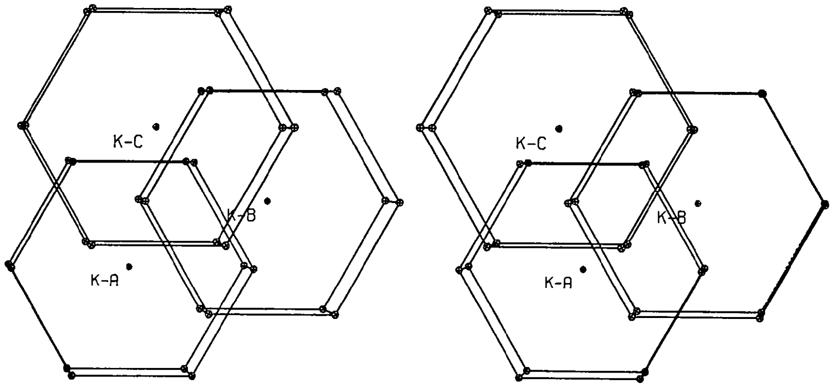

Fig. 3. *ABC* stacking of α-KTh_6F_{25}. F ions are omitted. Th ions are not labeled.

BRUNTON, G. (1971). *Acta Cryst.* **B27**, 245.
BRUNTON, G. D., INSLEY, H., MCVAY, T. N. & THOMA, R. E. (1965). USAEC Report ORNL-3761, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). USAEC Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
THOMA, R. E. & CARLTON, T. S. (1961). *J. Inorg. and Nucl. Chem.* **17**, 88.
THOMA, R. E., INSLEY, H., LANDAU, B. S., FRIEDMAN, H. A. & GRIMES, W. R. (1958). *J. Amer. Ceram. Soc.* **41**, 538.
ZACHARIASEN, W. H. (1948). *J. Amer. Chem. Soc.* **70**, 2147.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.
ZACHARIASEN, W. H. (1968). *Acta Cryst.* **A24**, 212.

Acta Cryst. (1972). **B28**, 147

The Crystal Structure of the Molecular Complex between Antimony Trichloride and Phenanthrene

BY A. DEMALDÉ, A. MANGIA, M. NARDELLI, G. PELIZZI AND M. E. VIDONI TANI

Istituto di Chimica Generale ed Inorganica, Università degli Studi, Parma, Italy
Centro di Studio per la Strutturistica Diffrattometrica del C.N.R.

(*Received* 21 *December* 1970)

$2SbCl_3$.phenanthrene gives triclinic ($P\bar{1}$) crystals: $a=8{\cdot}990(6)$, $b=11{\cdot}10(1)$, $c=10{\cdot}44(1)$ Å, $\alpha=90{\cdot}7(1)$, $\beta=80{\cdot}4(1)$, $\gamma=69{\cdot}1(1)°$, $Z=2$. The structure has been determined by three-dimensional Fourier methods and refined using block-diagonal least-squares down to $R=3{\cdot}8$%. The structure consists of alternating double layers of $SbCl_3$ and phenanthrene molecules. The coordination around Sb corresponds to a distorted trigonal bipyramid. Two independent Sb atoms are on opposite sides of the phenanthrene plane and their distances from that plane are not equal (3·27, 2·94 Å). The interactions between the metal atom and the aromatic molecule concern the π-electron system. Distorted octahedral coordination around the Sb atoms is completed by Sb···Cl contacts (3·260, 3·49, 3·41, 3·55 Å) significantly shorter than the sum of van der Waals radii.

