The Crystal Structure of (CH₃)₄NCl·5SeOCl₂

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The crystal structure of $(CH_9)_4NCl.5SeOCl_9$ has been determined and refined from three-dimensional X-ray data. The crystals are monoclinic (space group $P2_1/n$), and there are four molecules in the unit cell of dimensions:

 $a = 15.540 \text{ Å}, b = 10.845 \text{ Å}, c = 16.550 \text{ Å} \text{ and } \beta = 95^{\circ}32'.$

The structure consists of discrete tetramethylammonium ions and solvated chloride ions. Each anion is octahedrally surrounded by six SeOCl₂ molecules, two of which are shared by an adjacent octahedron. One of these molecules, with a Cl⁻...Se distance of 4.02 Å, is much more remote than the other five, which have Cl⁻...Se distances ranging between 2.93 Å and 3.09 Å.

In a study concerning the coordination in complexes of the strongly ionizing non-aqueous solvent seleninyldichloride, SeOCl₂, the structures of two molecular addition compounds, SnCl₄·2SeOCl₂ and SbCl₅·SeOCl₂, have been reported previously.^{1,2} The present investigation includes the structure determination of an ionic complex formed between tetramethylammonium chloride and seleninyldichloride. Such a study might give information pertinent to the interaction between the SeOCl₂ molecule and the chloride ion in solutions, since the reaction SeOCl₂ = SeOCl⁺ (solvent) + Cl⁻ (solvent) occurs according to the self-ionization theory.

In the system $(CH_3)_4NCl-SeOCl_2$ three intermediate phases occur:³ $(CH_3)_4NCl\cdot 2SeOCl_2$, $(CH_3)_4NCl\cdot 3SeOCl_2$, and $(CH_3)_4NCl\cdot 5SeOCl_2$. As no suitable crystals of the first two compounds could be obtained it was only possible to make an X-ray study of the last one. The structure determination of $(CH_3)_4NCl\cdot 5SeOCl_2$ was undertaken from three-dimensional single-crystal diffraction data.

EXPERIMENTAL

The solid solvate $(CH_3)_4NCl.5SeOCl_2$ was prepared by cooling a heated mixture of $(CH_3)_4NCl$ and $SeOCl_2$ in the mole ratio 1:5. Attempts to get crystals of the 1:2 and 1:3 compounds in a similar manner were unsuccessful. The compounds are very rapidly hydrolyzed unless kept in closed and dried vessels. For this reason single crystals of $(CH_3)_4NCl.5SeOCl_2$ were made in thin-walled glass capillaries according to a method described in a previous paper. The melting point of the crystals, $+45^{\circ}C$, was in close

agreement with the value $+45^{\circ}$ to $+47^{\circ}$ C previously reported. The diameter of the glass capillaries was about 0.10 mm, and the wall thickness 0.01-0.03 mm. The cylindrical single crystal used for collecting intensity data had a diameter of 0.070 mm, and for the determination of the cell parameters a single crystal with a diameter of about 0.080 mm was used.

With the crystal rotating about the c axis, equi-inclination Weissenberg photographs of the zones $0 \le l \le 11$ were recorded with CuK radiation. The relative intensities were estimated visually by the multiple-film technique (four films) using a calibrated intensity scale obtained from one of the reflexions from the same crystal. 2129 independent reflexions were measured within an intensity range 1 to 5210. The data were corrected for the Lorentz and polarization effects. Corrections for absorption were not applied ($\mu R = 0.65$). The rotation axis and the capillary axis were not coincident. The interlayer scaling was carried out by the least squares refinement described below. The X-ray photographs indicated that the crystals used were stable during the time of exposure.

