

The Crystal Structure of $\text{SeOCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}$

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The crystal structure of the addition compound $\text{SeOCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}$ has been determined and refined using three-dimensional X-ray data. There are two molecules in the triclinic unit cell with the constants $a = 8.19$, $b = 11.72$, $c = 10.82$ Å, all ± 0.05 Å and $\alpha = 135.6 \pm 0.8^\circ$, $\beta = 110.8 \pm 0.6^\circ$, and $\gamma = 90.5 \pm 0.6^\circ$. The space group is $P\bar{1}$. The crystal consists of molecules in which the coordination polyhedron around the central selenium atom is a tetragonal pyramid. The two chlorine atoms and the two nitrogen atoms of the pyridine rings are bonded in the basal plane with atoms of the same kind in *trans* positions. The oxygen atom occupies the apex of the pyramid. The relevant bond distances and bond angles are: $\text{Se}-\text{Cl}_1 = 2.57 \pm 0.15$, $\text{Se}-\text{Cl}_2 = 2.39 \pm 0.15$, $\text{Se}-\text{N}_1 = 2.19 \pm 0.02$, $\text{Se}-\text{N}_2 = 2.20 \pm 0.02$, and $\text{Se}-\text{O} = 1.59 \pm 0.02$ Å, and $\text{Cl}_1-\text{Se}-\text{Cl}_2 = 165.2 \pm 0.2$, $\text{N}_1-\text{Se}-\text{N}_2 = 173.8 \pm 0.7$, $\text{O}-\text{Se}-\text{Cl}_1 = 95.1 \pm 0.7$, $\text{O}-\text{Se}-\text{Cl}_2 = 99.7 \pm 0.7$, $\text{O}-\text{Se}-\text{N}_1 = 90.9 \pm 1.0$, and $\text{O}-\text{Se}-\text{N}_2 = 92.3 \pm 1.0^\circ$. The molecules show a certain tendency to secondary dimerisation over weak chlorine bridges. The bridging chlorine atom completes the distorted octahedron around the central selenium at a distance of 3.65 Å.

The nature of the chemical bonds and the problem of chloride-ion transfer processes in solutions of pyridine in selenium oxychloride are briefly discussed.

1. Introduction

As part of a rather extensive investigation of the addition compounds formed by AsCl_3 , POCl_3 , and SeOCl_2 we have studied systems in which they probably function as acceptor molecules. Typical examples are the adducts with pyridine, $\text{AsCl}_3 \cdot \text{C}_5\text{H}_5\text{N}$, $\text{AsCl}_3 \cdot 2 \text{C}_5\text{H}_5\text{N}$ and $\text{SeOCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}$. The relations between the structures of the acceptor molecules and the adduct molecules are of great interest and we have started with a study of $\text{SeOCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}$.

2. Preparation of crystals

The phase diagram of the system $\text{SeOCl}_2-\text{C}_5\text{H}_5\text{N}$ has been studied by methods described earlier (Agerman *et al.*, 1958). It shows a flat melting point maximum of $+110^\circ \text{C}$. at the composition $\text{SeOCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}$. (This compound was first prepared by Edgington & Firth (1936).) Orange single crystals were prepared in sealed capillary tubes (the compound is very hygroscopic) by a method of zone melting. The crystals darkened during the X-ray work but did not decompose appreciably as far as we could judge from the X-ray photographs.

3. X-ray work

A 1.6 mm. long crystal in a thin-walled Pyrex glass capillary tube of 0.17 mm. outer diameter was used for the X-ray study.

Measurements on zero-layer Weissenberg photographs taken with Cu K -radiation around three different rational axes gave the constants of the triclinic cell

$$\begin{array}{ll} a = 8.19 \pm 0.05 \text{ \AA} & \alpha = 135.6 \pm 0.8^\circ \\ b = 11.72 \pm 0.05 & \beta = 110.8 \pm 0.6 \\ c = 10.82 \pm 0.05 & \gamma = 90.5 \pm 0.6 \end{array}$$

The value 1.5405 Å was used for the Cu $K\alpha_1$ wave length.

The calculated density for the crystal assuming two molecules in the unit cell is 1.734 g.cm.⁻³. The density of an ideal mixture between selenium oxychloride and pyridine in the mole ratio 1:2 would be 1.41 g.cm.⁻³. As the density cannot easily be measured because the crystals are too hygroscopic, we started with the assumption that there were two molecules in the unit cell, the space group being $P\bar{1}$. This has been confirmed by the structure determination.