Introduction

It is of interest to study the structure of the complexes formed by antimony trihalides with aromatic hydrocarbons, to determine the nature of the bonding interactions between the constituents and to obtain information on the mechanism of the catalytic effect which the antimony trihalides exert in Friedel–Crafts type reactions. The structure study of $2SbCl_3$.phenanthrene has been carried out to make a contribution to understanding the nature of the interactions between the inorganic and aromatic constituents, which could be related to the donor properties of the π system of phenanthrene and to the acceptor properties of $SbCl_3$. From the study of the pure quadrupole resonance spectrum of $2SbCl_3$.benzene, Okuda, Nakao, Shiroyama & Negita (1968) suggested that in this compound there is a charge transfer from the π system of benzene to a chlorine atom of $SbCl_3$, but a subsequent X-ray analysis carried out by Hulme & Szymanski (1969) showed that the transfer of π charge occurs to the antimony atom; this result is confirmed by the present study and by other X-ray analyses on similar compounds (Hulme, 1970).

Experimental

Single crystals suitable for X-ray work were grown by mixing together carbon disulphide solutions of the components, in stoichiometric ratio. In this way triclinic flattened prisms extremely unstable to air were obtained. For the X-ray analysis a crystal enclosed in a Lindemann glass capillary with the mother liquor was used. It had a mean diameter of about 0·4 mm.

The crystal data are as follows:

$(SbCl_3)_2.C_{14}H_{10}$, $M=634{\cdot}2$,
$a=8{\cdot}990$ (6), $b=11{\cdot}10$ (1), $c=10{\cdot}44$ (1) Å,
$\alpha=90{\cdot}7$ (1), $\beta=80{\cdot}4$ (1), $\gamma=69{\cdot}1$ (1)°,
$V=956{\cdot}5$ Å^3, $Z=2$, $D_x=2{\cdot}16$, $D_c=2{\cdot}20$ g.cm^{-3},
$\mu=36{\cdot}7$ cm^{-1},
space group: $P\bar{1}$ (from structural analysis).

Cell constants and intensity data have been determined by means of a single-crystal Siemens diffractometer on line to a 304 P computer. 5097 independent reflexions were collected using Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å, $2\theta_{max}=58°$); of these 1084 have been excluded from the refinement having $I<2\sigma(I)$. After correction for Lorentz and polarization factors, the structure amplitudes were put on an absolute scale, first by Wilson's method, then by correlating the observed with the calculated values. No absorption correction was made. The structure was solved by means of three-dimensional Patterson and Fourier methods and refined with block-diagonal least-squares using anisotropic thermal parameters and unit weights. The final R is 0·038. In Table 1 the final positional and thermal parameters with their estimated standard deviations are listed. The table of observed and calculated structure factors is stored at the National Lending Library (Boston Spa, Yorkshire, England) and copies are available on request.

The scattering factors used throughout the calculations are those of Cromer & Waber (1965). All the calculations were performed on the C.D.C. 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna), using the programmes of Immirzi (1967).

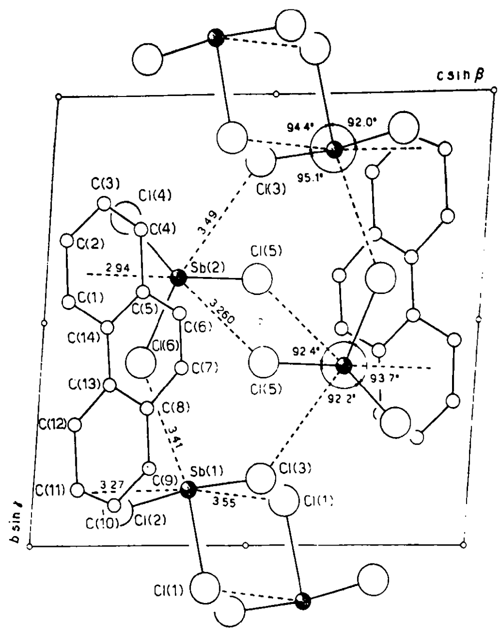

Fig. 1. Projection of the structure along [100].

