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The Crystal Structure of $\mathrm{SnCl_4.2\,SeOCl_2}$

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The crystal structure of the addition compound $\mathrm{SnCl_4.2\,SeOCl_2}$ has been determined and refined from three-dimensional X-ray data. The unit-cell dimensions are

$$a = 9{\cdot}24 \pm 0{\cdot}03,\; b = 9{\cdot}24 \pm 0{\cdot}03,\; c = 16{\cdot}26 \pm 0{\cdot}03\ \text{Å};\; \beta = 95^\circ\ 34' \pm 10'.$$

There are four molecules per unit cell and the space group is $C2/c$. The crystal consists of discrete $\mathrm{SnCl_4.2\,SeOCl_2}$ molecules. The tin atom is situated on a twofold axis, surrounded by a distorted octahedron of two oxygen atoms in *cis* position and four chlorine atoms. The oxygen atoms form bridges between the tin and the selenium atoms. The $\mathrm{SeOCl_2}$-parts of the molecule are pyramid-shaped. The angle Sn–O–Se is 121·5°. A tendency to secondary acceptor-donor interaction within and between the adduct molecules can be recognized from the interatomic distances. A distorted octahedral coordination around the selenium atom is obtained, if all nearest neighbours are considered. In this compound selenium oxychloride acts as a donor as well as an acceptor molecule, although the donor action is predominant.

1. Introduction

It is well known that many oxychlorides give stable complexes. Several investigations have been made to establish the structure of such complexes in solution and the nature of the acceptor-donor reactions.

To give a more detailed study of the behaviour in solution a knowledge of the structure of the solvate is necessary. Groeneveld (1956) has suggested that the addition of an oxychloride to a Lewis acid gives a stable compound owing to the polar bond to oxygen. This has been confirmed by the X-ray study of $\mathrm{SbCl_5.POCl_3}$ (Lindqvist & Brändén, 1959). Furthermore Lindqvist (1958) has pointed out that the formation of an adduct molecule leads to an increase in coordination of the acceptor molecule, while the donor molecule is essentially unchanged. This proposal should be valid for a compound like $\mathrm{SnCl_4.2\,SeOCl_2}$, and if the oxygens act as donor atoms, it is of interest to know whether they are in *cis*- or *trans*-positions.

2. Preparation of crystals

The compound $\mathrm{SnCl_4.2\,SeOCl_2}$ was first isolated by Weber (1865), but the complete system $\mathrm{SnCl_4}$–$\mathrm{SeOCl_2}$ has been described by Agerman *et al.* (1958). The phase diagram shows a congruent melting point of 52–54 °C. at the composition $\mathrm{SnCl_4.2\,SeOCl_2}$. Single crystals of the very hygroscopic compound were prepared in sealed capillary tubes by a method of zone melting. A capillary tube with an outer diameter of 0·11 mm. was used for the X-ray work. The crystal was stable during the time of exposure, judging from X-ray photographs.

3. X-ray measurements

The lattice constants of the monoclinic cell were determined by a method first described by Weisz, Cochran & Cole (1948). Systematic errors were eliminated by an extrapolation method (Löfgren, 1960; see also Hermodsson & Strandberg, 1957). The results are:

$$a = 9{\cdot}24 \pm 0{\cdot}03,\ b = 9{\cdot}24 \pm 0{\cdot}03,\ c = 16{\cdot}26 \pm 0{\cdot}03\ \text{Å};$$
$$\beta = 95^\circ\ 34' \pm 10'.$$

Systematic extinctions were found for *hkl* reflexions with $h+k$ odd and for $h0l$ reflexions with l odd. The space group is thus $C2/c$ or Cc. The choice of the centrosymmetrical space group was confirmed by the structure determination. With four molecules per unit cell the density was calculated to be 2·85 g.cm.$^{-3}$; the experimental value is 2·80 g.cm.$^{-3}$.

Weissenberg photographs were taken about the [110]-axis with Cu K radiation. Five layer lines (0–4) were recorded. Connection between the zones was obtained by comparing symmetry-related reflexions in different layers. The intensity of the reflexions were visually estimated by means of a calibrated scale. Use was made of the multiple-film technique.

Lorentz and polarization factors were taken into account using a modified Lu-procedure (Löfgren, 1960) and an approximate correction for absorption was made, for which the crystal was assumed to be a cylindrical rod ($\mu r \approx 0{\cdot}9$). In this way the structure factors of 1095 independent reflexions were obtained.