UNIT CELL AND SPACE GROUP

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

$$a = 15.540 \pm 0.025 \text{ Å}$$

 $b = 10.845 \pm 0.010 \text{ Å}$
 $c = 16.550 \pm 0.015 \text{ Å}$
 $\beta = 95^{\circ}32' \pm 5'$

The rotation axis c, the b axis, and the reciprocal cell element a^* were determined from quartz-calibrated rotation and zero-layer Weissenberg photographs. The angle β was determined from higher layer lines by the method of angular lag.⁴ Quartz was also used in this case as the calibration substance $(a = 4.913 \text{ Å}, c = 5.405 \text{ Å} \text{ for } \alpha\text{-quartz}, \lambda \text{ (Cu}K\alpha_1) = 1.54051 \text{ Å}, \lambda \text{ (Cu}K\alpha_2) = 1.54433 \text{ Å}, \lambda \text{ (Cu}K\beta_1) = 1.39217 \text{ Å}. I am indebted to Mr. P. Nes for help with the determination of the cell parameters).$

The only systematic absences observed were h0l for h+l odd and 0k0 for k odd. The space group was accordingly taken to be $P2_1/n$ on the assumption that these are space group extinctions. The density calculated on the basis of four molecules $(CH_3)_4NCl\cdot 5SeOCl_2$ per unit cell is $2.25~g\cdot cm^{-3}$ in agreement with the density observed, $2.22~g\cdot cm^{-3}$. This value was obtained from the volume and the weight of a homogeneous crystal in a cylindrical capillary of uniform thickness. The volume was measured with a microscope, the weight being known from the preparation.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

Assuming the space group to be $P2_1/n$, the diffraction and density data indicate that the atoms are in the general 4-fold positions: (x,y,z); $(\bar{x},\bar{y},\bar{z})$; (1/2-x,1/2+y,1/2-z); (1/2+x,1/2-y,1/2+z). This gives 78 positional parameters to be determined, corresponding to five selenium, eleven chlorine, five oxygen, one nitrogen, and four carbon atoms in the asymmetric unit (the hydrogen atoms being neglected). The positional parameters of the five selenium atoms were approximately derived from a three-dimensional Patterson synthesis calculated on a modified Hägg-Laurent machine. Starting from these coordinates it was possible to locate the eleven chlorine atoms by means

of successive three-dimensional electron density calculations. After the last Fourier synthesis the signs of 1779 observed reflexions were determined. A three-dimensional difference synthesis with $(F_{\rm o}-F_{\rm Se}-F_{\rm Cl})$ as Fourier coefficients was computed. From this calculation it was possible to assign approximate coordinates to the nitrogen atom, the five oxygen atoms and the four carbon atoms. At this stage the signs were determined for all the structure factors.

To obtain more accurate parameters, particularly for the lightest atoms, a new set of three-dimensional Fourier syntheses was calculated. The syntheses were as follows: an observed and a calculated electron density map for obtaining back-shift corrections for the selenium and the chlorine atoms, and a difference map for refining positional parameters of the nitrogen, oxygen and the carbon atoms. The discrepancy index R after these improvements was 0.21 $(R = \sum ||F_o| - |F_c||/\sum |F_o|$; all R values in this paper are based on observed reflexions only). These Fourier calculations were made on the electronic computer BESK in Stockholm using the programs designated SNUSKMUS and SUPERMUS written by Asbrink $et\ al.^6$,7

The atomic parameters were then further refined by the method of least squares. The first series of these calculations was made on the computer FACIT EDB with a program (SFLS) devised by Åsbrink and Brändén,8 which minimizes the function $\sum w(|F_o|-|F_c|)^2$ and uses a block-diagonal approximation. The weights w were calculated according to an equation $w=1/(a+|F_o|+c|F_o|^2)$ suggested by Cruickshank et al.9 The final values for these constants were a=34, c=0.0050. Reflexions too weak to be observed were given zero weight. The 116 parameters to be refined were atomic coordinates, individual isotropic temperature factors and twelve scale factors, one for each layer line. After about fifteen cycles of refinement the shifts for all the parameters were less than one tenth of their standard deviations. During the last cycles, fifteen reflexions affected by extinction, or lying at the film edges, or otherwise uncertain were omitted. The R factor then decreased to 0.099.

The second series of least squares refinements was carried out on a CD 3600 computer using a full matrix program LALS written by Gantzel, Sparks and Trueblood ¹⁰ and modified by Zalkin, Berkeley, and by Brändén, Liminga, and Lundgren in Uppsala. The previous weighting scheme was used. After two cycles no parameter shift exceeded one seventh of the respective standard deviation. The R value showed an insignificant decrease to the value 0.098. No significant deviations in the final parameters compared to those given in the last SFLS refinement were found. In the second series of refinements the same structure factors as previously were omitted. This did not significantly alter the atomic coordinates.² The R value for all 2129 observed reflexions was 0.102.