Table 1. *Final atomic fractional coordinates* ($\times 10^4$) *and thermal parameters*† ($\times 10^2$ Å^2) *with e.s.d.'s*

	$x/a(\sigma)$	$y/b(\sigma)$	$z/c(\sigma)$	$B_{11}(\sigma)$	$B_{22}(\sigma)$	$B_{33}(\sigma)$	$B_{12}(\sigma)$	$B_{13}(\sigma)$	$B_{23}(\sigma)$
Sb(1)	866 (1)	1239 (1)	6430 (1)	383 (2)	329 (2)	373 (2)	−123 (2)	−49 (2)	55 (2)
Sb(2)	780 (1)	3993 (1)	3004 (1)	260 (2)	308 (2)	268 (2)	−93 (1)	−40 (1)	13 (1)
Cl(1)	1520 (3)	−970 (2)	5864 (2)	628 (12)	357 (8)	543 (10)	−215 (8)	−118 (9)	40 (7)
Cl(2)	2544 (3)	778 (2)	7999 (2)	643 (12)	411 (9)	601 (12)	−130 (9)	−295 (10)	57 (8)
Cl(3)	2836 (3)	1462 (2)	4748 (2)	465 (10)	464 (10)	563 (11)	−156 (8)	64 (8)	102 (8)
Cl(4)	−36 (3)	2679 (2)	1735 (2)	617 (11)	491 (10)	379 (8)	−292 (9)	−113 (8)	−45 (7)
Cl(5)	−1240 (2)	4067 (2)	4853 (2)	298 (6)	437 (8)	295 (6)	−183 (6)	−12 (5)	−6 (5)
Cl(6)	−916 (2)	5929 (2)	2296 (2)	356 (7)	343 (7)	476 (9)	−91 (6)	−131 (6)	106 (6)
C(1)	3034 (9)	4503 (8)	526 (7)	347 (29)	482 (36)	270 (26)	−158 (27)	15 (22)	−30 (24)
C(2)	3446 (10)	3174 (8)	397 (8)	439 (36)	507 (39)	368 (33)	−199 (31)	94 (27)	−104 (29)
C(3)	4427 (10)	2357 (9)	1205 (9)	395 (36)	478 (40)	534 (43)	−105 (30)	112 (31)	−47 (33)
C(4)	5023 (9)	2890 (9)	2098 (9)	259 (29)	525 (42)	576 (44)	−7 (27)	30 (28)	137 (34)
C(5)	4615 (8)	4277 (8)	2230 (7)	217 (24)	607 (42)	336 (30)	−117 (26)	−17 (21)	28 (28)
C(6)	5278 (10)	4816 (10)	3143 (8)	333 (33)	765 (55)	438 (38)	−176 (35)	−77 (28)	−24 (36)
C(7)	4953 (10)	6054 (10)	3269 (8)	334 (32)	835 (59)	399 (35)	−265 (36)	−23 (26)	−41 (36)
C(8)	3930 (9)	6913 (8)	2511 (7)	318 (29)	558 (40)	361 (31)	−216 (28)	62 (23)	−81 (28)
C(9)	3649 (11)	8241 (9)	2661 (9)	544 (45)	569 (47)	530 (44)	−294 (38)	132 (35)	−138 (36)
C(10)	2687 (13)	9084 (10)	1868 (12)	691 (57)	567 (51)	833 (66)	−341 (46)	336 (49)	−200 (46)
C(11)	1933 (12)	8679 (9)	995 (10)	509 (45)	501 (44)	675 (54)	−141 (36)	129 (38)	129 (39)
C(12)	2214 (10)	7304 (8)	866 (8)	402 (35)	468 (38)	417 (35)	−117 (29)	36 (28)	62 (29)
C(13)	3216 (8)	6438 (7)	1611 (6)	262 (25)	438 (32)	267 (25)	−140 (23)	27 (19)	−9 (22)
C(14)	3597 (7)	5089 (7)	1452 (6)	225 (22)	393 (29)	247 (24)	−102 (21)	15 (18)	19 (20)

† The B_{ij} values refer to the formula: $\exp -(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)$ in which $b_{11}=\frac{1}{4}a^{*2}B_{11}, b_{12}=\frac{1}{2}a^*b^*B_{12}$, *etc.*

