

The Crystal Structure of $\text{SbCl}_5 \cdot \text{SeOCl}_2$

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The crystal structure of the addition compound $\text{SbCl}_5 \cdot \text{SeOCl}_2$ has been determined and refined from three-dimensional X-ray data. The crystals are monoclinic, space group $P2_1/c$, with eight formula units in the unit cell of dimensions:

$$a = 13.19 \text{ \AA}, b = 14.49 \text{ \AA}, c = 12.03 \text{ \AA} \text{ and } \beta = 104^\circ 58'$$

The structure consists of discrete $\text{SbCl}_5 \cdot \text{SeOCl}_2$ molecules packed together with relatively short intermolecular contacts along the a axis. The antimony atom is octahedrally coordinated by five chlorine atoms and one oxygen atom. The SeOCl_2 part of the molecule has a pyramidal shape. The mean bond distances in Ångström units are: $\text{Sb}-\text{Cl} = 2.34$, $\text{Sb}-\text{O} = 2.08$, $\text{Se}-\text{Cl} = 2.12$, $\text{Se}-\text{O} = 1.69$. The angle $\text{Sb}-\text{O}-\text{Se}$ is 121.5° .

During several years, structural studies of addition compounds formed between metal halides and oxygen donor molecules have been made at this Institute.¹ As part of this investigation X-ray studies of solid solvates formed with the non-aqueous ionizing solvent seleninyldichloride, SeOCl_2 , have been undertaken by the present author. The structure of $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ has been reported earlier.² This compound shows a strong interaction between the metal halide and the solvent molecule through oxygen bonds to the tin atom. The oxygen atoms are in *cis*-position. The present investigation involves the determination of the crystal structure of a solvate in the system $\text{SbCl}_5-\text{SeOCl}_2$.

The existence of a compound between seleninyldichloride and antimony pentachloride was first established by Weber³ in 1865. Weber interpreted his analytical data as corresponding to the formula $\text{SbCl}_5 \cdot 2\text{SeOCl}_2$, whereas a re-calculation of his results with modern atomic weights gives a $\text{Sb}:\text{Se}:\text{Cl}$ ratio of 1:1:7, leading to the formula $\text{SbCl}_5 \cdot \text{SeOCl}_2$. Wise⁴ has later reported the compound $\text{SbCl}_5 \cdot 2\text{SeOCl}_2$. This phase was, however, not found by Agerman *et al.*⁵ Their melting point diagram for the system $\text{SbCl}_5-\text{SeOCl}_2$ indicates only one intermediate compound, $\text{SbCl}_5 \cdot \text{SeOCl}_2$, with a melting point of $79-80^\circ\text{C}$.

EXPERIMENTAL

Crystals of $\text{SbCl}_5 \cdot \text{SeOCl}_2$ are very rapidly hydrolyzed unless kept in a closed and well dried vessel. For this reason single crystals were prepared in the following way. After careful melting of a sample of crystalline $\text{SbCl}_5 \cdot \text{SeOCl}_2$ in a small nitrogen-filled vessel, the liquid was sucked into a thin-walled glass capillary, which was then quickly sealed off. A single crystal was grown from the polycrystalline mass by moving an electrically heated wire slowly along the capillary, using one of the original crystals as seed. The diameter of the glass capillaries was 0.10–0.20 mm, with a wall thickness of about 0.02 mm. The cylindrical single crystal used for X-ray work had a diameter of 0.050 mm.

Equi-inclination Weissenberg photographs were taken about the c axis with nickel-filtered CuK radiation. The angle between the rotation axis and the capillary axis was about 20° . Ten layer lines (0–9) were recorded. The relative intensities were estimated visually by the multiple-film technique (four films) and comparison with an intensity scale made with the same crystal. 1908 independent reflexions were recorded. The data were corrected for the Lorentz and polarization effects. Corrections for absorption were not applied ($\mu R = 1.0$). Attempts were made to reduce the absorption effects by using MoK radiation, but the data obtained with this radiation were not very satisfactory. The data for different layers were first scaled relative to each other by a zone connection method but were finally adjusted by the least squares refinement described below. The crystal used was stable during the time of exposure, as judged from the X-ray photographs.

UNIT CELL AND SPACE GROUP

The unit cell is monoclinic. The dimensions and estimated errors are:

$$\begin{aligned} a &= 13.19 \pm 0.01 \text{ \AA} \\ b &= 14.49 \pm 0.01 \text{ \AA} \\ c &= 12.03 \pm 0.03 \text{ \AA} \\ \beta &= 104^\circ 58' \pm 10' \end{aligned}$$

The lattice constants were determined by a single crystal method first described by Weisz, Cochran and Cole⁶ and subsequently further developed by Löfgren.⁷ As the reflexions were relatively more diffuse in the higher layers and it was impossible to rotate around another crystal axis, the uncertainty in the determination of the c axis was greater.

