References

Bream, R. A., Estes, E. D. & Hodgson, D. J. (1975). *Inorg. Chem.* **14**, 1672–1675.

Duckworth, V. F. & Stephenson, N. C. (1969). *Acta Cryst.* B**25**, 1795–1803.

Dunitz, J. D. (1957). *Acta Cryst.* **10**, 307–313.

Hatfield, W. E. (1974). *Extended Interactions Between Metal Ions*, edited by L. V. Interrante, *ACS Symp. Ser.* **5**, 108–141.

Helis, H. M., Goodman, W. H., Wilson, R. B., Morgan, J. A. & Hodgson, D. J. (1977). *Inorg. Chem.* **16**, 2412–2416.

Hodgson, D. J. (1975). *Prog. Inorg. Chem.* **19**, 173–241.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kupčik, V. & Ďurovič, S. (1960). *Czech. J. Phys. B*, **10**, 182–190.

Luukkonen, E. & Pajunen, A. (1973). *Suom. Kemistil. B*, **46**, 292–296.

Mégnamisi-Bélombé, M. & Novotny, M. A. (1978). *Inorg. Chem.* Submitted.

Pauling, L. (1960). *The Nature of the Chemical Bond.* 3rd ed., p. 225. Ithaca: Cornell Univ. Press.

Phelps, D. W., Goodman, W. H. & Hodgson, D. J. (1976). *Inorg. Chem.* **15**, 2266–2270.

Singh, P., Jeter, D. Y., Hatfield, W. E. & Hodgson, D. J. (1972). *Inorg. Chem.* **11**, 1657–1661.

Svedung, D. H. (1969). *Acta Chem. Scand.* **23**, 2865–2878.

Wilson, R. B., Hatfield, W. E. & Hodgson, D. J. (1976). *Inorg. Chem.* **15**, 1712–1716.

Acta Cryst. (1978). B**34**, 3739–3741

Antimony Trichloride 2 : 1 Complex with 1,3,5-Triacetylbenzene

By William A. Baker and Donald E. Williams

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

(*Received* 23 *August* 1977; *accepted* 25 *July* 1978)

Abstract. $2SbCl_3.C_{12}H_{12}O_3$, triclinic, $P\bar{1}$, $Z = 2$, $a = 8{\cdot}933$ (4), $b = 14{\cdot}045$ (4), $c = 8{\cdot}663$ (5) Å, $\alpha = 103{\cdot}70$ (5), $\beta = 104{\cdot}69$ (5), $\gamma = 95{\cdot}24$ (6)°, $D_m = 2{\cdot}06$, $D_c = 2{\cdot}07$ g cm^{-3}. Both Sb atoms have approximately octahedral configurations. Sb(1) is coordinated to three O atoms at 2·694, 3·023 and 3·040 Å. Sb(2) is coordinated to one O at 2·851 and two Cl atoms at 3·320 and 3·323 Å. The Sb(1) octahedra share an edge to form a bridged dimer with a nonbonded Sb···Sb distance of 3·777 Å.

Introduction. In a previous paper (Baker & Williams, 1978) the crystal structures of 1 : 1 adducts of antimony trichloride with terephthaldehyde and *p*-diacetylbenzene were described. The coordination about Sb in the terephthaldehyde adduct was found to be distorted pentagonal bipyramidal, described as AX_6E by valence-shell electron-pair repulsion (VSEPR) theory (Gillespie, 1967), with the lone pair axial. In the *p*-diacetylbenzene adduct the coordination about Sb was found to be distorted octahedral, described as AX_6 by VSEPR theory, with the lone pair not located. We have now examined the 2 : 1 complex with 1,3,5-triacetylbenzene in order to obtain more information about the nature of the coordination in antimony trichloride adducts with organic carbonyl compounds.

