

- RAO, C. N. R. & RAO, G. V. S. (1974). *Natl Stand. Ref. Data Ser. Natl Bur. Stand.* **49**, 117–122.
- SALJE, E. (1975). *Acta Cryst.* **A31**, 360–363.
- SALJE, E. (1976). *Ferroelectrics*, **12**, 215–217.
- SALJE, E. (1977). *Acta Cryst.* **B33**, 574–577.
- SALJE, E. & VISWANATHAN, K. (1975). *Acta Cryst.* **A31**, 356–359.
- SAWADA, S. & DANIELSON, G. C. (1959). *Phys. Rev.* **113**, 803–808.
- SCHIRMER, O. F., WITTEW, V., BAUR, W. & BRANDT, G. (1977). *J. Electrochem. Soc.* **124**, 749–753.
- SCHRÖDER, F. A. (1976). *Acta Cryst.* **A32**, 342–344.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- TANISAKI, S. (1960a). *J. Phys. Soc. Jpn*, **15**, 573–581.
- TANISAKI, S. (1960b). *J. Phys. Soc. Jpn*, **15**, 566–573.

*Acta Cryst.* (1978). **B34**, 1111–1116

## Antimony Trichloride 1:1 Complexes with Terephthaldehyde and *p*-Diacetylbenzene

BY WILLIAM A. BAKER AND DONALD E. WILLIAMS

*Department of Chemistry, University of Louisville, Louisville, Kentucky 40208, USA*

(Received 29 March 1977; accepted 20 July 1977)

The crystal and molecular structures of 1:1 adducts of  $\text{SbCl}_3$  with organic carbonyl compounds were determined by X-ray diffraction. The terephthaldehyde adduct ( $\text{C}_8\text{H}_6\text{O}_2\text{SbCl}_3$ ) crystallized in space group *Pnma* with  $Z = 4$  and lattice constants  $a = 8.433$  (1),  $b = 21.556$  (2), and  $c = 6.279$  (1) Å. The Sb atom is strongly coordinated to two carbonyl O atoms, and weakly coordinated to a Cl, in a distorted pentagonal bipyramidal configuration. The *p*-diacetylbenzene adduct ( $\text{C}_{10}\text{H}_{10}\text{O}_2\text{SbCl}_3$ ) crystallized in space group *Pbca* with  $Z = 8$  and lattice constants  $a = 17.689$  (2),  $b = 17.639$  (2), and  $c = 8.996$  (2) Å. In this structure there are two kinds of *p*-diacetylbenzene molecules, of which one has coplanar acetyl groups and one has acetyl groups non-coplanar by  $9.9^\circ$ . The Sb atom is strongly coordinated to two carbonyl O atoms and to a Cl in a distorted octahedral configuration.

### Introduction

Over a half century ago Menshutkin (1912) reported the existence of over 60 compounds which were adducts of antimony trichloride with organic molecules. Recently, Park (1969) has examined 119 adducts formed between antimony trichloride and various organic molecules. The detailed crystal structures of several adducts have been determined. These include 2:1 adducts with naphthalene (Hulme & Szymanski, 1969) and phenanthrene (Demaldé, Mangia, Nardelli, Pelizzi & Tani, 1972) and a 1:1 adduct with aniline (Hulme & Scruton, 1968).

Antimony trichloride itself has a pyramidal structure both in the crystal (Lindquist & Niggli, 1956) and in the gas phase observed by electron diffraction (Allen & Sutton, 1950) or microwave spectroscopy (Kisliuk, 1954). Although antimony trichloride is in Group V of the periodic table and has a lone pair of electrons on Sb, its normal mode of coordination is in the role of electron acceptor from the coordinated ligand atoms.