Systematic absences of $h0l$ reflexions occurred for l odd, and $0k0$ for k odd, which corresponds to the space group $P2_1/c$, assuming that the absences are space group extinctions. The assumption that there are eight $\text{SbCl}_5 \cdot \text{SeOCl}_2$ units per cell gives the reasonable value of $2.78 \text{ g}\cdot\text{cm}^{-3}$ for the density.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

Since the cell contains eight formula units and the general position is fourfold the atomic coordinates of two sets of $\text{SbCl}_5 \cdot \text{SeOCl}_2$ units have to be determined. The positional parameters of the two antimony atoms and the two selenium atoms were obtained approximately from a three-dimensional Patterson function calculated on a modified Hägg-Laurent machine.⁸ After applying back-shift corrections to these atoms a three-dimensional $F_o - F_c$ synthesis based on the refined parameters was computed. All atoms except three chlorine atoms and one oxygen atom were unambiguously located by

this calculation. The remaining atomic positions could then readily be established from a three-dimensional F_o synthesis and the previously determined parameters were simultaneously obtained with greater accuracy. A larger number of the structure factors was used in this last computation (about half the number of the reflexions), this being rather more than the number in the previous case. The programs used in the last two Fourier syntheses were written by Åsbrink *et al.*^{9,10} and designated SNUSKMUS and SUPERMUS. The calculations were performed on the electronic computer BESK in Stockholm.

A least squares refinement was then started using a program (SFLS) devised by Åsbrink and Brändén,¹¹ which minimizes the function $\sum w(|F_o| - |F_c|)^2$ and uses a block-diagonal approximation. The weighting factor w was calculated according to an equation $w = 1/(a + |F_o| + c|F_o|^2)$ suggested by Cruickshank *et al.*¹² Reflexions too weak to be observed were given zero weight. At this stage, all of the 1908 observed reflexions were included in the calculations. The parameters refined (90 in number) were atomic coordinates, individual isotropic temperature factors, and ten scale factors, one for each layer line. This refinement was terminated when the shifts for all the parameters were less than one tenth of their standard deviations. The discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.098. All R values in this paper are based on observed reflexions only. During the last cycles reflexions strongly affected by extinction and some reflexions at the edges of the films or otherwise uncertain were omitted (a total of 22).

The structure was finally refined using the full-matrix program OR FLS written by Busing *et al.*¹³ and modified by Brändén to accommodate more parameters. The function minimized was the same as before. No significant deviations between the block-diagonal and full-matrix calculations were

Table 1. Final atomic parameters and their standard deviations.

Atom	x	y	z	$B \text{ \AA}^2$	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B) \text{ \AA}^2$
Sb(1)	0.2373	0.1449	0.2456	2.12	0.0001	0.0001	0.0002	0.05
Sb(2)	0.7435	0.1053	0.2545	2.41	0.0002	0.0001	0.0002	0.05
Se(1)	0.0481	-0.0062	0.2362	2.58	0.0003	0.0002	0.0004	0.07
Se(2)	0.5488	0.2515	0.2302	2.62	0.0003	0.0002	0.0004	0.08
Cl(1)	0.3000	0.1291	0.0827	4.11	0.0008	0.0007	0.0010	0.20
Cl(2)	0.3687	0.0471	0.3472	4.10	0.0008	0.0007	0.0010	0.21
Cl(3)	0.1599	0.1433	0.4010	4.78	0.0008	0.0008	0.0011	0.24
Cl(4)	0.0919	0.2282	0.1397	3.51	0.0007	0.0007	0.0010	0.18
Cl(5)	0.3336	0.2793	0.3104	3.13	0.0006	0.0006	0.0009	0.17
Cl(6)	0.1131	-0.1051	0.3613	4.93	0.0009	0.0008	0.0011	0.23
Cl(7)	-0.0245	-0.0963	0.0991	3.54	0.0007	0.0007	0.0009	0.18
Cl(8)	0.8208	0.1271	0.1030	4.43	0.0008	0.0008	0.0010	0.22
Cl(9)	0.8694	0.2010	0.3697	5.07	0.0009	0.0009	0.0011	0.25
Cl(10)	0.6505	0.1038	0.3974	4.64	0.0008	0.0008	0.0010	0.23
Cl(11)	0.6029	0.0268	0.1325	4.92	0.0009	0.0008	0.0011	0.25
Cl(12)	0.8334	-0.0288	0.3243	3.85	0.0007	0.0007	0.0010	0.19
Cl(13)	0.6017	0.3547	0.3560	5.15	0.0009	0.0009	0.0011	0.24
Cl(14)	0.4803	0.3386	0.0880	3.82	0.0007	0.0007	0.0009	0.19
O(1)	0.1509	0.0228	0.1881	2.78	0.0017	0.0016	0.0021	0.44
O(2)	0.6638	0.2243	0.1976	3.56	0.0019	0.0018	0.0024	0.52

Table 2. Weight analysis after the last SFLS cycle.

Interval $\sin \theta$	Number of reflexions	$\overline{w \Delta^2}$ (normalized)	Interval F_o	Number of reflexions	$\overline{w \Delta^2}$ (normalized)
0.00–0.46	318	1.02	0–34	84	1.01
0.46–0.58	321	1.21	34–68	823	1.07
0.58–0.67	279	1.05	68–102	463	0.86
0.67–0.74	212	1.00	102–136	256	0.87
0.74–0.79	189	0.92	136–170	120	0.77
0.79–0.84	165	0.98	170–204	64	1.00
0.84–0.89	131	0.90	204–238	46	1.50
0.89–0.93	111	0.96	238–340	30	2.62
0.93–0.97	123	0.57			
0.97–1.00	37	1.07			

found, the changes were all within the standard deviations. The influence of the extinction effects on the atomic parameters was examined by including all the observed reflexions. The R value increased to 0.111, the temperature factor decreased for all atoms and the scale factors applied to F_o increased, but the changes in the coordinates were all within the estimated standard deviations.