The 2 : 1 $SbCl_3$–triacetylbenzene adduct ($2SbCl_3.C_{12}H_{12}O_3$) was prepared (Park, 1969) by addition of 2·5 g of 1,3,5-triacetylbenzene (Eastman Chemical Co., m.p. 162–164 °C) to 100 ml of a solution of $CHCl_3$ containing 7·5 g of $SbCl_3$ (Baker Chemical Co., further purified by vacuum sublimation). The mixture was boiled and filtered. Light-yellow crystals were obtained on cooling and they were recrystallized from $CHCl_3$ (m.p. 122–124 °C). Elemental analysis for C, H, and Cl agreed with the above empirical formula.

X-ray intensity data were taken from a single crystal of approximate dimensions 0·2 × 0·2 × 0·3 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 27 high-angle reflections observed with Cr $K\alpha$ ($\lambda = 2{\cdot}28962$ Å) radiation. The conventional orientation for the reduced cell was obtained as described by Azaroff & Buerger (1958).

X-ray diffraction intensities for 2235 reflections were observed using Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). A manually controlled $\theta/2\theta$ scan method was used with graphically estimated backgrounds. A scintillation counter detector was used. No significant decomposition of the crystal occurred during data collection, as indicated by the measurement of reference intensities from the crystal. The data were corrected for the Lorentz and polarization factors in the usual manner to obtain observed structure factor amplitudes. The errors in the intensity measurements were estimated from $\sigma^2(I) = C_T + C_B + (0{\cdot}05C_T)^2 + (0{\cdot}05C_B)^2$, where C_T and C_B are the total and background counts respectively. The errors in the structure factors were calculated by a finite-difference method (Williams & Rundle, 1964).

Both Sb positions and one Cl position were obtained from a sharpened Patterson function map. A difference Fourier map was used to locate the remaining five Cl positions; a subsequent difference Fourier map based on all Sb and Cl positions revealed the remaining non-hydrogen atoms. The final weighted least-squares structure factor refinement (Busing, Martin & Levy, 1962) used calculated H positions and anisotropic temperature factors for all atoms. The ring H atoms were placed 1·04 Å from C on a line passing through the 1,4 C atoms. The methyl-group H atoms were assigned staggered tetrahedral positions. The scattering factor for H was that of Stewart, Davidson & Simpson (1965) and the H temperature factors were set equal to those of the C atoms to which they were bonded. For other atoms the scattering factors of Hanson, Herman, Lea, & Skillman (1964) were used.

Table 1. *Atomic coordinates* ($\times 10^4$) *and their standard deviations*

	x	*y*	*z*
Sb(1)	−413·7 (8)	4020·0 (5)	2964·6 (8)
Cl(1)	433 (4)	3913 (3)	615 (4)
Cl(2)	−1900 (3)	2406 (2)	2108 (4)
Cl(3)	1864 (3)	3512 (2)	4351 (3)
Sb(2)	1735·3 (8)	1250·6 (5)	1981·6 (9)
Cl(4)	1777 (3)	−402 (2)	723 (4)
Cl(5)	4386 (4)	1556 (2)	3338 (4)
Cl(6)	917 (5)	744 (3)	4110 (5)
C(1)	3390 (13)	6739 (7)	2819 (11)
C(2)	4113 (12)	7529 (8)	2373 (11)
C(3)	5428 (11)	7446 (7)	1811 (11)
C(4)	6005 (11)	6576 (8)	1709 (11)
C(5)	5258 (11)	5776 (7)	2146 (11)
C(6)	3954 (11)	5855 (7)	2703 (11)
C(7)	1983 (12)	6790 (8)	3490 (13)
C(8)	1210 (16)	7658 (10)	3485 (17)
C(9)	6286 (14)	8310 (8)	1345 (14)
C(10)	6071 (13)	9331 (10)	1946 (18)
C(11)	5959 (13)	4865 (7)	2077 (11)
C(12)	5179 (13)	4017 (8)	2592 (15)
O(1)	1470 (9)	6082 (6)	3999 (9)
O(2)	7159 (11)	8148 (6)	507 (11)
O(3)	7128 (9)	4827 (5)	1611 (9)
H(2)	3678	8196	2459
H(4)	6994	6514	1289
H(6)	3416	5274	3029
H(8)	253	7569	3944
H(8′)	851	7761	2305
H(8″)	1989	8299	4201
H(10)	6731	9822	1550
H(10′)	4895	9394	1527
H(10″)	6385	9517	3234
H(12)	5783	3417	2490
H(12′)	4024	3778	1864
H(12″)	5148	4235	3816