### Experimental

The 1:1  $\text{SbCl}_3$ -terephthaldehyde adduct ( $\text{C}_8\text{H}_6\text{O}_2\text{SbCl}_3$ ) was prepared (Park, 1969) by addition of 2.0 g of terephthaldehyde (Aldrich Chemical Co., m.p. 114–115°C) to a dry solution of 3.7 g  $\text{SbCl}_3$  (Baker Chemical Co., further purified by vacuum sublimation) in 100 ml  $\text{CCl}_4$ . The mixture was boiled and filtered. The resulting white crystals were recrystallized from  $\text{CCl}_4$ , m.p. 79–81°C. The density measured by flotation in  $\text{CBr}_4\text{-CCl}_4$  solution was  $2.05 \text{ g cm}^{-3}$ ; the calculated density was  $2.11 \text{ g cm}^{-3}$ . X-ray intensity data were taken from a single crystal of approximate dimensions  $0.3 \times 0.3 \times 0.4 \text{ mm}$  sealed in a glass capillary tube. Lattice constants were obtained by a least-squares fit (Williams, 1964) using the Nelson & Riley (1945) extrapolation function to ten high-angle reflections observed with  $\text{Cr } K\alpha$  ( $\lambda = 2.28962 \text{ Å}$ ) radiation.

The diffraction symmetry was orthorhombic and the systematically absent reflections indicated space groups

*Pnma* or *Pna2<sub>1</sub>*. The statistical distribution of intensities indicated the centrosymmetric space group *Pnma* and this was confirmed by the structure solution. X-ray diffraction intensities for 1693 reflections were observed using Zr-filtered Mo *K* $\alpha$  radiation ( $\lambda = 0.7107$  Å). The  $\theta$ - $2\theta$ -scan method of data collection was used, with stationary background counts taken before and after the scan. A scintillation counter detector was used. A systematic decline of reference intensities to about 60% of their initial values was observed. This decline was rapid initially, and then levelled off. The data were corrected for this apparent decomposition and the usual Lorentz and polarization corrections made to obtain observed structure factor amplitudes. The error in the intensity measurement was estimated from the formula

$$\sigma^2(I) = C_T + C_B + (0.05C_T)^2 + (0.05C_B)^2$$

where  $C_T$  and  $C_B$  are the total and background counts respectively. The error in the structure factor was calculated by the finite-difference method (Williams & Rundle, 1964).

The Sb and Cl positions were obtained from a sharpened Patterson function map. The remainder of the atoms were located from Fourier maps. The final weighted least-squares structure-factor refinement (Busing, Martin & Levy, 1962) used calculated H positions and anisotropic temperature factors for all atoms. The H atoms were placed 1.07 Å from C on a line passing through the 1,4 ring C atoms; the aldehyde H was placed with local  $C_{2v}$  symmetry at the carbonyl C. The scattering factor for H was that of Stewart, Davidson & Simpson (1965) and the H temperature factors were set equal to those of the bonded C atom. For other atoms the scattering factors of Hanson, Herman, Lea & Skillman (1964) were used.

67 parameters were adjusted by least-squares calculations. In the final cycle all shifts in the adjustable parameters were less than  $0.1\sigma$ . The final weighted agreement factor,

$$R_w = \{\sum \sigma^{-2}(F_o)[F_o - |F_c|]^2 / \sum \sigma^{-2}(F_o)\}^{1/2},$$

was 0.062.\*

The final atomic coordinates are given in Table 1. The atomic numbering system and the thermal ellipsoids (Johnson, 1965) are shown in Fig. 1.

The 1:1 SbCl<sub>3</sub>-*p*-diacetylbenzene adduct (C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>SbCl<sub>3</sub>) was prepared by addition of 1.6 g of *p*-diacetylbenzene (Aldrich Chemical Co., m.p. 112–114°C) to 80 ml of a dry solution of 3 g SbCl<sub>3</sub> in cyclohexane. The mixture was warmed and CHCl<sub>3</sub> added until all the *p*-diacetylbenzene dissolved (about 20 ml of

Table 1. Atomic coordinates ( $\times 10^4$ ) in fractions of the unit-cell edges and their estimated standard deviations

Terephthaldehyde adduct

	x	y	z
Sb(1)	6931 (1)	2500	-352 (1)
Cl(1)	8160 (4)	2500	2998 (4)
Cl(2)	8632 (3)	3280 (1)	-1803 (4)
C(1)	5560 (11)	4468 (4)	4094 (15)
C(2)	6046 (11)	4632 (4)	6140 (16)
C(3)	5454 (10)	5168 (4)	7052 (13)
C(4)	6189 (11)	3879 (5)	3137 (17)
O(1)	5807 (8)	3678 (4)	1428 (12)
H(2)	6870	4343	6976
H(3)	5774	5314	8624
H(4)	7024	3593	3962

