atoms. The two octahedra share one edge, forming an Al_2O_{10} group (Fig. 2). The mean Al—O distance is 1·94 Å. Principal distances are given in Table 3.

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An X-ray Structure Redetermination of Antimony Trichloride

By Annegret Lipka*

Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, Universitätsstrasse 1, 4000 Düsseldorf, Federal Republic of Germany

Abstract. $SbCl_3$, orthorhombic, Pnma, $a = 8·111$ (2), $b = 9·419$ (1), $c = 6·313$ (1) Å, $Z = 4$, $D_x = 3·14$ Mg m^{-3}. The structure has been redetermined from counter data; with 963 independent observed reflections the final R is 0·045. The main improvements and results of this more accurate study are (1) the space group, and thus the mirror symmetry of the $SbCl_3$ molecules, was confirmed, (2) the structure was refined with anisotropic thermal parameters, (3) Sb—Cl lengths differ significantly due to intermolecular interactions, (4) intermolecular contacts and the resulting eightfold coordination of the Sb atom are discussed.

Introduction. $SbCl_3$ molecules have been found as units of structures in adducts of $SbCl_3$ with different donor systems (Hulme & Scruton, 1968; Hulme, Mullen & Scruton, 1969; Hulme & Szymański, 1969; Hulme & Mullen, 1976; Demaldé, Mangia, Nardelli, Pelizzi & Vidoni Tani, 1972; Lipka & Mootz, 1978; Lipka, 1978).

Comparison with the structure of $SbCl_3$ as determined by Lindqvist & Niggli (1956) showed that the

shapes of the molecules are similar, but with regard to intermolecular contacts the coordination polyhedra are different. However, the accuracy of the above-mentioned work based on refinement by difference Fourier techniques was not sufficient to allow further discussion of structural details. The equivalence of the Sb—Cl lengths was just within large e.s.d.'s and the mirror symmetry of the molecules resulting from the adopted space group Pbmn was questionable, for accurate X-ray (Nyburg, Ozin & Szymański, 1971) and neutron (Bartl, 1975) structure determinations had shown that the isostructural $BiCl_3$ crystallizes in the noncentrosymmetric space group $Pn2_1a$. Therefore a complete X-ray structure redetermination of $SbCl_3$ was undertaken.

$SbCl_3$ p.a. was purified by reductive distillation over Sb under a nitrogen atmosphere. A bipyramidal-shaped single crystal grown from the melt was selected in a dry box under an argon atmosphere and sealed in a Lindemann-glass capillary ($\varnothing = 0·3$ mm). Photographs showed systematic absences $0kl$ for $k + l$ odd and $hk0$ for h odd, indicative of the space groups Pnma and $Pn2_1a$ (conventional setting $Pna2_1$). Cell dimensions were obtained by least-squares refinement from angular measurements of 15 reflections in the range $36 < 2\theta <$

* Present address: Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland.

43° on a Syntex $P2_1$ diffractometer. The density of 3·140 Mg m^{-3} (*Handbook of Chemistry and Physics*, 1974) corresponds to $Z = 4$. The intensities of 1114 independent reflections ($2\theta < 70°$) were measured on the diffractometer in the ω-scan mode with Mo $K\alpha$ radiation. 963 reflections were classified as observed ($|F_o| > 3·92\sigma_F$). Empirical absorption corrections were applied [μ(Mo $K\alpha$) $= 7·22$ mm^{-1}]. Least-squares refinement was started with the known positional parameters (Lindqvist & Niggli, 1956), which were transformed from *Pbnm* to the conventional *Pnma* for better comparison with other Group V trihalides. The final refinement with anomalous-scattering corrections and anisotropic temperature factors converged at $R = 0·045$ (0·052) and $R_w = 0·056$ (0·058).* Weights were derived from counter data by $1/w = \sigma_F^2 + (0·02|F_o|)^2$.

Further refinement of both sets of atomic parameters related by $\bar{1}$ symmetry in space group $Pn2_1a$ improved R only from 0·045 to 0·044, probably due to the increase of 14 in the number of variables, and resulted in a significantly different but chemically less reasonable model. Thus, within the limits of X-ray data, the structure is best described with the centrosymmetric space group *Pnma*, implying mirror symmetry for the molecules.

The final atomic parameters are listed in Table 1. All calculations were carried out on a 32-K Eclipse computer with the program system *EXTL* (Syntex).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34727 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The structure of SbCl$_3$ reported by Lindqvist & Niggli (1956) is fully confirmed. The structure consists of discrete molecules of pyramidal shape and mirror symmetry. Bond lengths, angles and intermolecular distances are given in Table 2.

Two equivalent bonds are 2·368 (1) Å long; the third bond of 2·340 (2) Å is significantly shorter. The bond angle of 90·98 (5)° opposite the short bond is smaller than the other two at 95·70 (5)°. Intermolecular Sb$\cdots$Cl contacts of 3·457 (2×), 3·609 (1×) and 3·736 Å (2×) are significantly shorter than the sum of the van der Waals radii (4·0 Å) and increase the coordination number of the Sb atom to eight. Further Sb$\cdots$Cl distances are >4·12 Å. The two long Sb—Cl bonds are *trans* to the two shortest intermolecular contacts and all these interactions as well as the two longest Sb$\cdots$Cl contacts involve the same independent Cl atom. Similar patterns have been observed in the octahedral coordination of Sb^{III} in structures of adducts (Lipka & Mootz, 1978). The eightfold coordination of the Sb atom is best described as a bicapped trigonal prism (Fig. 1*a,b*). One trigonal base is formed by the three bonded Cl atoms, the second by the three more distant Cl atoms. The two Cl atoms above rectangular faces are closer to the Sb atom than the Cl atoms building up the second prism base. [These distances have been interchanged in the description by Nyburg, Ozin & Szymański (1971).] The coordination number of the Sb atom is best described as 3 + 2 + 3. With regard to the intramolecular and intermolecular contacts a three-dimensional network is formed (Fig. 2). The packing of the Cl atoms can roughly be described as distorted hexagonal close packing.