Discussion

As shown in Figs. 1 and 2 the structure is built up by double layers of $SbCl_3$ which alternate with phenanthrene double layers tilted about 45° to [100]. Bond distances and angles in the $SbCl_3$ molecules are quoted in Table 2. Both antimony atoms, which are not crystallographically equivalent, are bounded to three chlorine atoms with distances a little shorter than the sum of covalent radii (2·40 Å) and in agreement with the values found in $2SbCl_3$. naphthalene (Hulme & Szymanski, 1969) and in $SbCl_3$ itself (Lindqvist & Niggli, 1956) in which these distances are in the range 2·35–2·37 Å. In each molecule of $SbCl_3$, two Sb–Cl bonds lie on a plane nearly parallel to that of the organic molecule (the dihedral angle in both cases is $\simeq 5°$), while the third bond is directly perpendicular to that plane. In this last direction the Sb atoms are respectively 3·27 and 2·94 Å away from the phenanthrene plane and face

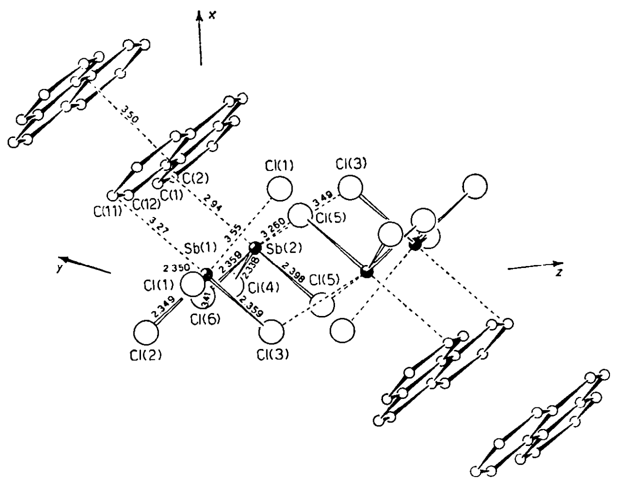

Fig. 2. Clinographic projection of the packing in the structure.

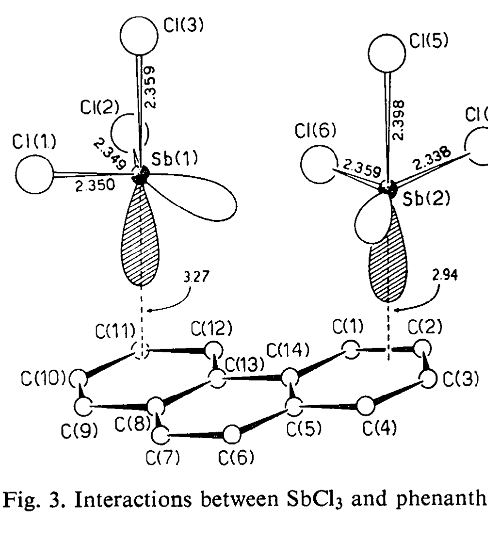

Fig. 3. Interactions between $SbCl_3$ and phenanthrene.

the terminal rings; more exactly Sb(2) is opposite a point on the ring very near to the midpoint of the C(1)–C(2) bond, while Sb(1) is almost exactly opposite C(11). A similar situation is present in $2SbCl_3$.naphthalene, but in this compound two $SbCl_3$ molecules, related by a centre of symmetry, are situated on opposite sides of the plane of the aromatic molecule, giving an alternating distribution of organic and inorganic layers. Moreover in $2SbCl_3$. naphthalene the distance between Sb and the plane of the organic molecule (3·20 Å) is of the same order of magnitude as the longer distance found in the phenanthrene derivative and appreciably longer than the shorter one. The distances between the antimony atoms and the π aromatic system are significantly longer than those found in π complexes of transition metals, *e.g.* 1·80 Å in phenanthrenechromium tricarbonyl (Muir, Ferguson & Sim, 1966), 1·75 Å in naphthalenechromium tricarbonyl (Kunz & Nowacki, 1967). Nevertheless, in the present compound there is electron donation from the aromatic system to the antimony atom through the π bonds in which both Sb atoms are involved. This is of the same kind as that observed in the naphthalene derivative (Hulme & Szymanski, 1969).