The final atomic parameters obtained after the last full matrix calculation including 1886 reflexions are listed in Table 1. The values for weighted $R = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$ and unweighted $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ were 0.123 and 0.099, respectively. An analysis of the weighting scheme for the last SFLS cycle is given in Table 2. The values $a = 30$ and $c = 0.0070$ were found suitable for the final SFLS refinement. These values were also used in the OR FLS cycles. Observed and calculated structure factors are presented in Table 3.

A comparison between calculated structure factors for unobserved reflexions and estimated upper limits of these structure factors shows that only in a few cases does the calculated magnitude exceed the upper limit, and then only within the range of error.

The atomic scattering factors used were those given by Thomas and Umeda¹⁴ for antimony and selenium, Tomiie and Stam¹⁵ for chlorine, and Berghuis *et al.*¹⁶ for oxygen.

The correctness of the structure determination was examined by computing $(F_o - F_c)$ and F_o syntheses with all atoms included. Both functions were three-dimensional and calculated over the asymmetric part of the unit cell at points spaced less than 0.3 Å apart. The maximum absolute value in the difference synthesis was 3.6 % of the largest observed electron density value. Furthermore the largest maxima and minima of the difference function were 1/4 and 1/2, respectively, of the oxygen peaks in the electron density map. These Fourier calculations were made by programs designated STRIX and PROFFS and written by Liminga and Olovsson.¹⁷

Table 3. Continued.

Table with 16 columns: k, l, |r_0|, |r_1|, k, l, |r_0|, |r_1|, k, l, |r_0|, |r_1|, k, l, |r_0|, |r_1|. The table contains numerical data organized in four groups of four columns each.

Table 3. Continued.