Three-dimensional intensity material was gathered by taking multiple-film Weissenberg photographs about the c -axis ($l = 0-9$). Mo K -radiation was used. The films in the pack were interleaved with 0.04 mm. iron foils. In order to get similarly shaped spots for all the reflexions in the layer, two photographs per layer line for $l \geq 1$ were taken, the crystal being turned by 180° for the second one. The intensities of 1134 independent reflexions were estimated by visual comparison with an intensity scale prepared with the crystal under investigation. The relative $|F_o|$ -values were derived using Lu's (1943) curves. No extinction or absorption corrections were applied. (The linear absorption coefficient is 36.7 cm.⁻¹ for Mo $K\alpha$.)

4. Structure determination and refinement

The selenium and chlorine positions were obtained from Patterson and electron-density projections along

the three axes and checked by bounded Patterson projections along the c -axis between the planes $z = 0$ and $z = \frac{1}{4}$ and between $z = \frac{1}{4}$ and $z = \frac{1}{2}$ as well as along the a -axis with boundaries $x = 0$ and $x = \frac{1}{2}$. The oxygen atom and the atoms of one pyridine ring showed up clearly in the corresponding bounded electron-density projections. About 50% of the observed structure factors were used whose signs could be determined on the basis of the selenium and

chlorine positions only. The structure thus determined permitted a reasonably safe assessment of the signs of 929 structure factors. A three-dimensional electron-density calculation was then made which showed well resolved peaks of the atoms of the second pyridine ring besides the maxima at the already known atomic positions.

The structure was refined by scaling the observed structure factors of each photograph against those calculated for the parameters obtained from the preceding three-dimensional electron-density function and by successive F_o -synthesis. Three such cycles of refinement were performed. After the first one the signs of all structure factors were fixed. Finally a F_c -synthesis was calculated to correct for series termination. The last column in Table 1 gives the final corrected coordinates.

The agreement between observed and calculated structure factors improved rapidly during the first two cycles of refinement and remained nearly constant in the last one. Table 2* compares the observed structure factors with the calculated values for the atomic coordinates contained in the second column of Table 1 which correspond to the second stage of refinement. Atomic scattering factor curves in the analytical representation given by Vand *et al.* (1957) were used. For selenium the constants in Table 4 of the quoted paper (Thomas-Fermi atomic scattering factor curves, without exchange) were taken, for chlorine those in Table 3 (Light elements without exchange), and for oxygen, nitrogen and carbon those in Table 1 (Light elements with exchange). The constants a and b given there are calculated for Cu $K\alpha$ -radiation and were therefore multiplied by the factor $1.54^2/0.7095^2$ in order to make them applicable to the Mo $K\alpha$ -radiation data. All observed reflexions lay within the limits in $\sin \theta$ claimed by Vand *et al.* (1957) for the validity of their approximation. An isotropic temperature factor with the value $B = 4.79 \text{ \AA}^2$ common to all atoms was applied. The reliability index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ for all observed reflexions is 0.150.

All projections were calculated on the Hagg-Laurent machine (1946). The structure factor and the three-dimensional electron-density calculations were performed on BESK, the high-speed electronic computer belonging to Statens Matematikmaskinnämnd, Stockholm, using programmes designed by Mr S. Westman and Mr S. Åsbrink. In the vicinity of the selenium and the chlorine atoms the electron density was evaluated at points $1/128$ of the cell edges apart and at points with twice this spacing for the lighter atoms. The maxima were located using the method given by Booth (1948) in combination with a graphical method. The results of these interpolations were checked in a few cases against values obtained by the analytical method of Shoemaker *et al.* (1950) and

Table 1. Atomic coordinates at various stages of refinement

		Second cycle of refinement	Final corrected parameters
Se	x	0.4559	0.4568
	y	0.0593	0.0600
	z	0.3127	0.3134
Cl ₁	x	0.7158	0.7158
	y	0.2052	0.2057
	z	0.6587	0.6593
Cl ₂	x	0.1770	0.1783
	y	-0.1275	-0.1279
	z	-0.0178	-0.0169
O	x	0.5636	0.5632
	y	0.1978	0.1989
	z	0.3431	0.3429
N ₁	x	0.2980	0.2976
	y	0.2183	0.2195
	z	0.4477	0.4484
C ₁	x	0.1594	0.1680
	y	0.1591	0.1641
	z	0.4527	0.4583
C ₂	x	0.0623	0.0597
	y	0.2452	0.2495
	z	0.5280	0.5319
C ₃	x	0.1045	0.0993
	y	0.4159	0.4144
	z	0.6123	0.6109
C ₄	x	0.2323	0.2283
	y	0.4722	0.4688
	z	0.6045	0.5949
C ₅	x	0.3302	0.3299
	y	0.3663	0.3670
	z	0.5119	0.5123
N ₂	x	0.5922	0.5858
	y	-0.1197	-0.1244
	z	0.1510	0.1466
C ₆	x	0.5943	0.5918
	y	-0.2432	-0.2472
	z	0.1323	0.1283
C ₇	x	0.6947	0.6885
	y	-0.3538	-0.3535
	z	0.0548	0.0515
C ₈	x	0.7617	0.7655
	y	-0.3382	-0.3383
	z	-0.0395	-0.0378
C ₉	x	0.7650	0.7594
	y	-0.2030	-0.2031
	z	-0.0127	-0.0145
C ₁₀	x	0.6506	0.6567
	y	-0.1172	-0.1103
	z	0.0550	0.0602

* Microfilm copies of Table 2 can be obtained from this Institute.

found to be consistent with the latter within the expected limits of error of the structure determination.

The standard deviations of the atomic coordinates were estimated by the formula given by Cruickshank (1949).

5. Description of the structure

One molecule of $\text{SeOCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ is shown in Fig. 1. All bond lengths and bond angles are given in Table 3 together with their standard deviations. The packing of the molecules is shown in Fig. 3(a), (b). The shortest packing distances between different molecules are collected in Table 4.

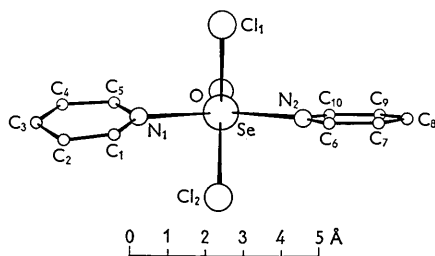


Fig. 1. The molecule of the addition compound $\text{SeOCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$.

Table 3. Bond distances and angles in $\text{SeOCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ and their standard deviations

Distance (Å)	S.D. (Å)	Angle (°)	S.D. (°)	
Se-Cl ₁	2.57	Cl ₁ -Se-Cl ₂	165.2	0.2
Se-Cl ₂	2.39	N ₁ -Se-N ₂	173.8	0.7
Se-O	1.59	O-Se-Cl ₁	95.1	0.7
Se-N ₁	2.19	O-Se-Cl ₂	99.7	0.7
Se-N ₂	2.20	O-Se-N ₁	90.9	1.0
		O-Se-N ₂	92.3	1.0
N ₁ -C ₁	1.31	Cl ₁ -Se-N ₁	92.8	0.7
N ₂ -C ₅	1.30	Cl ₁ -Se-N ₂	92.4	0.7
N ₂ -C ₆	1.31	Cl ₂ -Se-N ₁	87.3	0.7
N ₂ -C ₁₀	1.35	Cl ₂ -Se-N ₂	86.8	0.7
Mean	1.32	C ₅ -N ₁ -C ₁	121	3.0
C ₁ -C ₂	1.34	C ₁₀ -N ₂ -C ₆	120	3.0
C ₄ -C ₅	1.39	Mean	120.5	
C ₆ -C ₇	1.37	N ₁ -C ₁ -C ₂	125	3.0
C ₉ -C ₁₀	1.33	C ₄ -C ₅ -N ₁	120	3.0
Mean	1.36	N ₂ -C ₆ -C ₇	126	3.0
C ₂ -C ₃	1.41	C ₉ -C ₁₀ -N ₂	119	3.0
C ₃ -C ₄	1.35	Mean	122.5	
C ₇ -C ₈	1.42	C ₁ -C ₂ -C ₃	115	3.0
C ₈ -C ₉	1.42	C ₃ -C ₄ -C ₅	120	3.0
Mean	1.40	C ₆ -C ₇ -C ₈	114	3.0
		C ₈ -C ₉ -C ₁₀	120	3.0
		Mean	117.3	
		C ₂ -C ₃ -C ₄	120	3.0
		C ₇ -C ₈ -C ₉	119	3.0
		Mean	119.5	

* The uncertainty in the cell dimensions give the more realistic value of 0.015 Å.