208 parameters were adjusted by least squares. In the final cycle all shifts in the adjustable parameters were less than 0·1σ. 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 0·039. The final atomic coordinates are given in Table 1. Table 2 lists coordination distances and angles about the Sb atoms, and Table 3 shows deviations from the benzene least-squares plane and from the $Sb_2Cl_6O_2$ dimer plane.* The atomic numbering system and the thermal ellipsoids (Johnson, 1965) are shown in Fig. 1.

Discussion. The observed density indicated two formula units in the unit cell. Thus, in space group $P\bar{1}$ the asymmetric unit consists of two $SbCl_3$ molecules and one 1,3,5-triacetylbenzene molecule. The two Sb atoms have a different coordination environment.

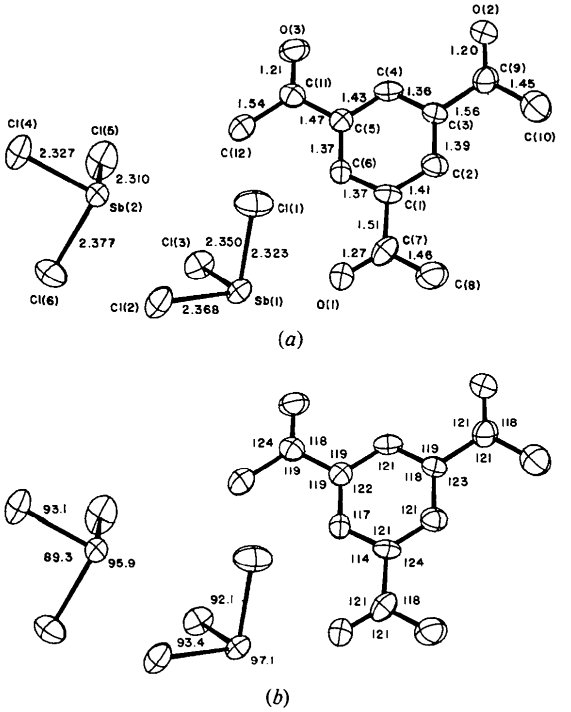

Fig. 1. (*a*) The atomic numbering system and the bond distances (Å). The standard deviations are: for Sb—Cl, 0·003 Å; all others, 0·012--0·018 Å. (*b*) The bond angles (°). The standard deviations are: for Cl—Sb—Cl, 0·11–0·16°; for others 1°.

---

* Lists of structure factors and anisotropic thermal parameters, and Tables 2 and 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33799 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

An overall view of the crystal structure is given in Fig. 2, viewed roughly perpendicular to the *bc* unit-cell face. Sb(1) is located near an inversion center at $(0,\frac{1}{2},\frac{1}{2})$, and Sb(2) is located near an inversion center at (0,0,0).

The 1,3,5-triacetylbenzene molecule is centered near $(\frac{1}{2},\frac{1}{2},\frac{1}{4})$ in a general position. The benzene ring is planar within experimental error; the deviations of the acetyl groups from the benzene ring plane are shown in Table 3(*a*). Acetyl group C(9)—C(10)—O(2) shows the largest deviations from the benzene plane; O(2) and symmetry-related O(*f*) are moved closer to Sb as a result of a 20° twist of this group. Acetyl group C(7)—C(8)—O(1) is twisted by 6°; the O of this group, as O(*a*) and O(*c*), is involved in the bridged dimer moiety. Acetyl group C(11)—C(12)—O(3) is nearly planar, with a twist angle of only 2°; O(3) as O(*b*) has the shortest distance to Sb at 2·694 Å. Fig. 1 shows the distances and angles in the 1,3,5-triacetylbenzene molecule; all are close to normally expected values.

The Sb—Cl distances in the two $SbCl_3$ molecules range from 2·310 to 2·377 Å. Since the estimated standard deviation is 0·003 Å, this difference is outside the experimental error. The Cl—Sb—Cl angles range from 89·3 to 97·1°; again this difference is outside the experimental error. Apparently $SbCl_3$ can adjust its geometry within these ranges.

Sb(2) is coordinated to two Cl atoms at nearly equal distances of 3·323 and 3·320 Å (Table 2) and to an O atom at 2·851 Å. The configuration is approximately octahedral, with the largest deviation from regular octahedral symmetry being the Cl(3)—Sb(2)—Cl(*e*) angle of 111°. There does not appear to be much surface area available for the Sb lone-pair electrons, as required by VSEPR theory (Gillespie, 1967). Cl(2) is 3·775 Å from Sb(2); since the sum of the van der Waals radii of Sb and Cl is 4·0 Å (Pauling, 1960), the interaction (if any) is weak. The nearest neighboring Sb is 4·543 Å away, across the inversion center at (0,0,0).

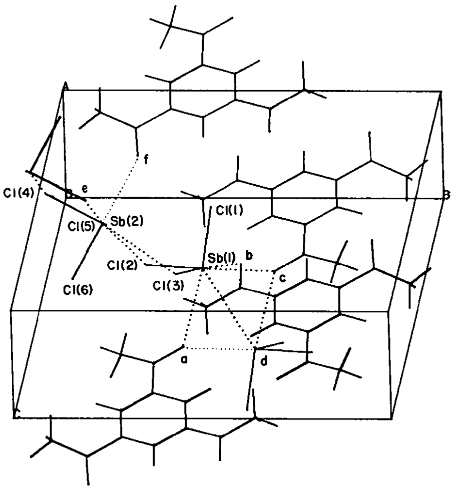

Fig. 2. The crystal structure viewed approximately perpendicular to the *bc* unit-cell face.

Sb(1) is coordinated to three O atoms at distances of 3·040, 2·694, and 3·023 Å. The two longer distances are to O atoms which bridge to another Sb atom across the inversion center at $(0,\frac{1}{2},\frac{1}{2})$. The bridged Sb—Sb distance is 3·777 Å, remarkably shorter than the van der Waals diameter for Sb of 4·4 Å (Pauling, 1960). Although the bridging of Sb atoms by bonded O atoms, as in Sb_2O_3 (Svensson, 1975), is well known, this appears to be the first observation of bridging through nonbonded O atoms. A view of the bridged dimer is given in Fig. 2. The deviations of the atoms from the dimer plane are given in Table 3(*b*).

The local configuration about Sb(1) is approximately octahedral, with an edge shared to form the dimer. The largest deviations from regular octahedral symmetry are angles O(*a*)—Sb(1)—O(*c*) and Cl(2)—Sb(1)—O(*a*) at 103 and 78° respectively. The Sb—O—Sb bridging angle is 77°. The 1,3,5-triacetylbenzene plane is tilted 55° from the dimer plane. Thus, the coordination about O is not consistent with an interaction of pure sp^2 orbitals on O. As was the case with Sb(2), there does not appear to be much surface area on Sb(1) available for the Sb lone-pair electrons. Thus the coordination type for both Sb atoms is AX_6 with the lone pair not located.

References

AZAROFF, L. V. & BUERGER, M. J. (1958). *The Powder Method in X-ray Crystallography*. New York: McGraw-Hill.

BAKER, W. A. & WILLIAMS, D. E. (1978). *Acta Cryst.* B**34**, 1111–1116.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

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.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc. London*, **57**, 160–177.

PARK, W. (1969). PhD dissertation, Univ. of Louisville, Kentucky, USA.

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.

SVENSSON, C. (1975). *Acta Cryst.* B**31**, 2016–2018.

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.