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	
-14	5	8	49.7	40.3	-9	9	8	123.4	103.4	-2	1	9	80.3	79.8	3	4	9	46.4	35.0	-12	7	9	65.5	63.9	
-15	5	8	50.0	35.4	-12	9	8	39.6	41.8	-3	1	9	91.3	93.3	3	4	9	48.9	49.3	-12	8	9	45.5	38.4	
-1	6	8	60.7	46.3	-13	9	8	57.8	47.0	-5	1	9	61.5	63.1	-3	4	9	83.7	70.2	-1	8	9	45.5	54.0	
-1	6	8	45.1	38.4	1	10	8	88.1	75.7	6	1	9	66.7	66.6	-9	4	9	41.8	52.7	1	7	9	41.5	58.2	
3	6	8	80.9	92.5	3	10	8	89.0	74.7	-6	1	9	116.9	110.2	-11	0	5	99	58.4	41.7	-7	8	9	48.9	40.2
5	6	8	137.6	137.4	-5	10	8	78.9	79.4	7	1	9	47.7	53.8	1	0	5	99	59.4	64.8	-7	8	9	75.4	64.0
-5	6	8	80.1	66.6	7	10	8	53.8	43.4	-8	1	9	98.4	94.9	-1	0	5	99	72.9	79.2	-7	8	9	35.7	47.3
-7	6	8	125.7	152.8	-9	10	8	89.6	75.1	9	1	9	34.4	32.1	-1	0	5	99	45.5	35.5	-13	1	9	104.9	91.7
-11	6	8	118.5	127.9	-11	10	8	65.9	51.0	10	1	9	40.9	40.1	-2	1	9	99	38.8	25.8	-1	2	3	83.0	84.1
-13	6	8	41.0	36.0	0	11	8	93.1	79.9	-12	1	9	44.6	60.1	-3	5	9	99	79.9	79.2	-2	3	9	104.0	98.7
-1	7	8	53.4	52.4	1	11	8	145.2	143.9	0	2	9	131.0	154.5	-3	5	9	41.2	35.5	-3	9	9	110.7	113.3	
-1	7	8	121.4	111.2	-1	11	8	90.5	89.6	1	2	9	40.6	38.9	-4	7	9	99	45.5	35.5	-3	9	9	110.7	113.3
-2	7	8	69.6	66.9	-2	11	8	66.8	67.6	-1	2	9	34.4	48.8	-4	7	9	99	86.1	81.9	-4	5	9	62.0	62.0
-3	7	8	120.8	123.6	3	11	8	59.8	58.0	2	2	9	134.4	148.9	-5	5	9	75.0	79.8	-5	9	9	71.0	56.2	
-3	7	8	59.0	44.9	-3	11	8	91.9	84.9	-2	2	9	88.0	98.5	-9	5	9	117.2	100.2	-7	9	9	59.4	64.9	
-5	7	8	76.6	87.7	-4	11	8	48.3	49.6	4	2	9	169.2	181.4	-9	5	9	46.7	50.4	-8	9	9	116.3	92.2	
-5	7	8	95.4	83.7	-5	11	8	41.6	38.7	-4	2	9	169.2	175.9	-10	5	9	74.7	91.2	-7	9	9	116.3	92.2	
-7	7	8	63.0	53.2	7	11	8	80.1	76.7	-6	2	9	176.8	169.1	-10	5	9	123.0	76.3	-8	9	9	116.3	92.2	
-7	7	8	98.3	103.8	-7	11	8	80.1	76.7	-6	2	9	176.8	169.1	-2	6	9	46.7	50.4	-9	9	9	86.1	69.9	
-8	7	8	86.7	75.2	-9	11	8	83.2	73.6	7	2	9	63.0	65.6	-2	6	9	150.4	178.4	-6	10	9	88.0	84.5	
-8	7	8	63.6	61.7	-10	11	8	37.7	29.0	8	2	9	81.5	94.0	-4	7	9	149.5	141.4	-8	10	9	51.1	46.7	
9	7	8	55.8	47.3	-11	11	8	47.7	40.9	-8	2	9	184.5	170.9	-5	6	9	48.3	63.4	-1	11	9	101.5	104.2	
-11	7	8	63.6	60.5	2	12	8	79.2	68.7	9	2	9	33.8	54.1	-5	6	9	46.7	35.4	1	11	9	70.7	55.4	
-11	7	8	60.7	69.7	-6	12	8	70.5	60.0	-10	2	9	133.8	144.9	-6	6	9	54.7	66.7	-4	11	9	122.1	49.7	
-12	7	8	147.1	144.3	3	13	8	46.5	40.3	-12	2	9	70.1	75.0	-8	6	9	160.9	124.2	-3	11	9	103.0	92.8	
-2	8	8	57.8	50.7	-1	13	8	142.9	113.6	-14	2	9	66.4	64.9	-8	6	9	56.9	46.3	-3	11	9	122.1	49.7	
4	8	8	150.0	152.7	3	13	8	74.3	69.6	-10	2	9	93.9	70.2	-8	6	9	124.6	130.7	-7	11	9	63.4	30.4	
-6	8	8	124.0	134.3	5	13	8	53.2	56.0	1	3	9	65.8	62.0	-10	6	9	124.6	130.7	-7	11	9	63.4	30.4	
-10	8	8	125.1	117.7	-5	13	8	118.8	102.2	-2	3	9	32.6	29.7	0	7	9	106.7	84.9	-9	11	9	46.4	49.6	
-12	8	8	40.5	43.4	-7	13	8	75.9	59.2	-2	3	9	80.0	78.2	-1	7	9	106.7	84.9	-11	11	9	67.7	63.6	
0	9	8	67.9	71.5	-9	13	8	40.5	36.2	-3	3	9	80.0	84.1	3	7	9	64.6	54.4	-11	11	9	67.7	63.6	
-2	9	8	134.9	38.6	-1	14	8	66.8	47.8	4	3	9	55.6	43.5	-3	7	9	57.5	52.3	-9	12	9	45.5	58.2	
3	9	8	113.9	105.7	-3	14	8	40.5	38.6	4	3	9	55.6	43.5	-6	7	9	73.2	91.7	-1	13	9	106.1	69.3	
-3	9	8	102.6	112.7	-7	14	8	70.8	74.9	7	3	9	52.6	50.5	-5	7	9	143.3	122.7	-1	13	9	45.5	58.2	
-4	9	8	63.0	58.0	-1	15	8	42.2	45.0	7	3	9	76.9	71.0	6	7	9	44.9	62.3	-3	13	9	41.2	49.5	
-5	9	8	68.2	59.0	-1	15	8	44.4	51.7	8	3	9	60.0	77.3	-6	7	9	71.4	38.6	-4	13	9	63.4	46.0	
7	9	8	95.9	85.0	-3	15	8	57.8	52.3	-8	3	9	82.4	87.7	7	7	9	76.9	22.6	-7	13	9	102.7	76.5	
-7	9	8	110.4	104.1	-5	15	8	59.8	58.4	-9	3	9	72.9	66.5	-7	7	9	109.2	82.4	-7	13	9	58.1	52.6	
-8	9	8	42.5	38.3	0	1	9	44.9	42.9	-10	3	9	86.0	61.7	9	7	9	48.6	48.4	-5	13	9	58.1	52.6	
-8	9	8	70.2	55.2	1	1	9	44.9	42.9	-13	3	9	64.6	77.6	-9	7	9	82.1	70.7	-4	14	9	37.5	35.6	
					1	1	9	67.4	71.2	-1	4	9	50.7	46.5	-11	7	9	55.4	52.2						

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of $\text{SbCl}_5 \cdot \text{SeOCl}_2$ is shown in Fig. 1. Bond distances are indicated in Fig. 2 and listed together with bond angles in Table 4. The standard deviations given in the table are calculated without correction for thermal motion by means of the program OR FFE devised by Busing *et al.*¹⁸ The errors of the atomic coordinates from the last OR FLS cycle were used.

As shown in Fig. 1, the structure is composed of discrete $\text{SbCl}_5 \cdot \text{SeOCl}_2$ molecules. There are two structurally non-equivalent molecules in the unit cell, but the differences between the dimensions of these two molecules are generally very small (Fig. 2 and Table 4). The rather large difference between the Sb—O lengths is discussed elsewhere in this paper. The two non-equivalent molecules are roughly related through an *a* glide plane at $y = 1/8$ parallel to (010).