*p*-Diacetylbenzene adduct

	x	y	z
Sb(1)	7474.8 (3)	7282.8 (2)	2138.7 (4)
Cl(1)	6435 (1)	8040 (1)	2844 (3)
Cl(2)	8310 (1)	8211 (1)	3148 (2)
Cl(3)	7449 (1)	6567 (1)	4370 (2)
C(1)	5667 (4)	5314 (4)	515 (8)
C(2)	5624 (4)	4543 (4)	239 (10)
C(3)	5043 (4)	5754 (4)	274 (10)
C(4)	6366 (4)	5671 (4)	1101 (9)
C(5)	7083 (5)	5246 (5)	1107 (18)
C(6)	9695 (4)	5666 (4)	550 (8)
C(7)	9623 (5)	4331 (5)	190 (11)
C(8)	9318 (5)	4983 (5)	757 (12)
C(9)	9358 (4)	6376 (5)	1119 (8)
C(10)	9747 (5)	7099 (5)	922 (13)
O(1)	6354 (3)	6321 (3)	1522 (6)
O(2)	8751 (3)	6354 (3)	1798 (6)
H(2)	6097	4177	425
H(3)	5080	6346	516
H(5)	7538	5576	1550
H(5')	7229	5051	18
H(5'')	7024	4754	1794
H(7)	9972	4819	354
H(8)	8800	4957	1368
H(10)	9436	7550	1429
H(10')	9833	7226	-229
H(10'')	10290	7085	1447

CHCl<sub>3</sub>). The solution was boiled and filtered. The light-yellow crystals were recrystallized from CHCl<sub>3</sub>-C<sub>6</sub>H<sub>12</sub>, m.p. 120–122°C. The density measured by flotation in CBr<sub>4</sub>-CCl<sub>4</sub> solution was 1.81 g cm<sup>-3</sup>; the calculated density was 1.85 g cm<sup>-3</sup>. X-ray intensity data were taken from a single crystal approximately 0.25 mm in diameter and 0.35 mm long sealed in a glass capillary tube. Lattice constants were obtained as described above from 15 high-angle reflections.

The diffraction symmetry was orthorhombic and the systematically absent reflections indicated the unique space group *Pbca*. X-ray diffraction intensities for 2489 reflections were observed as described above. No significant decomposition of the crystal occurred during data collection, as indicated by measurement of

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33190 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

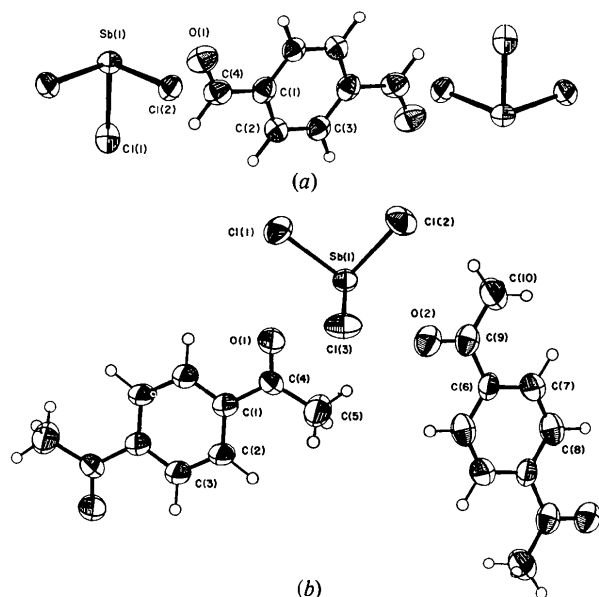


Fig. 1. The atomic numbering system and the thermal ellipsoids. (a) Terephthaldehyde adduct. (b) *p*-Diacetylbenzene adduct.

reference intensities from the crystal. The data were processed as described above.