The final atomic parameters obtained from the last LALS cycle are listed in Table 1. An analysis of the weighting scheme for this cycle is given in Table 2. Observed and calculated structure factors are presented in Table 3.

The correctness of the final structure was substantiated by calculating three-dimensional $(F_{\rm o}-F_{\rm c})$ and $F_{\rm o}$ syntheses at points spaced at intervals less than 0.35 Å throughout the asymmetric part of the unit cell. The largest

Table 1. Final atomic parameters and their standard deviations.

Atom	\boldsymbol{x}	$oldsymbol{y}$	$oldsymbol{z}$	$B~{ m \AA}^2$	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$ Å ²
Se(1)	0.6823	0.4634	0.6864	4.40	0.0002	0.0003	0.0002	0.07
Se(2)	0.2998	0.4672	0.5525	3.47	0.0002	0.0002	0.0002	0.06
$\mathbf{Se}(3)$	0.4791	0.6070	0.7762	3.34	0.0002	0.0002	0.0002	0.06
Se(4)	0.4330	0.2370	0.7987	4.31	0.0002	0.0003	0.0002	0.07
Se(5)	0.5151	0.3034	0.4871	2.90	0.0002	0.0002	0.0002	0.05
Cl(1)	0.6596	0.2823	0.7367	6.60	0.0006	0.0008	0.0006	0.20
Cl(2)	0.8242	0.4529	0.7092	7.37	0.0006	0.0009	0.0007	0.22
Cl(3)	0.2648	0.3289	0.6406	7.04	0.0006	0.0009	0.0006	0.21
Cl(4)	0.1667	0.5266	0.5154	6.94	0.0006	0.0009	0.0006	0.21
Cl(5)	0.4918	0.7571	0.8673	$\bf 5.22$	0.0005	0.0007	0.0005	0.16
Cl(6)	0.3409	0.6384	0.7387	5.63	0.0005	0.0007	0.0005	0.17
Cl(7)	0.4156	0.0474	0.7587	7.28	0.0006	0.0009	0.0006	0.22
Cl(8)	0.5203	0.1949	0.9051	7.11	0.0006	0.0009	0.0006	0.22
Cl(9)	0.4918	0.1854	0.3762	5.49	0.0005	0.0007	0.0005	0.17
Cl(10)	0.4893	0.1504	0.5705	5.11	0.0005	0.0007	0.0005	0.15
Cl(11)	0.4889	0.4695	0.6221	3.65	0.0004	0.0005	0.0004	0.12
O(1)	0.6582	0.5560	0.7555	5.85	0.0013	0.0019	0.0014	0.47
O(2)	0.3226	0.3893	0.4773	4.93	0.0012	0.0017	0.0013	0.40
O(3)	0.4795	0.4891	0.8322	5.67	0.0013	0.0018	0.0014	0.47
O(4)	0.3475	0.2668	0.8380	7.38	0.0016	0.0022	0.0016	0.58
O(5)	0.6192	0.3151	0.5002	4.35	0.0011	0.0016	0.0012	0.38
\mathbf{N}	0.2249	-0.0159	0.4965	3.28	0.0013	0.0017	0.0013	0.40
C(1)	0.2789	-0.0294	0.5736	6.44	$\boldsymbol{0.0022}$	0.0033	0.0023	0.80
C(2)	0.1330	0.0388	0.5064	9.16	0.0029	0.0042	0.0029	1.14
C(3)	0.2725	0.0581	0.4414	10.36	0.0032	0.0046	0.0032	1.32
C(4)	0.2083	-0.1446	0.4641	8.09	0.0026	0.0038	0.0026	1.00

Table 2. Final weight analysis.