By the formation of the adduct molecule the antimony atom has changed its coordination from trigonal bipyramidal in crystalline SbCl_5 ¹⁹ to distorted octahedral in the adduct, the ligands being five chlorine atoms and one oxygen atom. The deviation from regularity is revealed in Table 4. The angles Cl—Sb—O which do not involve the chlorine atom opposite the Sb—O bond are less than 90° while the angles Cl—Sb—Cl which do involve this chlorine atom are larger than 90°. The average values are 86.2° and 93.8°, respectively. This tendency for the nearest chlorine atoms to move in towards the donor-acceptor bond is also found in other similar adducts.²⁰ These deviations from ideal octahedral configuration of the acceptor atom have been explained as being due to two steric factors, the van der Waals radii of the ligand atoms and their distances from the central atom.²⁰ The mean value of the remaining approximate orthogonal Cl—Sb—Cl angles is 89.7°.

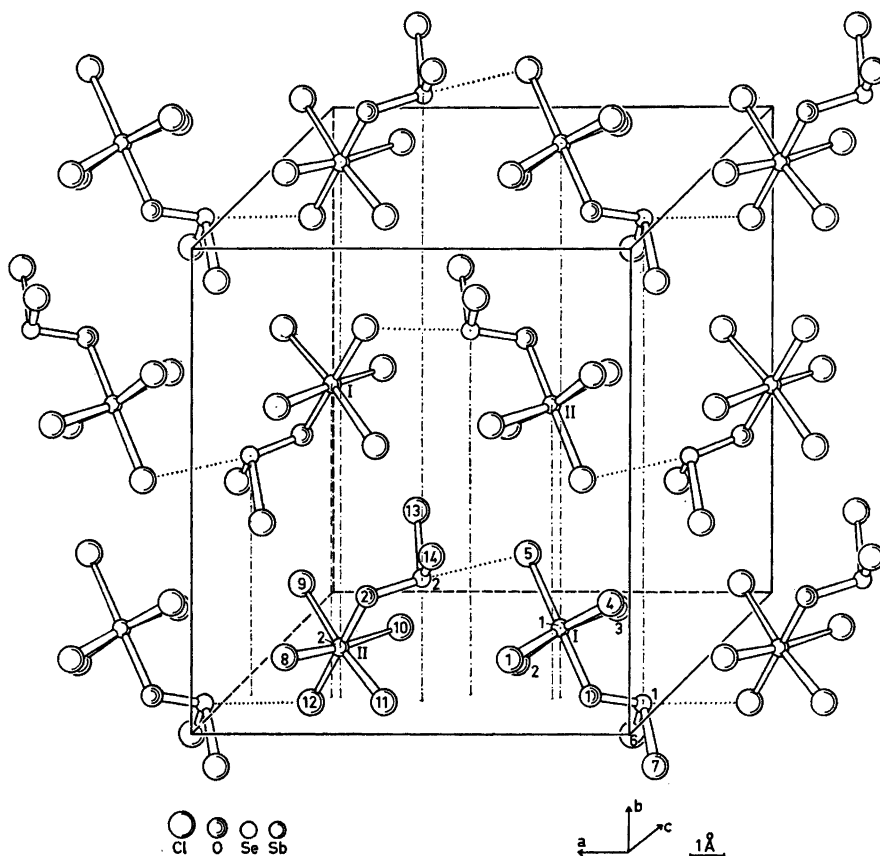


Fig. 1. Part of the crystal structure of $\text{SbCl}_5 \cdot \text{SeOCl}_2$. The glide plane operation has been omitted. Dotted lines indicate weak intermolecular contacts.

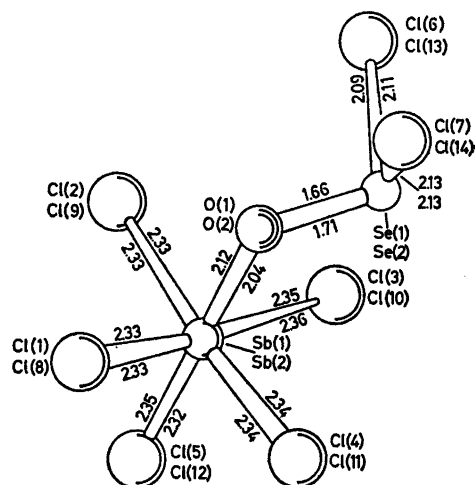


Fig. 2. Bond distances in $\text{SbCl}_5 \cdot \text{SeOCl}_2$. The upper sets of names and parameters correspond and likewise the lower. The orientation is the same as in Fig. 1.

Table 4. Bond distances and bond angles in $\text{SbCl}_5 \cdot \text{SeOCl}_2$, with standard deviations (including errors in cell parameters).