The Sb position was obtained from a sharpened Patterson function map. The remainder of the atoms were located from Fourier maps. The structure was refined as described above. The methyl-group H atoms were assigned staggered tetrahedral positions. 145 parameters were adjusted by least-squares calculations. In the final cycle all adjustable parameter shifts were less than  $0.1\sigma$ . The final weighted agreement index was 0.051.\*

### Description of the terephthaldehyde adduct structure

The observed density indicated four formula units in the unit cell. Thus, in space group *Pnma* the  $\text{SbCl}_3$  and terephthaldehyde molecules must lie on symmetry elements. The structure analysis indicated that the  $\text{SbCl}_3$  molecule was located on a mirror plane at  $y = 0.25$ . The terephthaldehyde molecule was located on an inversion center at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ , with the long axis of the molecule predominantly along **b** (see Fig. 2). The terephthaldehyde molecule is nearly planar. Table 2 shows that there is a slight twist of the carbonyl group with the O atom  $0.067 \text{ \AA}$  out of the plane defined by the benzene ring and the carbonyl C atoms. Fig. 3 shows the bond distances and angles in the terephthaldehyde molecule; all are in the normally expected range. The  $\text{SbCl}_3$  molecule is pyramidal with bond

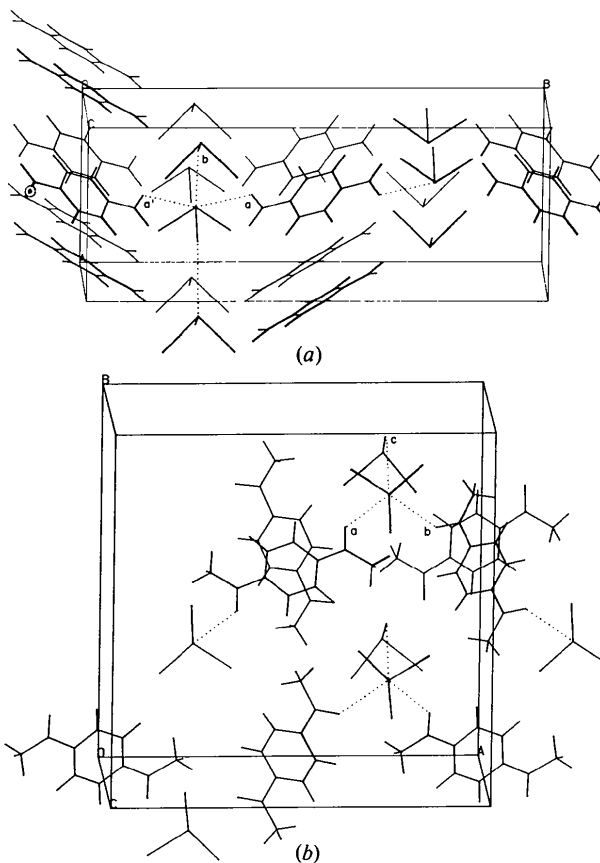


Fig. 2. Crystal structures of (a) the terephthaldehyde adduct, (b) the *p*-diacetylbenzene adduct.

Table 2. Least-squares planes and deviations of atoms ( $\text{\AA}$ )

The plane is fitted to the atoms indicated with an asterisk; atoms related by the inversion centre were included in the fitting.

#### Terephthaldehyde adduct

$$0.7723X + 0.5108Y - 0.3777Z = 7.5765$$

C(1)*	0.010	C(4)*	0.005
C(2)*	-0.000	O(1)	0.067
C(3)*	-0.010		

#### *p*-Diacetylbenzene adduct

$$\text{Plane A: } -0.3035X - 0.1597Y + 0.9394Z = -4.0928$$

$$\text{Plane B: } 0.4843X - 0.1357Y + 0.8643Z = 7.3697$$

	Distance from plane A		Distance from plane B
C(1)*	-0.011	C(6)*	0.007
C(2)*	-0.004	C(7)*	0.015
C(3)*	0.005	C(8)*	-0.009
C(4)*	0.008	C(9)*	-0.009
C(5)	-0.252	C(10)*	-0.003
O(1)	0.187	O(2)*	0.004

\* See deposition footnote.

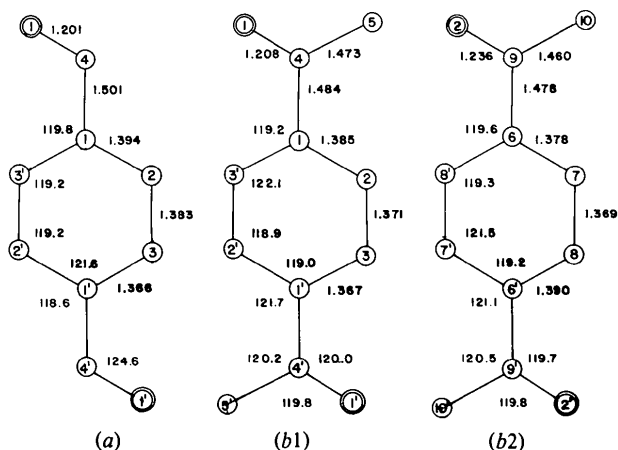


Fig. 3. Bond distances and angles (Å and deg) in (a) the terephthaldehyde molecule; (b1) the first *p*-diacetylbenzene molecule; and (b2) the second *p*-diacetylbenzene molecule. The O atoms are indicated by double concentric circles. The estimated standard deviations are 0.01 Å for the distances and 0.8° for the angles.

