remaining acceptor power of Se in the adduct must be very small.

In a solution of C_5H_5N in an excess of $SeOCl_2$, on the other hand, unreacted $SeOCl_2$ molecules might function as a kind of secondary acceptor molecules withdrawing chloride ions from the adduct molecules. Such an interaction would be stronger than the one found in the adduct and thus result in a more fargoing release of chloride ions. The experimental methods used to prove the existence of ion-transfer processes would register this effect as a chloride-ion transfer to the solvent (*cf.* for instance Andersson & Lindqvist, 1955). The structure determination has thus been of help towards a deeper understanding of what are generally called ionic-transfer processes in solution. The possible analogy with hydrogen bonds has been pointed out by Lindqvist (1955) and by Khotsianova (1957).

We wish to thank Mr S. Westman and Mr S. Åsbrink for their kind help with the introduction in the use of their programmes for BESK and Prof. G. Hägg for all facilities put at our disposal.

The work has been supported by grants from the Swedish Natural Science Research Council and from Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force, through its European Office under Contract No. AF 61(052)-43. These grants are gratefully acknowledged.

References

Abrahams, S. C. (1956). *Quart. Rev. Chem. Soc. Lond.* **10**, 407.
Agerman, M., Andersson, L. H., Lindqvist, I. & Zackrisson, M. (1958). *Acta Chem. Scand.* **12**, 477.
Amma, E. L. & Rundle, R. E. (1958). *J. Amer. Chem. Soc.* **80**, 4141.
Andersson, L. H. & Lindqvist, I. (1955). *Acta Chem. Scand.* **9**, 79.
Bak, B., Hansen, L. & Rastrup-Andersen, J. (1954). *J. Chem. Phys.* **22**, 2013.
Booth, A. D. (1948). *Fourier Technique in X-ray Organic Structure Analysis.* Cambridge: University Press.
Christofferson, G. D., Sparks, R. A. & McCullough, J. D. (1958). *Acta Cryst.* **11**, 782.
Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.
Dunitz, J. D. (1957). *Acta Cryst.* **10**, 307.
Edgington, B. & Firth, S. B. (1936). *J. Soc. Chem. Ind.* **55**, 1921.
Hägg, G. & Laurent, T. (1946). *J. Sci. Instrum.* **23**, 155.
Khotsianova, T. L. (1957). *Crystallographia*, **2**, 45. (American translation.)
Lindqvist, I. (1955). *Acta Chem. Scand.* **9**, 73.
Lindqvist, I. & Brändén, C. I. (1957). *Acta Chem. Scand.* **12**, 134.
Lu, C.-S. (1943). *Rev. Sci. Instrum.* **14**, 331.
Luzzati, V. (1951). *Acta Cryst.* **4**, 193.
McCullough, J. D. & Hamburger, G. (1942). *J. Amer. Chem. Soc.* **64**, 508.
McCullough, J. D. & Marsh, R. E. (1950). *Acta Cryst.* **3**, 41.
Shoemaker, D. P., Donohue, J., Schomaker, V. & Corey, R. B. (1950). *J. Amer. Chem. Soc.* **72**, 2328.
Vand, V., Eiland, P. F. & Pepinsky, R. (1957). *Acta Cryst.* **10**, 303.

Acta Cryst. (1959). **12**, 642

The Crystal Structure of $SbCl_5 . POCl_3$

By Ingvar Lindqvist and Carl-Ivar Brändén
Institute of Chemistry, University of Uppsala, Uppsala, Sweden

(*Received* 2 *February* 1959)

The crystal structure of $SbCl_5 . POCl_3$ has been determined from three-dimensional X-ray data. This is the first structure determination of an addition compound with an oxychloride functioning as donor molecule. The structure is built up of discrete $SbCl_5 . POCl_3$ molecules. The coordination around Sb is octahedral with an O atom from $POCl_3$ in the sixth corner. The approximately tetrahedral structure of $POCl_3$ is preserved. The bond angle Sb–O–P is 143·7°. The structure is briefly discussed.