Table 2. *Bond distances and angles in* $SbCl_3$ *molecules*

Sb(1)–Cl(1) = 2·350 (4) Å	Cl(1)–Sb(1)–Cl(2) = 92·0 (1)°
Sb(1)–Cl(2) = 2·349 (4)	Cl(1)–Sb(1)–Cl(3) = 94·4 (1)
Sb(1)–Cl(3) = 2·359 (3)	Cl(2)–Sb(1)–Cl(3) = 95·1 (1)
Sb(2)–Cl(4) = 2·338 (3)	Cl(4)–Sb(2)–Cl(5) = 92·2 (1)
Sb(2)–Cl(5) = 2·398 (3)	Cl(4)–Sb(2)–Cl(6) = 93·7 (1)
Sb(2)–Cl(6) = 2·359 (3)	Cl(5)–Sb(2)–Cl(6) = 92·4 (1)

Each Sb can be considered in a sp^3d hybridization state with two Sb–Cl bonds and the lone pair on the equatorial plane as shown in Fig. 3; the third Sb–Cl bond and the electrons donated by the π system lie in the axial direction of a distorted trigonal bipyramid. It is interesting to observe that the Sb–Cl bonds, opposite the newly filled orbitals, are not of the same length: for the longer Sb–phenanthrene contact, the opposite Sb(1)–Cl(3) distance is lengthened relative to the other Sb–Cl contacts: the shorter Sb–phenanthrene contact is opposite to the Sb(2)–Cl(5) bond which is a little, but significantly, longer than the other Sb–Cl bonds. Such an extension of an Sb–halogen bond has been already observed in other cases, particularly in $2SbCl_3$. naphthalene (Hulme & Szymanski, 1969), in $2SbCl_3$. *p*-xylene (Hulme, 1970) and in the 2:1 adduct between SbI_3 and 1,4 dithiane (Bjorvatten, 1966).

Unlike $2SbCl_3$.naphthalene and $SbCl_3$ itself, in the crystal structure of $2SbCl_3$.phenanthrene there are Sb···Cl contacts (3·260, 3·49, 3·41, 3·55 Å) which are appreciably shorter than the sum of the van der Waals radii (4·0 Å) and complete the distorted octahedral coordination around antimony.

In Table 3 bond distances and angles in the organic molecule are quoted. This molecule is not perfectly planar, but strict planarity is observed for each single ring, their least-squares planes being:†

C(1)C(2)C(3)C(4)C(5)C(14)
$$-0{\cdot}6939X-0{\cdot}2281Y+0{\cdot}6830Z=-2{\cdot}8270$$
C(5)C(6)C(7)C(8)C(13)C(14)
$$-0{\cdot}6737X-0{\cdot}2103Y+0{\cdot}7084Z=-2{\cdot}5842$$
C(8)C(9)C(10)C(11)C(12)C(13)
$$-0{\cdot}6807X-0{\cdot}1709Y+0{\cdot}7123Z=-2{\cdot}2260$$

The dihedral angles they form are:

[C(1)...C(14)] ∧ [C(5)...C(14)] = 177·9°
[C(5)...C(14)] ∧ [C(8)...C(13)] = 177·7°

with a very flattened boat conformation.