Table 4. Packing distances in $\text{SeOCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$

(See Fig. 3a and b)

Distance (Å)	Distance (Å)
Se-Cl 1-2 3.65	O-C 18-13 3.66
Cl-Cl 2-3 3.86	18-28 3.79
4-5 4.12	18-15 3.96
Cl-C 6-7 3.48	N-C 19-20 3.69
8-9 3.55	C-C 11-21 3.43
10-11 3.66	14-22 3.51
12-13 3.72	16-24 3.72
2-14 3.79	22-25 3.79
5-15 3.93	26-27 3.95
5-16 4.05	
4-17 4.05	

This is the first example of a molecule containing five-bonded selenium (cf. the survey article by Abrahams, 1956). The selenium atom is surrounded by a tetragonal pyramid of five neighbour atoms. The deviations from the ideal bond angles of 90° are easily explained by the spatial conditions.

The Se-O bond length, 1.59 Å, is shorter than in any earlier reported structure but there are not many comparisons to be made (see Abrahams' article). It is particularly regrettable that the structure of SeOCl_2 is not known.

The Se-N bond lengths 2.19 and 2.20 Å are much larger than the calculated single bond length, 1.87 Å. The latter is, however, in agreement with the value 1.83 ± 0.04 Å found by Luzzati (1951) in $\text{C}_6\text{H}_4\text{N}_2\text{Se}$. The nature of the chemical bond must thus be very different in the two cases as will be further discussed later in this paper.

The two Se-Cl bond lengths 2.57 and 2.39 Å are significantly different. They are both appreciably longer than the calculated single bond length, 2.16 Å. Earlier structure determinations by McCullough *et al.* (1942, 1950) show, however, good agreement with the shorter of the bond lengths found in this structure (2.30 and 2.38 Å). The 'long' Se-Cl bond length, 2.57 Å, to one of the chlorine atoms, Cl₁, can be correlated with the weak interaction between that chlorine atom and the selenium atom of a neighbouring molecule (the chlorine atom approaches the sixth corner of the incomplete octahedron).

This weak 'bridge' function is seen in Fig. 3(a), and is also demonstrated in the rather short intermolecular

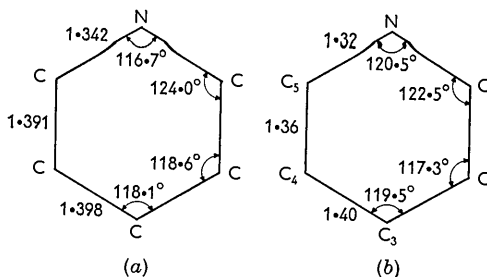


Fig. 2. Comparison of the interatomic distances and bond angles in the pyridine ring found by Bak *et al.* (1954), (a), and in the present work, (b).

Se-Cl distance 3.65 Å (the accepted van der Waals distance is 3.80 Å). The completion of the tetragonal pyramid to a distorted octahedron leads to a kind of secondary dimerisation in the crystalline state (cf. the

All packing distances have reasonable values (for Se-Cl = 3.65 Å see above).

6. Discussion

This is the first structure determination of an addition compound in which the acceptor molecule is an oxychloride. These molecules have generally a greater tendency to function as donor molecules with the oxygen atoms as donor atom (cf. the crystal structure of $\text{SbCl}_5 \cdot \text{POCl}_3$ described by Lindqvist & Brändén, 1957). The ability to function as acceptor as well as donor molecule is well established for SeOCl_2 , which is known also to form such compounds as $\text{SbCl}_5 \cdot \text{SeOCl}_2$ and $\text{SnCl}_4 \cdot 2 \text{SeOCl}_2$ (Agerman *et al.*, 1958).

An increase in coordination number around the acceptor atom by the formation of an adduct is typical for all acceptor molecules. The change from three to five neighbour atoms is connected with a drastic rearrangement around the selenium atom in this case. The donor molecule is generally much less influenced by the adduct formation, and no significant effects are found in the present case.

The atomic configuration of the tetragonal pyramid is supposed to be caused by sp^3d^2 hybridisation with an unshared electron pair in the sixth corner of the octahedron. It is obvious, however, that the Se-N bonds are far from being ordinary covalent bonds, and that the Se-Cl bonds also are too long to be easily interpreted in that way. The covalent bond picture of the compound is thus very unsatisfactory.

An ionic bond picture gives a reasonable interpretation of the Se-N distance as caused by ion-dipole interaction but is difficult to reconcile with the short Se-O bond and the existence of two different Se-Cl bonds.

A compromise would be to consider the short Se-Cl bond as covalent and the long one as ionic and describe the molecule as built up of one SeOCl^+ , one Cl^- , and two $\text{C}_5\text{H}_5\text{N}$ units. The chemical interaction in adducts of this type, however, cannot adequately be discussed in terms of those bond concepts which have been developed mainly on the basis of the empirical knowledge of such classes of compounds as typical molecules or salts. Therefore we think it advisable to refrain from further speculation about the nature of the chemical bonds until more structural and other information is available about compounds of this type.

It is quite clear, however, that one of the Se-Cl bond lengths is much longer than the other one, corresponding to a 'release' of one chloride ion whatever the exact nature of the chemical bond involved is. It is interesting to discuss the 'bridge dimerisation' in this connection, because it is the 'released' chloride ion which actually functions as a bridge. The distance to Se in a neighbour molecule is quite long, 3.65 Å, indicating a rather weak interaction. This is natural because the

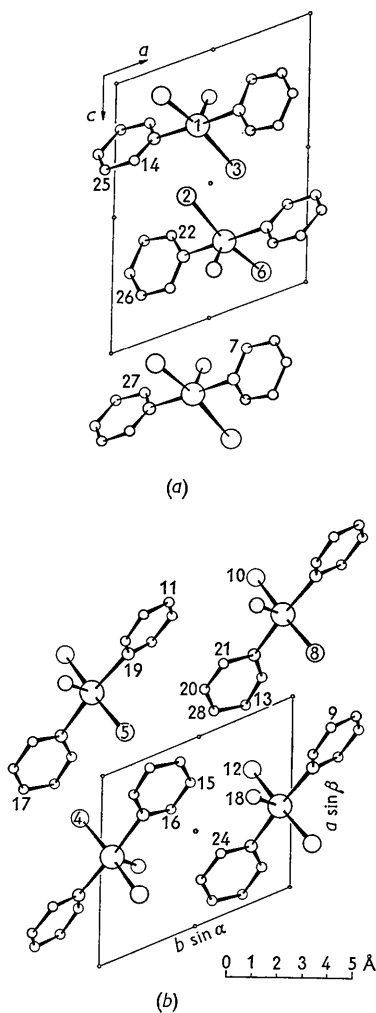


Fig. 3. (a) The packing of the molecules projected on (010). (b) The packing of the molecules seen along [001].

recent discussion of $\text{In}(\text{CH}_3)_3$ by Amma & Rundle, 1958). Similar indications of weak chlorine bridges in related compounds have been found in $\text{TeCl}_2(\text{CH}_3)_2$ (Christofferson *et al.*, 1958), in $\text{CuCl}_2 \cdot 2 \text{C}_5\text{H}_5\text{N}$ (Dunitz, 1957), and in $(\text{C}_6\text{H}_5)_2\text{JCl}$ (Khotsianova, 1957).

The pyridine rings, which are planar within the limits of error, are not in the equatorial plane through Se, O and N but are rotated around the Se-N bonds through angles of 4° and 22° respectively, both in the same direction. The bond lengths are not significantly different from those in pure pyridine. The values from the very accurate micro-wave work by Bak *et al.* (1954) are shown in Fig. 2 together with the averaged values for corresponding bond lengths and bond angles in this compound.

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

In a solution of $\text{C}_5\text{H}_5\text{N}$ 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).

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The Crystal Structure of $\text{SbCl}_5 \cdot \text{POCl}_3$

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The crystal structure of $\text{SbCl}_5 \cdot \text{POCl}_3$ 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 $\text{SbCl}_5 \cdot \text{POCl}_3$ 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