Table 1. *Atomic fractional coordinates and thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

Temperature factor $= \exp[-\frac{1}{4}(h^2 a^{*2} B_{11} + \ldots + 2klb^* c^* B_{23})]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sb	−0·01007 (5)	0·25	0·02499 (7)	2·49 (2)	2·49 (2)	2·25 (2)	0·0	0·29 (1)	0·0
Cl(1)	0·0715 (2)	0·25	−0·3306 (3)	3·94 (7)	4·20 (7)	2·25 (5)	0·0	0·16 (5)	0·0
Cl(2)	0·1761 (2)	0·0707 (1)	0·1343 (2)	4·79 (5)	2·46 (3)	3·74 (5)	0·41 (4)	−1·34 (4)	0·10 (3)

Table 2. *Interatomic distances* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

Sb—Cl(1)	2·340 (2)	
Sb—Cl(2) = Sb—Cl(2^I)	2·368 (1)	
Sb—Cl(2^{II}) = Sb—Cl(2^{III})	3·457 (1)	
Sb—Cl(1^{VI})	3·609 (2)	
Sb—Cl(2^{IV}) = Sb—Cl(2^V)	3·736 (1)	

Symmetry code

(I)	$x, \frac{1}{2} - y, z$	(IV)	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$
(II)	$-x, -y, -z$	(V)	$-\frac{1}{2} + x, y, \frac{1}{2} - z$
(III)	$-x, \frac{1}{2} + y, -z$	(VI)	$-\frac{1}{2} + x, y, -\frac{1}{2} - z$

Angles around Sb

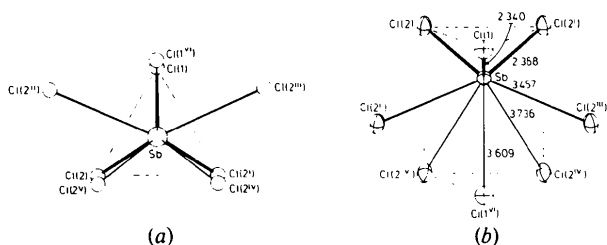|	Cl(1)	Cl(2)	Cl(2^I)	Cl(2^{II})	Cl(2^{III})	Cl(1^{VI})	Cl(2^{IV})
Cl(2^I)	95·70 (5)	90·98 (5)					
Cl(2^{III})	80·27 (4)	163·00 (4)	73·14 (4)	121·82 (3)			
Cl(1^{VI})	86·54 (4)	134·32 (4)		62·27 (3)			
Cl(2^V)	138·14 (4)	86·81 (4)	126·09 (4)	60·47 (3)	107·28 (3)	63·58 (3)	53·75 (3)

Fig. 1. *ORTEP* diagram (Johnson, 1976) of the bicapped trigonal prism of Cl atoms, which gives the eightfold coordination of Sb; (a) projection on the triangular base of bonded Cl atoms; (b) perspective view.
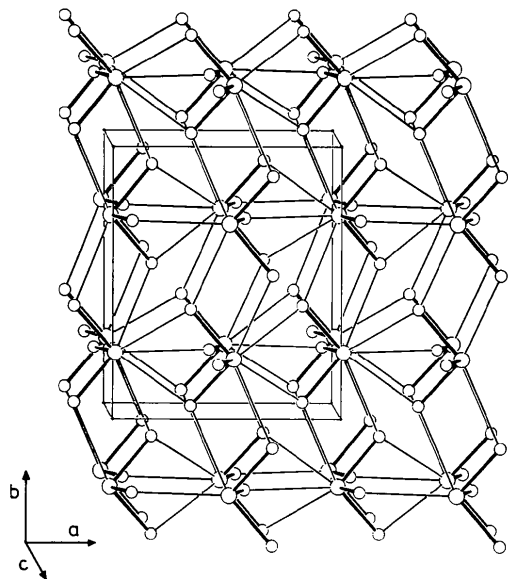

Fig. 2. *ORTEP* diagram (Johnson, 1976) of the structure of $SbCl_3$, showing a section of the three-dimensional network built up by Sb—Cl···Sb bridging.

The 3 + 2 + 3 coordination of the Sb atom is unique for the structure of $SbCl_3$. It is not found in structures of adducts of $SbCl_3$, where intermolecular contacts up to 3·5 Å often complete an octahedral or ψ-octahedral coordination of the Sb atom and where in cases of one or two short contacts in excess of six no simple polyhedral description of coordination can be given.

In the crystal structures of Group V*a* trichlorides and tribromides discrete MX_3 molecules are the primary units of structure. With regard to intermolecular contacts the eightfold coordination of a bicapped trigonal prism around the *M* atom seems to be a typical case: it is observed in the isostructural $SbCl_3$ and $BiCl_3$ (Nyburg, Ozin & Szymański, 1971) and in PBr_3 (Enjalbert & Galy, 1979) and β-$SbBr_3$ (Cushen & Hulme, 1962) and with more distortions in α-$SbBr_3$ (Cushen & Hulme, 1964). The related coordination polyhedron of a tricapped trigonal prism is found in $AsCl_3$ (Enjalbert & Galy, 1978). The structure of NCl_3 (Hartl, Schöner, Jander & Schulz, 1975) differs: The Cl atoms build up distorted octahedra, tetrahedra and trigonal prisms around the N atom.

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