1. Introduction

Groeneveld (1956) suggested in an interesting discussion that, in the oxychlorides, the oxygen atoms in many cases function as electron-pair donors by the formation of solid addition compounds. This has been confirmed by the present structure determination (preliminarily communicated by Lindqvist & Brändén, 1958) and by infra-red spectroscopy on different addition compounds (Sheldon & Tyree, 1958). The implications for the reactions in solution have briefly been discussed by Lindqvist (1958) and more extensively by Gutmann (1958).

2. Preparation of crystals

The liquidus curve in the system $SbCl_5$–$POCl_3$ shows the existence of an addition compound $SbCl_5.POCl_3$ with a congruent melting point of +117 °C. (Agerman *et al.*, 1958). (This compound was first described by Weber, 1865.) Single crystals of the very hygroscopic compound were prepared in sealed capillary tubes by a method of zone melting. The crystals were stable during the time of exposure.

3. Crystal data

The unit-cell dimensions of the orthorhombic crystals were determined by an extrapolation method (Lövgren, to be published) used earlier in this Institute (Hermodsson & Strandberg, 1957). The values are

$$a = 8{\cdot}06\pm0{\cdot}01,\quad b = 16{\cdot}42\pm0{\cdot}01,\quad c = 8{\cdot}93\pm0{\cdot}02\ \text{Å}\ .$$

The value 1·5405 Å was used for the Cu $K\alpha_1$ wave length.

The extinctions $h0l$ for $h+l$ odd and $hk0$ for k odd lead to the space groups *Pmnb* or $P2_1nb$. The centrosymmetrical space group *Pmnb* was confirmed by the structure determination.

The single crystal was rotated around the c-axis and Weissenberg photographs were taken with Cu K- and Mo K-radiation. 13 zones (0–12) were recorded with Mo K-radiation using multiple-film technique with Fe-foils between the films. Connection between the zones was obtained using a method described by Magnéli (1948). The 1124 independent intensities were estimated visually. The relative $|F|^2$ values were obtained after correction using the chart of Lu (1943). The number of molecules in the unit cell has been shown to be 4 (Gutmann *et al.*, 1957).

No correction was made for absorption errors. The capillary tube used had an inner diameter of 0·25 mm. The linear absorption coefficient is 44·4 cm.$^{-1}$ for Mo $K\alpha$.

4. Determination of the atomic positions

There are three different 4-fold positions in *Pmnb*. In order to determine the Sb-positions the Harker functions $P(0, y, z)$, $P(\frac{1}{2}, y, \frac{1}{2})$ and $P(0, \frac{1}{2}, z)$ were calculated.

The function $P(0, y, z)$ has its highest maximum in $y = 0{\cdot}5$, $z = 0{\cdot}350$ giving $z_{\text{Sb}} = \pm0{\cdot}075$. The function $P(\frac{1}{2}, y, \frac{1}{2})$ has its highest maximum in $y = 0{\cdot}217$ giving $y_{\text{Sb}} = 0{\cdot}142$ or $0{\cdot}358$. This is in agreement with Sb in the fourfold position $4(c)$. The parameters arbitrarily chosen were $y_{\text{Sb}} = 0{\cdot}142$ and $z_{\text{Sb}} = 0{\cdot}075$.

From some of the other peaks in the function $P(0, y, z)$ four other atoms could be placed in the mirror plane $x = \frac{1}{4}$. These atoms approximately occupy four corners of an octahedron around the Sb-atom. The other two corners of the octahedron should then be on opposite sides of the mirror plane with approximately the same y- and z-coordinate as the Sb-atom. The function $P(x, 0, 0)$ was calculated and showed a maximum at $x = 0{\cdot}289$ which was interpreted as an Sb–Cl vector in the x-direction. For the preliminary determination of the signs of $F(0, k, l)$ all these atoms were assumed to be Cl-atoms.

Signs of 107 of the 130 observed structure-factors $F(0, k, l)$ were determined from the parameters thus obtained and used for calculation of the electron-density projection $\varrho(y, z)$.