Molecule I		Molecule II	
Bond	Distance (Å)	Bond	Distance (Å)
Sb(1)—Cl(1)	2.326 ± 0.013	Sb(2)—Cl(8)	2.328 ± 0.014
Sb(1)—Cl(2)	2.326 ± 0.011	Sb(2)—Cl(9)	2.327 ± 0.013
Sb(1)—Cl(3)	2.351 ± 0.014	Sb(2)—Cl(10)	2.356 ± 0.014
Sb(1)—Cl(4)	2.345 ± 0.010	Sb(2)—Cl(11)	2.342 ± 0.013
Sb(1)—Cl(5)	2.346 ± 0.009	Sb(2)—Cl(12)	2.318 ± 0.010
Sb(1)—O(1)	2.122 ± 0.023	Sb(2)—O(2)	2.042 ± 0.025
Se(1)—Cl(6)	2.094 ± 0.013	Se(2)—Cl(13)	2.114 ± 0.013
Se(1)—Cl(7)	2.127 ± 0.011	Se(2)—Cl(14)	2.130 ± 0.012
Se(1)—O(2)	1.661 ± 0.023	Se(2)—O(2)	1.709 ± 0.025

Bonds		Bonds	
	Angle(°)		Angle(°)
Cl(1)—Sb(1)—Cl(2)	90.2 ± 0.4	Cl(8)—Sb(2)—Cl(9)	89.8 ± 0.5
Cl(1)—Sb(1)—Cl(3)	172.3 ± 0.4	Cl(8)—Sb(2)—Cl(10)	171.2 ± 0.4
Cl(1)—Sb(1)—Cl(4)	90.7 ± 0.4	Cl(8)—Sb(2)—Cl(11)	90.7 ± 0.5
Cl(1)—Sb(1)—Cl(5)	94.7 ± 0.4	Cl(8)—Sb(2)—Cl(12)	96.4 ± 0.4
Cl(1)—Sb(1)—O(1)	85.5 ± 0.7	Cl(8)—Sb(2)—O(2)	85.1 ± 0.8
Cl(2)—Sb(1)—Cl(3)	89.6 ± 0.4	Cl(9)—Sb(2)—Cl(10)	89.8 ± 0.5
Cl(2)—Sb(1)—Cl(4)	173.2 ± 0.4	Cl(9)—Sb(2)—Cl(11)	172.3 ± 0.5
Cl(2)—Sb(1)—Cl(5)	93.8 ± 0.4	Cl(9)—Sb(2)—Cl(12)	93.7 ± 0.4
Cl(2)—Sb(1)—O(1)	85.9 ± 0.7	Cl(9)—Sb(2)—O(2)	85.6 ± 0.8
Cl(3)—Sb(1)—Cl(4)	88.5 ± 0.4	Cl(10)—Sb(2)—Cl(11)	88.6 ± 0.4
Cl(3)—Sb(1)—Cl(5)	93.0 ± 0.4	Cl(10)—Sb(2)—Cl(12)	92.4 ± 0.4
Cl(3)—Sb(1)—O(1)	86.8 ± 0.7	Cl(10)—Sb(2)—O(2)	86.1 ± 0.8
Cl(4)—Sb(1)—Cl(5)	92.8 ± 0.3	Cl(11)—Sb(2)—Cl(12)	93.9 ± 0.4
Cl(4)—Sb(1)—O(1)	87.5 ± 0.7	Cl(11)—Sb(2)—O(2)	86.8 ± 0.8
Cl(5)—Sb(1)—O(1)	179.6 ± 0.7	Cl(12)—Sb(2)—O(2)	178.4 ± 0.8
Sb(1)—O(1)—Se(1)	121.1 ± 1.3	Sb(2)—O(2)—Se(2)	121.9 ± 1.5
Cl(6)—Se(1)—Cl(7)	99.0 ± 0.5	Cl(13)—Se(2)—Cl(14)	98.6 ± 0.5
Cl(6)—Se(1)—O(1)	101.8 ± 0.9	Cl(13)—Se(2)—O(2)	100.3 ± 0.9
Cl(7)—Se(1)—O(1)	97.4 ± 0.9	Cl(14)—Se(2)—O(2)	99.8 ± 1.0

The observed average value for the Sb—Cl bond lengths, 2.34 Å, is consistent with those reported by Brändén and Lindqvist²¹ in $\text{SbCl}_5 \cdot \text{POCl}_3$, 2.33 Å, and $\text{SbCl}_5 \cdot \text{PO}(\text{CH}_3)_3$, 2.34 Å, by Hansson^{22,23} in $\text{SbCl}_5 \cdot \text{SO}(\text{C}_6\text{H}_5)_2$, 2.35 Å, and $\text{SbCl}_5 \cdot \text{SO}_2(\text{CH}_3)_2$, 2.32 Å, and by Brun and Brändén²⁴ in $\text{SbCl}_5 \cdot \text{HCON}(\text{CH}_3)_2$, 2.34 Å. According to a theory by Lindqvist,²⁵ these Sb—Cl distances should be shorter than in regular octahedral SbCl_6^- ions. Unfortunately this cannot yet be verified, as no information exists about such Sb(V)—Cl bond lengths. The only data known are those for some irregular chloro complexes. In ISbCl_8 where approximately octahedral SbCl_6^- ions are linked with weak bonds to ICl_2^+ ions, the averages of the Sb—Cl bond lengths are 2.31 Å for the non-bridging chlorine atoms and 2.43 Å for the two bridging ones.²⁶ In comparison with the adducts formed by coordination through an oxygen atom, a somewhat longer Sb—Cl distance (2.39 Å) has been found in the adduct $\text{SbCl}_5 \cdot \text{S}_4\text{N}_4$.²⁷ This elongation conforms with the ideas suggested by Lindqvist.²⁵ In Rb_2SbCl_6 , which apparently has a disordered arrangement of SbCl_6^- and SbCl_6^{3-} ions, a Sb—Cl distance of 2.47 Å is found.²⁸ In this case, however, the lower oxida-

tion number of antimony may be a possible explanation for the longer Sb—Cl distance.