$\begin{array}{c} \text{Interval} \\ \sin \theta \end{array}$	Number of reflexions	$w \Delta^2$ (normalized)	$\begin{matrix} \text{Interval} \\ F_{\mathbf{o}} \end{matrix}$	Number of reflexions	$w \Delta^2$ (normalized)
0.00 - 0.46	526	1.06	0- 28	213	1.08
0.46 - 0.58	465	1.02	28 - 33	209	0.93
0.58 - 0.67	348	0.89	33 - 38	212	1.12
0.67 - 0.74	247	1.09	38-43	211	1.13
0.74 - 0.79	171	0.71	43 - 50	214	1.08
0.79 - 0.84	146	0.77	50 - 59	209	0.96
0.84 - 0.89	122	0.68	59 - 72	211	1.04
0.89 - 0.93	56	0.82	72 - 90	212	0.84
0.93 - 0.97	27	1.11	90 - 127	211	0.87
0.97 - 1.00	6	1.85	127 - 463	$\frac{1}{212}$	0.97

maximum and minimum values of the difference Fourier were less than one half of the carbon peaks in the $F_{\rm o}$ synthesis. Chemical considerations excluded all the positions for these maxima as possible atomic sites with the reservation that in some cases they could be hydrogen atoms. The maximum value of the difference function was furthermore only 3.1 % of the largest electron density value. The Fourier calculations were performed on the computer FACIT EDB using the programs designated STRIX and PROFFS written by Liminga and Olovsson. 11

Table 3. Observed and calculated structure factors. Reflexions marked with an asterisk were omitted during the last cycles of refinement. These reflexions were strongly affected by extinction, lay at the edges of the film, or were otherwise uncertain.

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Table 3. Continued.

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Table	2	Continued.
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The atomic scattering factors used in the LALS calculations were those given in the *International Tables*, Vol. III p. 202, corrected for the real part $\Delta f'$ of the anomalous scattering (*International Tables*, Vol. III p. 214). For the negatively charged chlorine atom, Cl(11), the scattering factor for Cl⁻ was taken. The other atoms were considered as neutral atoms. In all previous calculations the following f values for neutral atoms were used: Se, Thomas and Umeda; Cl, Tomiie and Stam; O, N, and C, Berghuis $et\ al.$

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of $(CH_3)_4NCl\cdot 5SeOCl_2$ is shown in Fig. 1. Bond lengths, bond angles, and intermolecular contacts are given in Tables 4—8 and Figs.

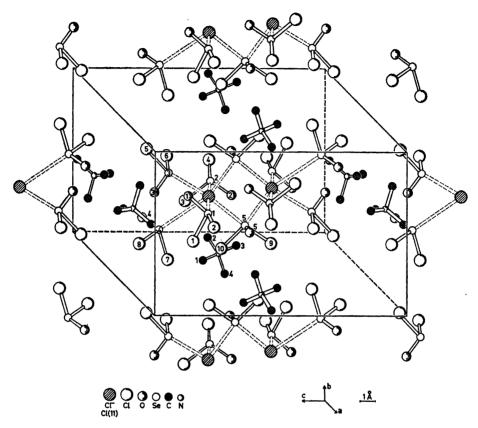


Fig. 1. The crystal structure of $(CH_3)_4NCl-5SeOCl_2$. For clarity only parts of the cell content are shown. The glide plane operation has been omitted. Double dashed lines indicate weak ion-dipole interactions.

2, 4, and 5. These distances and angles are based on the atomic parameters listed in Table 1 and were calculated using the program DISTAN devised by Zalkin *et al*. The standard deviations of the distances and angles were computed from the errors of atomic coordinates and cell-dimensions. The influence of the errors in the cell-dimensions was insignificant.

As indicated in Fig. 1 the structure is composed of discrete tetramethyl-ammonium ions and chloride ions surrounded by six seleninyldichloride molecules with the selenium atoms at the corners of a somewhat distorted octahedron. In accordance with the SeOCl₂:Cl⁻ ratio of 5:1, two of these molecules are common to an adjacent Cl(SeOCl₂)₆ octahedron. In the resulting binuclear complex ion Cl₂(SeOCl₂)₁₀²⁻, the two halves are related by a symmetry center (Fig. 2). This picture of an ion-solvent dipole interaction is consistent with the Se···Cl⁻ distances. Five of these distances are rather short (Fig. 2), being about midway between that for the sum of normal covalent

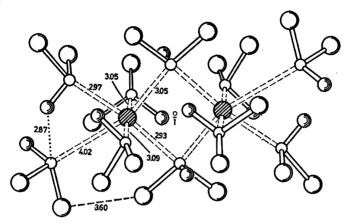


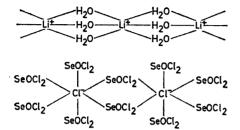
Fig. 2. The arrangement of SeOCl₂ molecules around chloride ions in $(CH_3)_4NCl.5SeOCl_2$. The orientation and notation of the atoms is the same as in Fig. 1.