The Sb position and three of the Cl positions in the mirror plane were confirmed. The height of the maximum of the fourth position in the mirror plane was about half the heights of the other Cl peaks and the distance from this position to the Sb atom was 0·2 Å shorter than the other distances. This strongly indicated the presence of an oxygen atom.

The ratio of the heights of the Sb-peak and the Cl-peaks was about 5:1 which confirms the Cl-positions on opposite sides of the mirror-plane. ($|\text{Sb+Cl+Cl}|/\text{Cl}$ should be approximately 5:1.) The P atom and the remaining three Cl atoms in the $POCl_3$ group could be located from the other maxima of the projection. Two of these Cl atoms are in a general position.

From the parameters obtained at this stage signs could be determined for almost all observed $F(h, k, l)$. (An approximate x-parameter of the Cl-atom in the general position was calculated using a P–Cl distance 2·0 Å.) These signs were used for a three-dimensional electron-density calculation. (These and the earlier Fourier-summations were made on the Hägg–Laurent (1946) machine.) All the atomic positions were confirmed and no extra peaks were obtained. The parameters obtained from this calculation have been published earlier (Lindqvist & Brändén, 1958).

5. Refinement and assessment of accuracy

Using these atomic positions, the structure factors $F(h, k, l)$ were calculated with a temperature factor of 2·73 Å^2. This and the following structure-factor and Fourier calculations were made on the electronic computer BESK in Stockholm. The program for the structure factor calculation uses analytical representation of the scattering-factors (Vand *et al.*, 1957). The F-values for $\sin\theta/\lambda \geq 0{\cdot}7.10^8$ were calculated separately using the following scattering factors: P and Cl (Tomiie & Stam, 1958), Sb (Thomas & Umeda, 1957), O (Berghuis *et al.*, 1955).

A three-dimensional back-shift correction was carried out. To obtain a rough estimate of the standard deviations in the atomic coordinates Cruickshank's method (1949) was used. The standard deviations obtained with the calculated structure factors from the atomic positions before the back-shift correction are given in Table 1. (We have checked that the standard deviations do not change appreciably by the back-shift correction.)

Table 1. *Standard deviations of the atomic coordinates*

	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
Sb	—	0·001	0·001
P	—	0·007	0·005
O	—	0·016	0·017
Cl_1	—	0·006	0·005
Cl_2	—	0·007	0·006
Cl_3	—	0·008	0·005
Cl_4	—	0·008	0·007
Cl_5	0·007	0·008	0·006
Cl_6	0·006	0·007	0·005

By the back-shift correction most of the atomic positions had been shifted more than the standard deviation. A new set of structure factors were calculated and a final three-dimensional back-shift correction was carried out. (A copy of the observed and calculated F-values before the final back-shift correction can be obtained by request.)

The final parameters are:

4 Sb	in x = 0·2500	y = 0·1450	z = 0·0797
4 P	in x = 0·2500	y = 0·0742	z = 0·7142
4 O	in x = 0·2500	y = 0·0706	z = 0·8774
4 Cl_1	in x = 0·2500	y = 0·2585	z = 0·9195
4 Cl_2	in x = 0·2500	y = 0·0202	z = 0·2048
4 Cl_3	in x = 0·2500	y = 0·2249	z = 0·2938
4 Cl_4	in x = 0·2500	y = 0·4644	z = 0·8699
8 Cl_5	in x = 0·0558	y = 0·1314	z = 0·6327
8 Cl_6	in x = 0·9617	y = 0·1405	z = 0·0597

6. Description and discussion of the structure

This is the first structure determination of an addition compound in which the donor molecule is an oxychloride.

The structure of one adduct molecule is shown in Fig. 1 and the bond lengths and bond angles are given in Table 2, together with their standard deviations. The packing of the molecules is indicated in Fig. 2. The shortest packing distances between different molecules are collected in Table 3.