Table 3. Distances (Å) and angles (°) and their estimated standard deviations about the Sb atom

See Fig. 2 for identification of lettered atoms.

Terephthaldehyde adduct

Sb(1)—Cl(1)	2.345 (3)	Cl(1)—Sb(1)—Cl(2)	94.4 (1)
Sb(1)—Cl(2)	2.391 (2)	Cl(1)—Sb(1)—O(a)	78.5 (2)
Sb(1)—O(a)	2.932 (4)	Cl(1)—Sb(1)—Cl(b)	91.3 (1)
Sb(1)—Cl(b)	3.507 (3)	Cl(2)—Sb(1)—Cl(2')	89.4 (2)
		Cl(2)—Sb(1)—O(a)	74.3 (2)
		Cl(2)—Sb(1)—O(a')	161.5 (2)
		Cl(2)—Sb(1)—Cl(b)	134.8 (1)
		O(a)—Sb(1)—O(a')	120.0 (5)
		O(a)—Sb(1)—Cl(b)	63.0 (2)

*p*-Diacetylbenzene adduct

Sb(1)—Cl(1)	2.360 (2)	Cl(1)—Sb(1)—Cl(2)	89.5 (1)
Sb(1)—Cl(2)	2.385 (2)	Cl(1)—Sb(1)—Cl(3)	93.4 (1)
Sb(1)—Cl(3)	2.372 (2)	Cl(1)—Sb(1)—O(a)	80.6 (1)
Sb(1)—O(a)	2.668 (5)	Cl(1)—Sb(1)—O(b)	170.7 (1)
Sb(1)—O(b)	2.806 (5)	Cl(1)—Sb(1)—Cl(c)	80.8 (1)
Sb(1)—Cl(c)	3.213 (2)	Cl(2)—Sb(1)—Cl(3)	93.2 (1)
		Cl(2)—Sb(1)—O(a)	167.5 (1)
		Cl(2)—Sb(1)—O(b)	86.8 (1)
		Cl(2)—Sb(1)—Cl(c)	82.6 (1)
		Cl(3)—Sb(1)—O(a)	79.8 (1)
		Cl(3)—Sb(1)—O(b)	78.3 (1)
		Cl(3)—Sb(1)—Cl(c)	172.7 (1)
		O(a)—Sb(1)—O(b)	101.8 (5)
		O(a)—Sb(1)—Cl(c)	103.3 (1)
		O(b)—Sb(1)—Cl(c)	107.2 (1)

angles 94.4, 94.4, and 89.4°. The Sb—Cl bond distances are 2.391, 2.391, and 2.345 Å (Table 3). There are also two O atoms and a Cl close to the Sb atom in a distorted pentagonal bipyramidal arrangement. The coordination about Sb is discussed further below.

### Description of the *p*-diacetylbenzene adduct structure

The observed density indicated eight formula units in the unit cell. Thus, in space group *Pbca* both the SbCl<sub>3</sub> and the *p*-diacetylbenzene molecules could be located in general positions. The structural analysis indicated that the SbCl<sub>3</sub> molecule was indeed in a general position. The Sb atom was placed near  $\frac{3}{4}, \frac{3}{4}, \frac{1}{4}$ . However, the structural analysis indicated that there were two crystallographically different *p*-diacetylbenzene molecules. Each molecule was centrosymmetric; thus the asymmetric unit was two half-molecules located on different inversion centers. Molecule 1 was located at  $\frac{1}{2}, \frac{1}{2}, 0$  and molecule 2 was located at  $1, \frac{1}{2}, 0$ . Table 2 shows that molecule 2 is planar, except for the methyl H atoms. In molecule 1 the acetyl groups are significantly twisted. The twist angle between the plane of the ring and the plane of the acetyl group is 9.9°. Since the observed twist angle does not result in a shorter Sb—O coordinated distance as compared to a planar acetyl-group conformation, the nonplanarity must be caused by van der Waals packing considerations. The molecules stack alternately in columns along *c* via a screw axis; the two crystallographic molecular types are rotated by about 90° from each other (Fig. 2).