All five chlorine atoms seem to be at the same distance from the antimony atom. No difference between the length of the four basal chlorine atoms and the axial chlorine atom is observed.

It would be of interest to know if there is any significant difference between the present Sb—Cl bond lengths and those found in solid SbCl_5 , 2.29 Å for the three basal chlorine atoms and 2.34 Å for the apical chlorine atoms,¹⁹ but as the accuracy in the latter determination is not sufficiently great, no valid comparisons can be made.

The difference between the Sb—O bond lengths for the two non-equivalent molecules seems to be quite large, about three times the standard deviation. An analysis of the steric conditions gives no obvious explanation of this difference, however. It may be mentioned that the distance between the antimony atom and the selenium atom is practically the same in the two molecules, 3.30 Å and 3.28 Å, and the angles Sb—O—Se do not differ significantly from each other, 121.1° and 121.9°. The average value of 2.08 Å may probably be accepted as the actual Sb—O bond length. This short distance indicates a strong interaction between the antimony pentachloride and the seleninyldichloride parts of the adduct molecule. In the complexes previously discussed the Sb—O distances range from 1.94 to 2.23 Å.

It has been suggested by the present author² that the angle subtended at the oxygen atom in adducts of this type is partly correlated with the electronegativity of the ligands at this atom. Thus an increase in electronegativity decreases the angle (cf. Gillespie and Nyholm²⁰). This would imply that the bond angle at the oxygen atom in $\text{SbCl}_5 \cdot \text{SeOCl}_2$ should be smaller than that in $\text{SbCl}_5 \cdot \text{POCl}_3$ but larger than the angle in $\text{SbCl}_5 \cdot \text{SO}(\text{C}_6\text{H}_5)_2$. The observed values of 121.5°, 145.0°,²¹ and 117.6°,²² respectively, are compatible with this suggestion. However, the angle of 121.5° in $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ ² and 124.5° in $\text{SbCl}_5 \cdot \text{HCON}(\text{CH}_3)_2$ ²⁴ shows that other factors are also of importance, particularly steric factors as has been pointed out by Lindqvist.¹

The geometry of the SeOCl_2 groups in the present structure is very similar to that observed in $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$,² but, as expected, different from that in $\text{SeOCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ³⁰ in which SeOCl_2 acts as an acceptor molecule (see Table 5). This is in agreement with previous observations showing that the dimensions of the donor molecule vary very little in different adducts. Furthermore the

Table 5. Bond lengths (Å) and bond angles (°) in the SeOCl_2 part of different molecular complexes.

	$\text{SbCl}_5 \cdot \text{SeOCl}_2$		$\text{SnCl}_4 \cdot 2\text{SeOCl}_2$	$\text{SeOCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$	
Se—O	1.66,	1.71	1.73	1.59	
Se—Cl	2.11,	2.12	2.14	2.39,	2.57
Cl—Se—Cl	99.0,	98.6	97.6	165.2	
Cl—Se—O	99.6,	100.1	101.1	95.1,	99.7

mean value of the Se—O bond length, 1.69 Å, is consistent with the observed value in other compounds having trigonal pyramidal configuration about a selenium atom. The latest reported is 1.71 Å, found in $\text{ZnSeO}_3 \cdot 2\text{H}_2\text{O}$.³¹ As regards the Se—Cl bonds in compounds with a similar hybridization of the selenium atom, no further distances have been published. In diphenylselenium dichloride and 1,1,4,4-tetrachloro-1,4-diselenane, where the bonding situation about the selenium atom is best described by a sp^3d -hybridization, the reported Se—Cl bond lengths are 2.30 Å³² and 2.24 Å.³³

An examination of the intermolecular distances listed in Table 6 reveals the occurrence of relatively short distances between molecules packed along the a axis. Thus two of the Se...Cl distances are much shorter, 3.25 Å and 3.29 Å, than the sum of the van der Waals radii, 3.8 Å, indicating an interaction between the two non-equivalent molecules. There is evidently a tendency for the molecules to be linked together, forming chains parallel to the a axis. The linking arrangement is shown in Fig. 1, in which the two short contacts are indicated by dotted lines. It must be emphasized, however, that the interaction seems to be quite weak, as no elongations are observed in the corresponding covalent Sb—Cl bonds.