radii (2.2 Å), and the normal van der Waals distance (3.8 Å). The sixth distance, Se(4)···Cl⁻, however, is much longer (4.02 Å) than the others. The main cause of this lengthening is probably the intermolecular interaction between this selenium atom and an oxygen atom bound to a neighbouring molecule (cf. the discussion below) and, to a lesser extent, a chlorine-chlorine repulsion (see Fig. 2). Taking into account the orientation of the sixth seleninyldichloride molecule and the disposition of neighbouring groups around it, there is no reason why it should not be considered as coordinated to the chloride ion. The present structure thus exhibits an example of a solvated anion.

As may be expected the tetramethylammonium ion does not seem to be solvated since the distances from the methyl groups to the chlorine and oxygen atoms are comparable with the corresponding sums of the van der Waals radii (3.8 Å and 3.4 Å, respectively). The shortest C···Cl distance is 3.65 Å and the shortest C···O distance 3.26 Å (cf. Table 8). Thus the structure may be described as composed of solvated anions of composition $\text{Cl}_2(\text{SeOCl}_2)_{10}^{2-}$ and $(\text{CH}_3)_4\text{N}^+$ cations situated in holes between the dimeric anions. The positions of these groups in the unit cell are shown in Fig. 1.

The arrangement of solvent molecules around the anion in the present structure can be compared with that of cations in hydrates, in particular those hydrates for which the oxygen coordination number is greater than the available number of water molecules, e.g. LiClO₄·3H₂O. In this case the Li⁺—H₂O chains ¹⁵ are analogous to the Cl⁻—SeOCl₂ dimer (Fig. 3).

The conditions for neutral molecules to be incorporated in an ionic crystal structure depend primarily upon the polarity and the size of the molecules. The most common examples are the molecules of water and ammonia on account of their smallness and large dipole moments. However, the present structure illustrates that even quite large molecules can be incorporated. This unusual situation probably also exists in the structure of KF.4SbF₃ ¹⁶ in view of the large difference between the two types of Sb—F distances (2.0 and 2.9 Å).



*Fig. 3. Comparison of ion-solvent interactions in LiClO₄·3H₂O and (CH₃)₄NCl·5SeOCl₂.

An analysis of the individual bond lengths and bond angles in the five SeOCl₂ molecules shows no significant differences between distances of the same type with the possible exception of the Se(5)—Cl(9) distance, which exceeds the average by an amount about four times the standard deviation (Table 4). The average values of bond lengths and bond angles are: Se—Cl 2.198 Å, Se—O 1.586 Å, Cl—Se—Cl 95.0°, and Cl—Se—O 102.9°. In comparison with the dimensions found in the molecular complexes SnCl₄·2SeOCl₂¹ and SbCl₅·SeOCl₂² these values differ significantly, which is to be expected in view of the weaker bonding of the SeOCl₂ groups in the present structure. Thus the Se—Cl bond length of 2.198 Å is greater than the distances reported in the addition compounds, 2.14 Å and 2.12 Å, respectively. The shortness of the Se—O bond length, 1.586 Å, suggests a more pronounced double bond character in (CH₃)₄NCl·5SeOCl₂. This also agrees with the increase in the Cl—Se—O angle. Nearly the same Se—O distance, 1.59 Å, has been found in SeOCl₂·2C₅H₅N ¹⁷ and in the tetragonal form of SeO₃, ¹⁸ 1.54 Å and 1.56 Å for

Table 4. Bond distances and bond angles with standard deviations within the five SeOCl₂ molecules in (CH₃)₄NCl-5SeOCl₂.

$\begin{array}{c} {\rm Bond} \\ {\rm Se}(1) - {\rm Cl}(1) \\ {\rm Se}(1) - {\rm Cl}(2) \\ {\rm Se}(1) - {\rm O}(1) \end{array}$	$\begin{array}{c} \text{Distance (Å)} \\ 2.175 \pm 0.010 \\ 2.205 \pm 0.011 \\ 1.592 \pm 0.022 \end{array}$	$\begin{array}{c} