Crystal Structure of the 2 : 1 Antimony Trichloride : *p*-Xylene Intermolecular Compound at −110 °C

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A three-dimensional *X*-ray structure analysis by the heavy-atom method of $2SbCl_3{\cdot}C_6H_4Me_2$ is described. Crystals are monoclinic, space group $P2_1/c$, $a = 9.13(4)$, $b = 8.44(2)$, $c = 12.79(4)$ Å, $\beta = 125.35(20)°$, $Z = 2$. Least-squares refinement of photographic data led to R 0.11 for 920 independent reflections. The structure is essentially layered, with alternate $SbCl_3$ and *p*-xylene layers. The $SbCl_3$ molecules occur with an 'incipient dimer' configuration. Sb–Cl bond distances are 2.30, 2.32, and 2.37 Å. The shortest Sb ··· C distance is 3.18 Å.

MENSHUTKIN, in 1912, prepared and characterised several complexes formed between antimony trichloride and various substituted aromatics.[1-4] The crystallographic interest in these systems has arisen from a need to account for the non-bonded interactions which apparently exist between the component molecules.

The most common $SbCl_3$–aromatic-hydrocarbon ratio [5] is 2 : 1, but the $SbCl_3$–*p*-xylene system exhibits both a 1 : 1 and a 2 : 1 ratio. We report structural data for the 2 : 1 compound.

EXPERIMENTAL

Materials.—*p*-Xylene (AnalaR) was freed from traces of *o*- and *m*-xylene by a fractional freezing process. Commercial-grade carbon tetrachloride was dried (calcium hydride) and redistilled. Chloroform was dried (phosphorus pentoxide) for a few hours and then distilled. $SbCl_3$ (reagent grade) was recrystallised (×3) from dry chloroform. The decantation of solvent from crystals was carried out in a dry box.

Preparation of $2SbCl_3{\cdot}C_8H_{10}$ *Crystals.*—The hygroscopic nature of $SbCl_3$ and its complexes with *p*-xylene made it necessary to carry out all preparative work in a dry box (phosphorus pentoxide). *p*-Xylene (*ca.* 0.3 ml) was added to $SbCl_3$ (*ca.* 0.25 g) and the two components were melted together. It was found that a small volume of carbon tetrachloride (0.5 ml) was necessary as a diluent to prevent rapid solidification of the mass. On slow cooling colourless plate-like needles of the 2 : 1 compound formed with $[10\bar{1}]$ as the needle axis. Single crystals, showing cross extinction, were selected for *X*-ray examination and were sealed in Lindemann glass tubes in the dry box.

Analysis.—The composition of the crystals was determined from a bromate titration [5,6] for the antimony component. The mean result (1.94 : 1) corresponded closely to the ideal $2SbCl_3{\cdot}C_8H_{10}$.

Crystal Data.—$2SbCl_3{\cdot}C_6H_4Me_2$, $M = 562.4$, Monoclinic, $a = 9.13(4)$, $b = 8.44(2)$, $c = 12.79(4)$ Å, $\beta = 125.35(20)$, $U = 804$ Å^3, $D_m = 2.16$ (flotation in $CHCl_3$–C_2H_5I mixtures), $Z = 2$, $D_c = 2.32$, $F(000) = 524$. $\lambda(\text{Mo-}K_\alpha) = 0.710\,7$ Å; $\mu(\text{Mo-}K_\alpha) = 42.8$ cm^{-1}. Space group $P2_1/c$ (No. 14) from systematic absences: $h0l$ when $l = 2n + 1$, $0k0$ when $k = 2n + 1$. Cell dimensions were determined at -110 ± 10 °C from Mo-K_α (Zr-filtered) photographs. a^*, c^*, and β^* were determined from an $h0l$ Weissenberg photograph, and b^*, c^* from an $0kl$ photograph. The cell dimensions differ by *ca.* 1% from those obtained at room temperature.[6]

Integrated intensity data were obtained from equi-inclination multiple-film Weissenberg photographs taken with Zr-filtered Mo-K_α radiation at −110°. Layers $0kl$—$6kl$ about the a axis were collected, and two b axis cross-level photographs were also taken for the purpose of layer scaling. Some difficulty was experienced in obtaining these photographs because the crystals tended to split and break up at low temperature.

The intensities were estimated by comparison with a standard calibrated wedge. Film factors placed all intensities in each layer on the same scale prior to Lorentz and polarisation corrections being applied. No corrections were made for absorption. Intensities from the seven layers about a were placed on a provisional common arbitrary scale by multiplication with the appropriate layer factor. With only limited cross-layer data available, these factors were obtained roughly, by equating the sum of intensities common to each layer and the zero cross-layer. The relative values corresponded reasonably well to a second set of factors obtained by reference to the first cross-layer. Individual layer scales were subsequently refined by least squares in two of the rounds of co-ordinate refinement (see later).

Structure Determination.—A three-dimensional Patterson map revealed the antimony position. A subsequent three-dimensional electron-density map phased on this antimony position alone revealed the three chlorine positions and resolved the *p*-xylene molecule in the special position about a centre of symmetry. The R factor for the model based on antimony alone was 0.38. Inclusion of the three chlorine atoms followed by rescaling of the layers lowered R to 0.15. Inclusion of all atoms (four independent carbon atoms in addition to antimony and three chlorine) gave R 0.13 for 800 reflections after five rounds of least-squares refinement. The following weighting scheme was used: $w = F_m/F_o$ if $F_o \geqslant F_m$; otherwise $w = F_o/F_m$, where F_m is the mean of all the observed structure amplitudes. After a final least-squares rescaling of the individual layers and inclusion of all 920 observed reflections R was 0.118, with isotropic temperature factors.

The *p*-xylene molecule showed slight deviations from the ideal configuration in two respects. First, the molecule was not completely planar in that the substituent methyl groups were bent out of the plane of the benzene ring. Second, the ring C–C bond lengths had deviated from the ideal value of 1.395 Å. The *p*-xylene molecule was idealised therefore and refinement continued with this molecule included as a rigid body. PARIBLES, the partial rigid-body least-squares refinement programme used, was written by one of us (R. H.) for an IBM 360/44 computer in Fortran IV. This programme refines the rigid-body position and orientation by optional adjustment of its centre (3 parameters) and its tilt (3 angular parameters

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[1] B. N. Menshutkin, *Chem. Zentr.*, 1910, 378.

[2] B. N. Menshutkin, *Chem. Zentr.*, 1912, 1436.

[3] B. N. Menshutkin, *J. Russ. Phys. Chem. Soc.*, 1912, **43**, 1805.

[4] B. N. Menshutkin, *J. Russ. Phys. Chem. Soc.*, 1912, **43**, 1329.

[5] S. A. A. Jayaweera, M.Sc. Thesis, University of London, 1964.

[6] J. T. Szymanski, Ph.D. Thesis, University of London, 1963.

referred to a set of orthogonal axes) as well as refining all isotropic temperature factors, the conventional co-ordinates of the free part of the structure, and individual layer scales (twice required here). In this particular case, adjustment of the molecular centre of the p-xylene was not required as it is fixed at a centre of symmetry. After three rounds of such refinement, with R at 0.110, all atom positions were set free again for a final round of refinement. The same deviations from ideality appeared again in the p-xylene molecule. The final R for 920 relections remained at 0.110, despite the additional parameters.

TABLE 1

Fractional co-ordinates and isotropic temperature factors (Å^2), with standard deviations in parentheses

Atom	x	y	z	B
Sb	0.389 9(04)	0.107 2(03)	0.099 5(02)	1.06(02)
Cl(1)	0.332 0(15)	0.345 7(11)	−0.005 3(09)	2.92(20)
Cl(2)	0.499 1(13)	0.223 3(10)	0.296 2(08)	2.02(16)
Cl(3)	0.679 3(13)	0.087 4(12)	0.143 2(08)	2.60(18)
C(1)	0.010 5(65)	0.313 7(47)	0.108 0(38)	3.2(8)
C(2)	0.065 2(58)	0.017 2(46)	0.127 6(36)	2.8(8)
C(3)	0.055 7(48)	−0.139 3(43)	0.070 9(29)	2.2(7)
C(4)	0.012 5(56)	0.153 8(46)	0.056 0(34)	2.9(8)

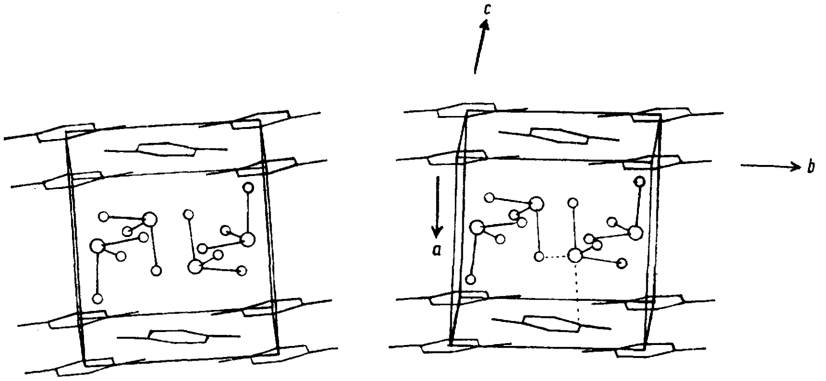

FIGURE 1 Stereoview of the structure of $2SbCl_3 \cdot C_6H_4Me_2$

As the free atom co-ordinates may suggest meaning, even though they are not significantly different from the rigid ones, we report in Table 1 the final free atomic co-ordinates. Bond lengths and angles are in Table 2 and measured structure amplitudes with calculated structure factors are listed in Supplementary Publication No. SUP 21638 (7 pp., 1 microfiche).*

RESULTS AND DISCUSSION

The essential feature of the structure is the layer-like nature of the molecular arrangements, layers of antimony trichloride alternating with those of p-xylene molecules. This is shown in Figure 1, a general stereoscopic view of the unit cell. The numbering system of the atoms is shown in Figure 2.

The $SbCl_3$ molecules are orientated with their dipoles antiparallel, and are too far apart for formal halogen bridging to occur. Nevertheless, the 'dimeric' $Sb \cdots Cl_3'$ distance is 3.24 Å, which is much shorter than the corresponding distance (3.58 Å) observed in the naphthalene–antimony trichloride structure.[7] Furthermore, the same relative orientation of $SbCl_3$ molecules occurs both in antimony trichloride itself[8] and in the naphthalene–antimony trichloride structure,[7] and it must therefore be considered an 'incipient dimer'.

TABLE 2

Interatomic distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Intramolecular bond distances and angles			
Sb–Cl(1)	2.304(11)	Cl(2) $\cdots$ Cl(3)	3.40(2)
Sb–Cl(2)	2.320(13)	C(1)–C(4)	1.51(6)
Sb–Cl(3)	2.369(14)	C(2)–C(3)	1.48(6)
Cl(1) $\cdots$ Cl(2)	3.38(2)	C(2)–C(4)	1.37(7)
Cl(1) $\cdots$ Cl(3)	3.38(2)	C(3′)–C(4)	1.37(5)
Cl(1)–Sb–Cl(2)	94.1(4)	C(1)–C(4)–C(3′)	119.3(3.9)
Cl(1)–Sb–Cl(3)	92.8(5)	C(2)–C(4)–C(3′)	117.4(2.7)
Cl(2)–Sb–Cl(3)	93.1(5)	C(3)–C(2)–C(4)	121.4(5.0)
C(1)–C(4)–C(2)	123.0(4.8)	C(4′)–C(3)–C(2)	121.2(2.7)
(*b*) Intermolecular distances and angles			
Sb $\cdots$ C(2)	3.28(5)	Sb $\cdots$ Sb′	4.40(6)
Sb $\cdots$ C(4)	3.18(6)	Sb $\cdots$ Cl(3′)	3.235(14)
Sb $\cdots$ C(3′)	3.33(4)		
Cl(3) – Sb $\cdots$ C(4)	175.8(9)		

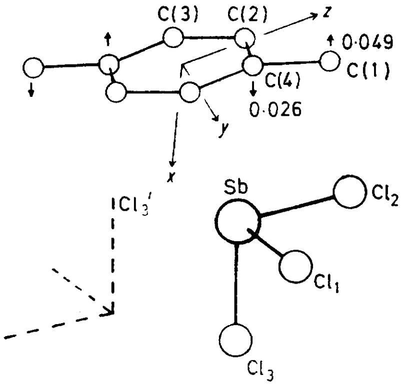

FIGURE 2 Atom numbering scheme for the intermolecular compound showing distances (Å) of C(1) and C(4) from the mean plane C(2), C(2′), C(3), C(3′). The equation of the plane referred to orthogonal Å axes, $X \| a, Y \| b, Z \| c^*$, is $4.054X + 0.574Y + Z = 0$

Indeed, the positions of the $SbCl_3$ moieties in the naphthalene and p-xylene compounds are remarkably

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

[7] R. Hulme and J. T. Szymanski, *Acta Cryst.*, 1969, **B25**, 753.

[8] I. Lindqvist and A. Niggli, *J. Inorg. Nuclear Chem.*, 1956, **2**, 345.

similar, despite significantly different cell dimensions. We observe again two Sb–Cl distances which are sensibly equal at 2.31 Å (shorter than the 2.347 Å in the naphthalene compound), with the third one somewhat longer at 2.37 Å (*cf.* 2.367 Å in the naphthalene compound).

The distance from the antimony atom to the plane of the *p*-xylene molecule is 3.09 Å, and to the nearest carbon atom, C(4), 3.18 Å, both distances being much shorter than the van der Waals distance of 3.5 Å. The carbon atom in question is the ring atom bonded to the substituent methyl group. A projection down the longer Cl(3)–Sb bond (Figure 3) shows that the atoms Cl(3)–Sb–C(4) are almost collinear at 175.8°.

The *p*-xylene molecule (Figure 2) shows irregular C–C distances with C(1) and C(4) a little out of plane, but these deviations are not significant in themselves. Nevertheless, taken together with the deviations in the $SbCl_3$ molecule, they suggest a weak antimony–*p*-xylene interaction involving some small tendency to localisation of the π-electron aromatic system similar to that postulated for the naphthalene compound.[7]

The 1 : 1 $SbCl_3 : C_8H_{10}$ compound [6,9] is very similar to the 2 : 1 compound in its layer-like nature, its bond distances, and the antimony trichloride–aromatic interactions. Both compounds crystallise in the space group $P2_1/c$, with closely similar *a*, *b*, and β values. To accommodate the additional *p*-xylene molecules the *c* axis is longer (17.65 Å) in the 1 : 1 unit cell.

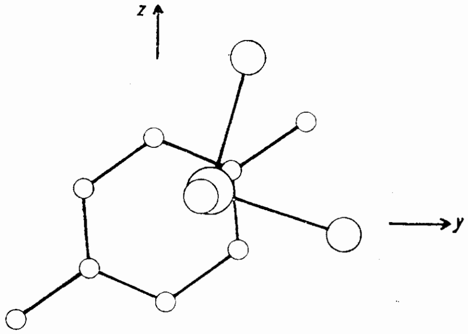

FIGURE 3 The $SbCl_3$–*p*-xylene interaction

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[5/1442 *Received*, 21*st July*, 1975]

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[9] D. W. Cushen, R. Hulme, and J. T. Szymanski, to be published.