4. Determination of the structure

Since the general positions are eightfold and the special positions fourfold in the space group $C2/c$, the four tin atoms were placed in

$$4(e) = \pm(0, y, \tfrac{1}{4};\ \tfrac{1}{2}, \tfrac{1}{2}+y, \tfrac{1}{4})$$

and the other atoms in

$$8(f) = \pm(x, y, z;\ \bar{x}, y, \tfrac{1}{2}-z;\ \tfrac{1}{2}+x, \tfrac{1}{2}+y, z;\ \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}-z)\,.$$

From the Harker line $P(0, y, \frac{1}{2})$, the Harker section $P(x, 0, z)$ and the section $P(x, \frac{1}{4}, z)$, the tin and the selenium parameters were determined. From a three-dimensional Patterson synthesis, together with electron-density projections along the a and b axis, the chlorine positions were obtained. The complete set of vectors between the tin, selenium and chlorine atoms were identified in the Patterson function. All these calculations were made on the Hägg–Laurent (1946) machine.

From the parameters obtained, a three-dimensional electron-density function was calculated, from which the oxygen positions could be determined. The resulting parameters led to an improvement in the reliability index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for all observed reflexions from 0·25 to 0·17. All structure factors and three-dimensional electron-density functions were calculated on the electronic computer BESK in Stockholm. (The author is indebted to Mr S. Westman and Mr S. Åsbrink for the use of their programmes. The atomic scattering factors were evaluated by a two-term expansion of Gaussian functions, with constants given by Vand *et al.* (1957).

5. Refinement and accuracy of determination

A three-dimensional electron-density calculation with all signs determined gave new coordinates, which were refined by successive three-dimensional back-shift corrections (Booth, 1946). The temperature factors used were assumed to be isotropic and equal for all atoms. After each calculation of the structure factors the scale factor and the temperature factor were determined by comparison of the calculated and observed structure factors. Before the first back-shift correction, ln F_o/F_c was plotted against the calculated intensity giving a straight line. The linear variation of ln F_o/F_c was assumed to depend mainly on secondary extinction (Vand, 1955), and the correction was applied to the calculated F-values. After the second cycle the shifts were smaller than the standard deviation and further refinements were not made. The standard deviation in the final coordinates due to experimental errors in the structure factors were calculated by the method proposed by Cruickshank (1949).

Table 1. *Final atomic parameters and their standard deviations*

Atom	x	y	z	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
Sn	0·0000	0·7988	0·2500	—	0·0014	—
Se	0·1566	0·0638	0·3695	0·0024	0·0022	0·0026
Cl_1	0·4372	0·7408	0·0703	0·0064	0·0056	0·0066
Cl_2	0·2633	0·4468	0·0218	0·0065	0·0057	0·0063
Cl_3	0·2591	0·8346	0·2571	0·0061	0·0054	0·0059
Cl_4	0·0092	0·3652	0·8616	0·0057	0·0057	0·0065
O	0·5013	0·4722	0·1646	0·0134	0·0138	0·0180

The final parameters and their standard deviations are listed in Table 1. Using a temperature factor of 2·21 Å^2, the reliability index for all observed reflexions is 0·14 after the last cycle. (A copy of the observed and calculated F-values after the final back-shift correction can be obtained upon request.)

6. Description and discussion of the structure

A drawing of the final structure is shown in Fig. 1. Table 2 contains bond lengths, bond angles and their standard deviations calculated according to Cruickshank & Robertson (1953). The unit cell seen along the monoclinic axis is given in Fig. 2 and all intermolecular distances smaller than 4·0 Å are collected in Table 3.

In this structure, the acceptor atom, tin, has changed its coordination from a tetrahedron to a distorted octahedron by accepting two oxygen atoms, situated

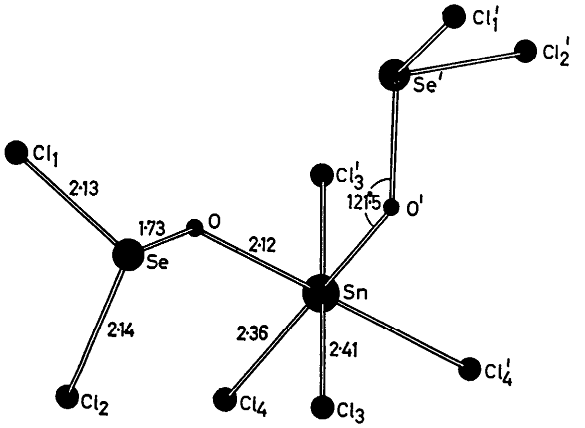

Fig. 1. The molecule of the addition compound $SnCl_4.2SeOCl_2$. All distances given in Å.

in *cis* position. The two selenium oxychlorides are related to each other by the twofold axis on which the tin atom is placed. Thus in this compound as in $SbCl_5.POCl_3$ (Lindqvist & Brändén, 1959) oxygen functions as a donor atom.