The SbCl<sub>3</sub> molecule is again pyramidal with bond angles 89.5, 93.4, and 93.2°. The Sb—Cl bond distances are 2.360, 2.385 and 2.372 Å. There are also two O atoms and a Cl close to the Sb atom in a distorted octahedral arrangement. The coordination about Sb is discussed further below.

### Discussion

According to valence-shell electron-pair repulsion (VSEPR) theory, lone-pair electrons should occupy an equal or greater surface area on a coordinated central atom than ligand groups (Gillespie, 1967). Thus, SbCl<sub>3</sub> is an *AX<sub>3</sub>E* type which is nominally tetrahedral. The angles observed in SbCl<sub>3</sub> are less than tetrahedral because of the larger surface area required by the lone-pair electrons.

In the crystal additional coordination may occur. The usual criterion used to decide if a neighboring atom is coordinated is the smallness of the interatomic distance relative to the normally expected van der Waals distance. The normal Sb—Cl and Sb—O van der Waals distances are 4.0 and 3.6 Å respectively (Pauling, 1960). If three additional atoms are coordinated to Sb, the coordination type is *AX<sub>6</sub>E*, seven coordinate. The geometry of seven-coordination is complex and depends on the softness of the atoms (Claxton & Benson, 1966). 1:3:3, 1:4:2, or 1:5:1 arrangements are possible.

In crystalline SbCl<sub>3</sub> (Lindquist & Niggli, 1956) the Sb atom has two Cl atoms near it at 3.447 Å\* and a

\* The original publication states incorrectly that there are no nonbonded distances less than 3.5 Å in the SbCl<sub>3</sub> crystal structure.

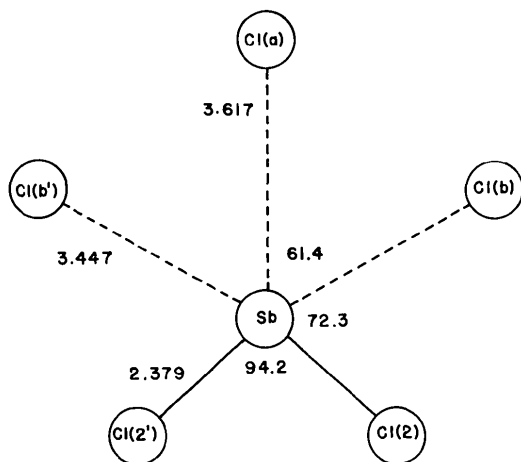


Fig. 4. Coordination of Sb in crystalline  $\text{SbCl}_3$ , looking down the  $\text{Cl}(1)\text{--Sb}$  bond. The primed atoms are related by mirror symmetry. The  $\text{Sb--Cl}(1)$  distance is 2.351 Å and the angles from  $\text{Cl}(1)$  are: to  $\text{Cl}(2)$ , 95.7°; to  $\text{Cl}(a)$ , 86.3°; and to  $\text{Cl}(b)$ , 80.6°. The data were taken from Lindquist & Niggli (1956).

third Cl at 3.617 Å, in addition to bonded Cl atoms at 2.351, 2.379, and 2.379 Å. The coordination about Sb is a distorted pentagonal bipyramid, the 1:5:1 configuration, with the lone pair axial. There is surface area available for the lone pair directly opposite one of the bonded Cl atoms (Fig. 4). If the coordination to  $\text{Cl}(a)$  were disregarded because of the longer distance to this atom, the configuration about Sb would be a distorted tetragonal pyramid, again with plenty of surface area available for a lone pair of electrons. The  $\text{Cl}(2)\text{--Sb--Cl}(2')$  bond angle is slightly smaller (94.2°) than the other two  $\text{Cl--Sb--Cl}$  angles (95.7°). The unique Cl has the shorter  $\text{Sb--Cl}$  distance (2.351 vs 2.379 Å).