This interaction may be a simple electrostatic attraction between dipoles but other interpretations are certainly possible. Short intermolecular Se...Cl distances have also been found in $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ ² and $\text{SeOCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$.³⁰ In the case of $\text{SeOCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ Gillespie³⁴ suggests that the interaction is due to the strong repulsion between the electron pairs in the valency shell of the selenium atom, which causes the lone pair on the selenium atom to be delocalized into a vacant $3d$ orbital on the chlorine atom of an adjacent molecule. This theory, however, hardly seems to be applicable to the present compound; firstly since the repulsion of the electron pairs in the valency shell of the three-bonded selenium is certainly not strong enough, and secondly since the free electron pair is not directed towards the chlorine atom. This chlorine

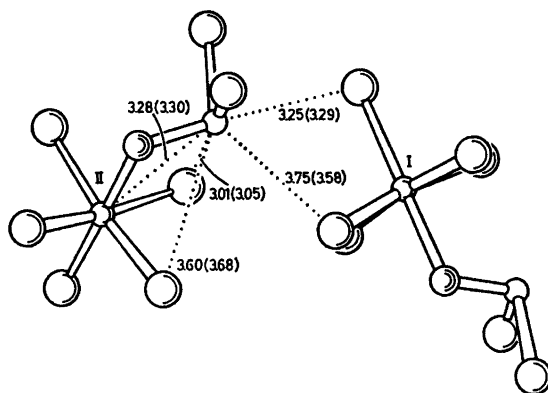


Fig. 3. The distances to the next nearest neighbours of a selenium atom. Distances in parantheses refer to the neighbours of Se(1). The orientation and notation of the atoms is the same as in Fig. 1.

atom lies close to the extension of the O—Se axis and seems to fit quite well into the pyramidal space between two bonding electron pairs and one lone electron pair. The angle O—Se...Cl is 171.8° (average value). It appears from the above discussion of the molecular interaction that the alternative interpretation of the short Se...Cl distances as due to packing effects cannot be excluded. The van der Waals forces should then be mainly responsible for the cohesion in the crystal.

There is in addition a further short selenium-chlorine distance in the structure (3.05 Å for Se(1) and 3.01 Å for Se(2)), but in this case the contact is intramolecular (Fig. 3). This fact may also complicate the attempts to obtain a true picture of the chemical bonding. Similar interactions have been found in $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ and $\text{SbCl}_5 \cdot \text{SO}(\text{C}_6\text{H}_5)_2$.²² It is noteworthy that the same intramolecular Se...Cl distance (3.01 Å) is observed in $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$.²

In addition to the neighbours of selenium discussed in the foregoing there are two more chlorine neighbours at larger distances, 3.68 Å and 3.58 Å for Se(1), for Se(2) 3.60 Å and 3.75 Å (Fig. 3).

Table 6. Intermolecular distances less than 4.0 Å in $\text{SbCl}_5 \cdot \text{SeOCl}_2$. Distances are given between the reference molecule of which the atomic coordinates are given in Table 1, and surrounding molecules designated as follows:

A:	x	y	z	G:	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
B:	$-1+x$	y	z	H:	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
C:	$-x$	$-y$	$-z$	I:	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
D:	$1-x$	$-y$	$-z$	K:	x	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
E:	$1-x$	$-y$	$1-z$	L:	$-1+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
F:	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$				

Contact	Distance (Å)	Contact	Distance (Å)
Se(1)...Cl(8)B	3.58	Cl(4)...Cl(12)G	3.65
Se(1)...Cl(12)B	3.29	Cl(5)...Cl(11)G	3.71
Se(2)...Cl(1)A	3.75	Cl(5)...Cl(12)G	3.65
Se(2)...Cl(5)A	3.25	Cl(5)...Cl(13)A	3.61
		Cl(5)...Cl(14)A	3.78
		Cl(5)...Cl(14)I	3.81
Cl(1)...Cl(5)K	3.67	Cl(6)...Cl(8)H	3.98
Cl(1)...Cl(7)C	3.76	Cl(6)...Cl(9)E	3.47
Cl(1)...Cl(11)D	3.89	Cl(6)...Cl(10)E	3.67
Cl(1)...Cl(14)A	3.85	Cl(6)...Cl(12)B	3.77
Cl(2)...Cl(10)A	3.70	Cl(7)...Cl(7)C	3.83
Cl(2)...Cl(10)E	3.83	Cl(7)...Cl(8)B	3.83
Cl(2)...Cl(13)H	3.79	Cl(7)...Cl(9)H	3.54
Cl(2)...Cl(14)H	3.59	Cl(7)...Cl(12)B	3.80
Cl(2)...Cl(14)I	3.33	Cl(8)...Cl(9)K	3.93
Cl(3)...Cl(4)I	3.72	Cl(8)...Cl(13)K	3.58
Cl(3)...Cl(9)B	3.84	Cl(10)...Cl(14)I	3.69
Cl(3)...Cl(12)E	3.68	Cl(11)...Cl(11)D	3.70
Cl(4)...Cl(6)F	3.62	Cl(11)...Cl(13)H	3.70
Cl(4)...Cl(7)C	3.37	Cl(11)...Cl(13)K	3.74
Cl(4)...Cl(8)B	3.78		
Cl(4)...Cl(9)L	3.91	Cl(7)...O(1)C	3.59

With the exception of the Se...Cl contacts mentioned above the packing of the $\text{SbCl}_5\cdot\text{SeOCl}_2$ molecules involves only chlorine-chlorine contacts. The shortest distance is 3.33 Å (Table 6), which may be compared with the normal van der Waals distance of 3.6 Å. Such a short Cl...Cl contact distance has also been found in other adducts, for example 3.31 Å in $\text{NbCl}_5\cdot\text{POCl}_3$ ²¹ and 3.41 Å in $\text{SbCl}_5\cdot\text{POCl}_3$.²¹ Ohlberg¹⁹ has reported 3.33 Å as the shortest packing distance in solid SbCl_5 .

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