By the rearrangement around tin the Sn–Cl distances have changed from 2·31 Å in the free molecule (Livingstone & Rao, 1959) to 2·36 Å and 2·41 Å in the addition compound, distances corresponding to those found in tin hexachloro complexes, e.g. 2·41 Å in $(NH_4)_2SnCl_6$ and 2·39 Å in Tl_2SnCl_6 (Engel, 1935). The observed bond length Sn–O, 2·12 Å, agrees with the calculated sum of the covalent radii, 2·11 Å, when using the octahedral covalent radius for tin. (All covalent radii used in this paper are taken from Pauling, 1948). This shows that the donor-acceptor interaction is rather strong.

Table 2. *Bond lengths and bond angles in* $SnCl_4.2SeOCl_2$ *and their standard deviations*

(cf. Fig. 1)

	Distance	σ		Angle	σ
Sn–Cl$_4$	2·360 Å	0·007 Å	Cl$_4$–Sn–Cl$_4'$	100·1°	0·2°
Sn–Cl$_3$	2·409	0·006	Cl$_4$–Sn–Cl$_3$	95·1	0·2
Sn–O	2·121	0·016	Cl$_4$–Sn–Cl$_3'$	95·0	0·2
Se–O	1·731	0·017	Cl$_4$–Sn–O	89·1	0·5
Se-Cl$_1$	2·132	0·008	Cl$_4$–Sn–O'	170·6	0·5
Se-Cl$_2$	2·141	0·009	Cl$_3$–Sn–Cl$_3'$	164·2	0·2
			Cl$_3$–Sn–O	86·2	0·4
			Cl$_3$–Sn–O'	81·9	0·4
			O'–Sn–O	81·9	0·6
			Se–O–Sn	121·5	0·9
			Cl$_2$–Se–Cl$_1$	97·6	0·3
			O–Se–Cl$_1$	98·9	0·6
			O–Se–Cl$_2$	103·3	0·6

The oxygen and the two chlorine atoms around the selenium atom form a distorted pyramid. If it is assumed that no drastic change of the arrangement of the donor molecule takes place at the adduct formation, the present study shows that selenium oxychloride has a pyramidal structure. Some evidence for this structure has been given by Gerding (1941).

The two Se–Cl bond distances (2·13 and 2·14 Å) are equal within experimental error and there is no significant difference from a normal single covalent bond (2·16 Å). These Se–Cl bond lengths are much smaller than the shortest found in $SeOCl_2.2C_6H_5N$, 2·38 Å (Lindqvist & Nahringbauer, 1959), in which compound selenium has a tetragonal-pyramidal configuration. The difference in bond lengths may be ascribed to the higher coordination of selenium (cf. the Se–Cl distances in selenium hexachloro complexes, 2·38 Å, in $(NH_4)_2SeCl_6$ (Engel, 1935)).

The Se–O distance of 1·73 Å lies between that for a single covalent bond length, 1·83 Å, and that for a double-bond length, 1·62 Å. From infrared spectra Sheldon & Tyree (1959) deduced a weakening in the Se–O bond due to the adduct formation. This effect might explain the difference between the Se–O distance in $SeOCl_2.2C_6H_5N$, 1·59 Å, and the present compound. But compared with the small change of the P–O bond length in the formation of $SbCl_5.POCl_3$, this difference seems too large. The knowledge of the Se–O distance in solid selenium oxychloride seems therefore desirable before any detailed discussion can be made. For comparison, the Se–O distance found in crystals of SeO_2: 1·76 Å (McCullough, 1937), H_2SeO_3: 1·74 Å (Wells & Bailey, 1949) and of $C_6H_5SeO_2H$: 1·71 and 1·77 Å (Bryden & McCullough, 1954) can be mentioned. The difference in the Se–O bond lengths in the last compound is significant and is caused by one of the oxygen atoms forming a hydrogen bond. In all these compounds selenium has a pyramidal configuration.