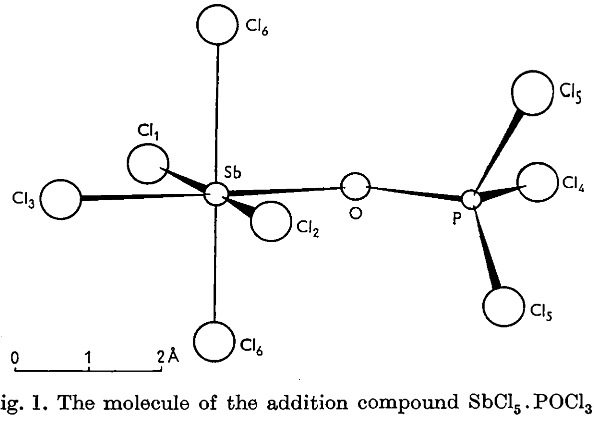

Fig. 1. The molecule of the addition compound $SbCl_5.POCl_3$.

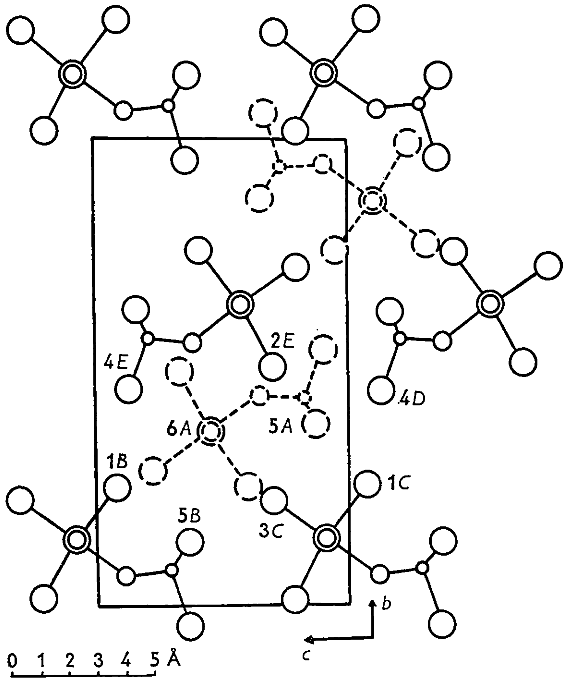

Fig. 2. Projection of the structure along [100], showing different Cl–Cl contacts. The dotted molecules are in the plane $x = \frac{3}{4}$. The other molecules are in $x = \frac{1}{4}$.

Table 2. *Bond distances and bond angles in* $SbCl_5.POCl_3$ *and their standard deviations*

	Distance (Å)	S.D. (Å)		Angle (°)	S.D. (°)
Sb–Cl_1	2·350	0·006	O–Sb–Cl_1	86·5	0·5
Sb–Cl_2	2·334	0·007	Cl_1–Sb–Cl_3	93·0	0·2
Sb–Cl_3	2·319	0·006	Cl_3–Sb–Cl_2	96·0	0·2
Sb–Cl_6	2·332	0·006	Cl_2–Sb–O	84·5	0·5
Sb–O	2·18	0·02	Cl_6–Sb–Cl_6	170·3	0·2
P–O	1·46	0·02	Cl_6–Sb–O	85·3	0·5
P–Cl_4	1·95	0·01	Cl_6–Sb–Cl_1	88·7	0·2
P–Cl_5	1·97	0·01	Cl_6–Sb–Cl_3	94·7	0·2
			Cl_6–Sb–Cl_2	90·5	0·2
			Sb–O–P	143·7	0·5
			O–P–Cl_5	112·9	0·7
			O–P–Cl_4	110·3	0·7
			Cl_4–P–Cl_5	107·4	0·4
			Cl_5–P–Cl_5	105·6	0·4

Table 3. *Packing distances in* $SbCl_5.POCl_3$
(*Cf.* Fig. 2)

		Distance (Å)
Cl–Cl	1–4	3·41
	6*A*–1*B*	3·85
	6*A*–4*E*	3·55
	6*A*–5*B*	3·78
	6*A*–3*C*	3·78
	5*A*–3*C*	3·70
	5*A*–1*C*	3·60
	5*A*–4*D*	3·75
	5*A*–2*E*	3·79

The bond lengths in the free donor molecule, $POCl_3$ (Badgley & Livingstone, 1954) have not been much changed by the adduct formation. The P–O bond length has changed from 1·45±0·05 Å to 1·46±0·02 Å and the P–Cl bond lengths from 1·995±0·02 Å to 1·97 and 1·95±0·01 Å. These changes are not significant in a mathematical sense.

Infra-red spectra indicate, however, that they may have physical significance. Sheldon & Tyree (1958) have thus interpreted the shift obtained in the P–O stretch frequency by adduct formation as due to a weakening of the P–O bond. A similar study of the P–Cl stretch frequency indicates a strengthening of that bond as probable (Kinell & Lindqvist, unpublished results). A more thorough discussion will be made in a future paper.

The Cl–P–Cl bond angles have changed from 103·5°±1 to 105·6° and 107·4°±0·4, too little to be of mathematical significance. A check of the validity of the concept of orthogonal hybridization of *s* and *p* orbitals can be made in the same way as described earlier for $K_2S_2O_5$ (Lindqvist & Mörtsell, 1957). The orthogonality condition would here be that

$$\cos 105{\cdot}6^\circ \cos 110{\cdot}3^\circ = \cos 107{\cdot}4^\circ \cos 112{\cdot}9^\circ.$$

The products are, however, significantly different and the description with orthogonal hybridization must be unsatisfactory in this case. The difference might be an effect of the packing of the molecules or due to partial use of *d* orbitals for the bonding.

The acceptor molecule $SbCl_5$ has changed its coordination from five (trigonal bipyramid) to six (octahedron). The Sb–Cl and Sb–O bond lengths and the Sb–O–P bond angle will be discussed in a subsequent paper on the very similar structure of $SbCl_5.PO(CH_3)_3$ where comparisons can be made between the values found with the two different donor molecules.

The packing distances between the different adduct molecules have reasonable values. One Cl–Cl distance is rather short (3·41 Å) but a still shorter van der Waals distance (3·3 Å) between chlorine atoms is found in solid Cl_2 (Collin, 1952).

We wish to thank Mr S. Westman and Mr S. Åsbrink for their kind help with the introduction in the use of their programmes for BESK and Prof. G. Hägg for all facilities put at our disposal. The work has been supported by grants from the Swedish Natural Science Research Council and from Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force, through its European Office under Contract No. AF 61(052)-43. These grants are gratefully acknowledged.

References

Agerman, M., Andersson, L.-H., Lindqvist, I. & Zachrisson, M. (1958). *Acta Chem. Scand.* **12**, 477.

Badgley, G. R. & Livingston, R. L. (1954). *J. Amer. Chem. Soc.* **76**, 261.

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Collin, R. L. (1952). *Acta Cryst.* **5**, 431.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.

Groeneveld, W. L. (1956). *Rec. Trav. chim. Pays-Bas*, **75**, 594.

Gutmann, V., Wittmann, A. & Nahringbauer, G. (1957). *Monatsh.* **88**, 403.

Gutmann, V. (1958). To be published.

Hermodsson, Y. & Strandberg, B. (1957). *Acta Cryst.* **10**, 434.

Hägg, G. & Laurent, T. (1946). *J. Sci. Instrum.* **23**, 155.

Lindqvist, I. & Mörtsell, M. (1957). *Acta Cryst.* **10**, 406.

Lindqvist, I. (1958). *Acta Chem. Scand.* **12**, 135.

Lindqvist, I. & Brändén, C.-I. (1958). *Acta Chem. Scand.* **12**, 134.

Lu, C.-S. (1943). *Rev. Sci. Instrum.* **14**, 331.

Magnéli, A. (1948). *Acta Chem. Scand.* **2**, 501.

Sheldon, J. C. & Tyree, S. Y. (1958). *J. Amer. Chem. Soc.* **80**. In press.

Thomas, L. H. & Umeda, K. (1957). *J. Chem. Phys.* **26**, 293.

Tomiie, Y. & Stam, C. H. (1958). *Acta Cryst.* **11**, 126.

Vand, V., Eiland, P. F. & Pepinsky, R. (1957). *Acta Cryst.* **10**, 303.

Weber, R. (1865). *Pogg. Ann. Physik*, **125**, 78.