Table 3. *Bond distances and angles in the phenanthrene molecule*

	C(1)—C(2)—C(3) = 121·1°
	C(2)—C(3)—C(4) = 119·3
	C(3)—C(4)—C(5) = 120·1
C(1)—C(2) = 1·39 Å	C(4)—C(5)—C(6) = 119·5
C(2)—C(3) = 1·42	C(5)—C(6)—C(7) = 120·8
C(3)—C(4) = 1·37	C(6)—C(7)—C(8) = 121·1
C(4)—C(5) = 1·45	C(7)—C(8)—C(13) = 120·5
C(5)—C(6) = 1·43	C(7)—C(8)—C(9) = 118·9
C(6)—C(7) = 1·30	C(13)–C(8)—C(9) = 120·5
C(7)—C(8) = 1·42	C(8)—C(9)—C(10) = 118·8
C(8)—C(13) = 1·41	C(9)—C(10)–C(11) = 123·1
C(8)—C(9) = 1·41	C(10)–C(11)–C(12) = 117·4
C(9)—C(10) = 1·41	C(11)–C(12)–C(13) = 120·5
C(10)–C(11) = 1·38	C(12)–C(13)–C(8) = 119·6
C(11)–C(12) = 1·46	C(8)—C(13)–C(14) = 118·4
C(12)–C(13) = 1·40	C(12)–C(13)–C(14) = 122·0
C(13)–C(14) = 1·41	C(13)–C(14)–C(1) = 123·2
C(14)–C(1) = 1·41	C(13)–C(14)–C(5) = 118·9
C(14)–C(5) = 1·41	C(1)—C(14)–C(5) = 117·9
	C(2)—C(1)—C(14) = 121·2
	C(4)—C(5)—C(14) = 120·3
	C(6)—C(5)—C(14) = 120·2

The e.s.d.'s for bond lengths are 0·01 Å, for angles are in the range 0·6–0·9°.

With respect to the bond distances in the phenanthrene layers, it must be pointed out that there are significant differences between some of the values measured in this complex and those measured which agree with those in phenanthrene itself calculated theoretically (Trotter, 1963). There is no shortening of C–C bonds in the region to which the axial sp^3d antimony orbital is pointing, in contrast with the situation found by Hulme & Szymanski in $2SbCl_3$. naphthalene. One more relevant fact is the quite unusual shortening of the C(6)–C(7) distance, which is 0·07–0·08 Å shorter than the experimental and molecular orbital calculated values for phenanthrene itself. No reason was found to justify this fact, which could be due to residual errors (*e.g.* absorption effects) uncorrected in the experimental data.

Packing is shown in Fig. 2. There are contacts between centrosymmetrical pairs of phenanthrene molecules which are 3·50 Å apart. The other packing contacts less than 3·5 Å are as follows:

$Cl(5)–Sb(2^{i}) = 3{\cdot}260$ (4) Å $Cl(6)–Cl(2^{i}) = 3{\cdot}45$ (1) Å
$Cl(6)–Sb(1^{i}) = 3{\cdot}41$ (1) $C(9)–Cl(1^{ii}) = 3{\cdot}49$ (1)

$$\text{i} = x,\ y+1,\ z$$
$$\text{ii} = \bar{x},\ 1-y,\ 1-z\,.$$

The authors wish to thank Dr R. Hulme for communicating his results prior to publication and for critically reading the manuscript.

† The transformation matrix from triclinic x, y, z to orthogonal X, Y, Z coordinates is:
$$\begin{pmatrix} \sin\gamma & 0 & -\sin\alpha\cos\beta^* \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\sin\beta^*. \end{pmatrix}$$

References

BJORVATTEN, T. (1966). *Acta Chem. Scand.* **20**, 1863.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
HULME, R. & SZYMANSKI, J. T. (1969). *Acta Cryst.* **B25**, 753.
HULME, R. (1970). Private communication.
IMMIRZI, A. (1967). *Ric. Sci.* **37**, 743.
KUNZ, V. & NOWACKI, W. (1967). *Helv. Chim. Acta*, **50**, 1052.
LINDQVIST, I. & NIGGLI, A. (1956). *J. Inorg. Nucl. Chem.* **2**, 345.
MUIR, K. W., FERGUSON, G. & SIM, G. A. (1966). *Chem. Commun.* p. 465.
OKUDA, T., NAKAO, A., SHIROYAMA, M. & NEGITA, H. (1968). *Bull. Chem. Soc. Japan*, **41**, 61.
TROTTER, J. (1963). *Acta Cryst.* **16**, 605.