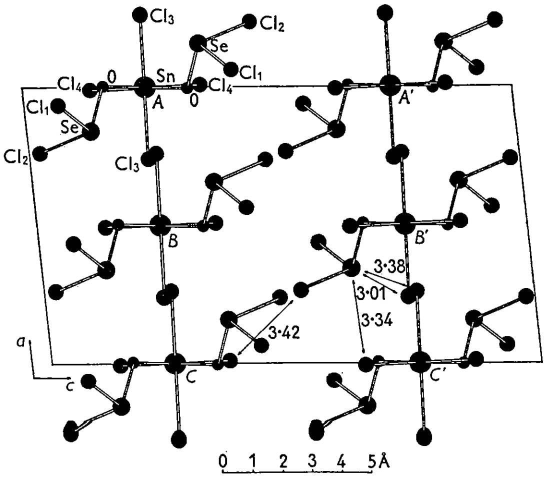

Fig. 2. The structure of $SnCl_4.2SeOCl_2$ viewed down the monoclinic axis. All distances given in Å.

The shortness of the distance Se–Cl$_3$, 3·01 Å, (see Fig. 2) suggests that $SeOCl_2$ also has a tendency to function as an acceptor molecule. The Sn–Cl$_3$ distance should therefore be elongated, and this is actually confirmed. Thus in this compound selenium oxychloride acts both as a donor and as an acceptor molecule, although the donor action is predominant. In $SeOCl_2.2\,C_6H_5N$, on the other hand, selenium oxychloride functions predominantly as an acceptor molecule with very weak donor properties (chloride ion donation).

Table 3. *Intermolecular distances smaller than* 4·0 Å (cf. Fig. 2)

Se–Cl	$Se(B')-Cl_3(C')$	= 3·38 Å
	$Se(B')-Cl_4(C')$	= 3·34
Cl : Cl	$Cl_1(B)-Cl_2(A')$	= 3·67 Å
	$Cl_1(B)-Cl_3(A)$	= 3·70
	$Cl_1(B)-Cl_4(B)$	= 3·82
	$Cl_1(B)-Cl_3(C)$	= 3·87
	$Cl_1(B)-Cl_2(C)$	= 3·71
	$Cl_1(B)-Cl_2(B')$	= 3·70
	$Cl_1(B)-Cl_4(B')$	= 3·70
	$Cl_2(B')-Cl_2(C)$	= 3·71
	$Cl_2(B')-Cl_4(C)$	= 3·42
	$Cl_2(B')-Cl_4(C')$	= 3·72
	$Cl_3(C)-Cl_4(B)$	= 3·89
Cl : O	$Cl_2(B')-O(B)$	= 3·97 Å

The angle Sn–O–Se of 121·5° can be compared with the Sb–O–P angle in $SbCl_5.POCl_3$ of 143·7°. The change might partly be correlated with the difference in electronegativity between selenium and phosphorus; tin and antimony are comparable (cf. Gillespie & Nyholm, 1957). It should be noted, however, that the interaction Se-Cl_3 must also have the effect of diminishing the Sn–O–Se angle.

From Table 3, giving packing distances, two relatively short distances (3·38 and 3·34 Å) between atoms in adjacent molecules are found, namely that of $Se(B')-Cl_3(C')$ and $Se(B')-Cl_4(C')$, (see Fig. 2). The sum of the van der Waals radii is 3·80 Å. These two chlorine atoms together with the chlorine atom (Cl_3) from the $SnCl_4$-part of the molecule give rise to hexacoordination around the selenium atom. Such a completion to a distorted octahedron by the next nearest neighbours is also found in SeO_2, H_2SeO_3 and $SeOCl_2.2\,C_6H_5N$ (see Fig. 3).

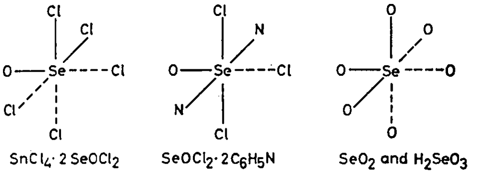

Fig. 3. A schematic drawing of the completion to a distorted octahedron around a selenium atom by the next nearest neighbours, denoted by broken lines.

The other packing distances have reasonable values. One Cl–Cl distance is rather short, 3·42 Å (see Fig. 2), but the same van der Waals distance between chlorine atoms has been found in $SbCl_5.POCl_3$ and a shorter one in solid Cl_2 (Collin, 1952).

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