In the  $\text{SbCl}_3\text{--terephthaldehyde}$  adduct the coordination about Sb appears to be quite similar to the coordination in  $\text{SbCl}_3$  itself, except that the two shorter  $\text{Sb--Cl}$  coordinated distances are replaced by  $\text{Sb--O}$  coordinated distances of 2.932 Å. The angles about Sb (Table 3) are remarkably similar to those in  $\text{SbCl}_3$  itself; even the mirror-plane symmetry is present. The coordination type is thus 1:5:1  $AX_6E$ , a distorted pentagonal bipyramid with a lone pair probably located opposite one bonded Cl in an axial location. The  $\text{Cl}(2)\text{--Sb--Cl}(2')$  bond angle (89.4°) is significantly smaller than the other two  $\text{Cl--Sb--Cl}$  angles (94.4°). The unique Cl has the shorter  $\text{Sb--Cl}$  distance (2.345 vs 2.391 Å).

The  $\text{SbCl}_3\text{--}p\text{-diacetylbenzene}$  adduct structure has a different coordination geometry. The coordination about Sb is a distorted octahedron (Table 3). No large surface area is available for the lone pair and the coordination appears to be of the  $AX_6$  type. The two  $\text{Sb--O}$  distances of 2.668 and 2.806 Å are significantly shorter than the corresponding distances in the

terephthaldehyde adduct structure. Also, the Cl atom is coordinated more closely (3.213 Å) as compared to either  $\text{SbCl}_3$  itself (3.617 Å) or the  $\text{SbCl}_3\text{--terephthaldehyde}$  adduct (3.507 Å). Thus the octahedral  $AX_6$   $\text{SbCl}_3\text{--}p\text{-diacetylbenzene}$  adduct shows a tighter coordination than the pentagonal bipyramidal  $AX_6E$  structure of  $\text{SbCl}_3\text{--terephthaldehyde}$ . The  $\text{Cl}(1)\text{--Sb--Cl}(2)$  bond angle (89.5°) is significantly smaller than the other two  $\text{Cl--Sb--Cl}$  angles (93.4 and 93.2°). The unique Cl has the shorter  $\text{Sb--Cl}$  distance (2.365 vs 2.385 and 2.372 Å).

The geometry about the carbonyl groups is consistent with  $sp^2$  hybridization of the lone pairs on O. The Sb is always *trans* to the benzene ring and is near the organic molecular plane. The  $\text{Sb--O--C}$  coordination angles are 124.5, 137.3 and 131.0°. The carbonyl stretching frequency of *p*-diacetylbenzene decreases from 1682  $\text{cm}^{-1}$  in the uncomplexed molecule to 1677  $\text{cm}^{-1}$  in the adduct (Park, 1969), corresponding to the tighter coordination in this adduct. The terephthaldehyde carbonyl stretching frequency of 1710  $\text{cm}^{-1}$  is unchanged in the complex. The lack of a frequency shift in the latter case was one of the factors which led Park to conclude that O was not ligated with Sb. We see that in fact Sb is ligated with O in both instances, but the weaker coordination in the terephthaldehyde complex did not show a detectable shift in the carbonyl stretching frequency.

The 1:1  $\text{SbCl}_3\text{--aniline}$  structure (Hulme & Scruton, 1968) shows a trigonal bipyramidal  $AX_4E$  coordination about Sb, with the lone pair equatorial. The 2:1  $\text{SbCl}_3\text{--naphthalene}$  (Hulme & Szymanski, 1969) and 2:1  $\text{SbCl}_3\text{--phenanthrene}$  (Demaldé *et al.*, 1972) adducts also show this trigonal bipyramidal configuration about Sb. The present adduct structures cannot be described as  $AX_4E$ , even if the more distant Cl coordination is neglected. The two O atoms at close coordination distances in both structures result in at least five ligands surrounding the Sb.

We thank Professors C. P. Brock and D. E. Sands and the University of Kentucky Computer Center for assistance in preparing the ORTEP plots.

## References

- ALLEN, P. W. & SUTTON, L. E. (1950). *Acta Cryst.* **3**, 46–72.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.  
 CLAXTON, T. A. & BENSON, G. C. (1966). *Can. J. Chem.* **44**, 157–163.  
 DEMALDÉ, A., MANGIA, A., NARDELLI, M., PELIZZI, G. & TANI, M. E. V. (1972). *Acta Cryst.* **B28**, 147–150.  
 GILLESPIE, R. J. (1967). *Angew. Chem. Int. Ed. Engl.* **6**, 819–830.

- HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.
- HULME, R. & SCRUTON, J. C. (1968). *J. Chem. Soc. A*, pp. 2448–2452.
- HULME, R. & SZYMANSKI, J. T. (1969). *Acta Cryst.* **B25**, 753–761.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KISLIUK, P. (1954). *J. Chem. Phys.* **22**, 86–92.
- LINDQUIST, I. & NIGGLI, A. (1956). *J. Inorg. Nucl. Chem.* **2**, 345–347.
- MENSHUTKIN, B. (1912). *Zh. Russ. Fiz. Khim. Ova*, **44**, 1079–1145.
- NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc. London*, **57**, 160–177.
- PARK, W. (1969). PhD Dissertation, Univ. of Louisville, Louisville, Kentucky.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. Ithaca: Cornell Univ. Press.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WILLIAMS, D. E. (1964). *A Fortran Lattice Constant Refinement Program*, US Atomic Energy Commission Report, IS-1052.
- WILLIAMS, D. E. & RUNDLE, R. E. (1964). *J. Am. Chem. Soc.* **86**, 1660–1666.

*Acta Cryst.* (1978). **B34**, 1116–1120

## The Crystal Structures of Hexahalouranates.

### I. Bis(triphenylethylphosphonium) Hexachlorouranate(IV) and Bis(triphenylethylphosphonium) Hexabromouranate(IV)

BY M. R. CAIRA AND J. F. DE WET\*

*Crystallography Group, Chemistry Department, University of Port Elizabeth, Port Elizabeth 6000, South Africa*

AND J. G. H. DU PREEZ AND B. J. GELLATLY†

*Uranium Chemistry Research Unit, University of Port Elizabeth, Port Elizabeth 6000, South Africa*

(Received 2 August 1977; accepted 2 September 1977)

The crystal structures of the bis(triphenylethylphosphonium) hexahalouranates(IV),  $[\text{P}(\text{C}_6\text{H}_5)_3\text{C}_2\text{H}_5]_2[\text{U}X_6]$  [ $X =$  (I) chlorine, (II) bromine], have been determined from three-dimensional X-ray diffraction data collected on an automatic Philips PW 1100 four-circle diffractometer using 2894 (I) and 1448 (II) structure amplitudes from independent reflexions. The compounds crystallize in the (I) triclinic  $P\bar{1}$ , and (II) monoclinic  $P2_1/n$  space groups with the lattice constants (I):  $a = 10.53$  (1),  $b = 10.95$  (1),  $c = 10.31$  (1) Å,  $\alpha = 113.22$  (5),  $\beta = 105.20$  (5),  $\gamma = 80.40$  (5)°; and (II):  $a = 10.45$  (1),  $b = 13.51$  (1),  $c = 15.46$  (1) Å,  $\beta = 96.67$  (5)°. In both structures the U atoms are situated at centres of symmetry [ $Z = 1$  (I) and 2 (II)]. Trial atomic coordinates, obtained by the usual heavy-atom techniques, were refined by blocked-full-matrix least-squares refinement procedures to values for the conventional  $R$  of 0.029 (I) and 0.055 (II). The mean values of the U– $X$  bond lengths and their estimated standard deviations are U–Cl = 2.624 (1) and U–Br = 2.770 (2) Å.

#### Introduction

The increasing number of accurate crystal-structure determinations in recent years on oxo-halo complexes of uranium with oxidation states  $\text{U}^{\text{IV}}$  to  $\text{U}^{\text{VI}}$ , as well as those of the type  $\text{UX}_4\text{L}_2$  ( $X = \text{Cl}, \text{Br}$ ;  $L$  a neutral oxygen donor ligand) has provided sufficient structural

data to permit important conclusions to be drawn with regard to the nature of the bonding by U in such complexes. Thus, de Wet & du Preez (1977) have adduced strong evidence that the nature of the bonding between U and its coordination neighbours is predominantly ionic, since ligand–ligand repulsions can account for the observed bonding distances as well as the shifts in U– $X$  ( $X = \text{oxygen}, \text{halogen}$ ) bond lengths which accompany changes in charge density, donor strength and coordination position of the ligands. For

\* Author to whom correspondence should be addressed.

† Present address: Chemistry Department, University of Reading, Reading, England.