hadži, 1977). In this case the *trans* influence is in concordance with the Lewis basicity. The angle at O is smaller in complexes of Sb and triphenylarsine oxide. This should be expected because of the differences in electronegativities of the metal and the consequent changes in s and p character of the donating orbital on O (Bent, 1961) in the first case; in the second the angle is sterically dependent because the As—O bonds are appreciably longer than the P—O bonds (Lindqvist, 1963). The bond lengths around Bi are left out of the correlation because of different bonding conditions in Bi iodine-bridged binuclear complexes.

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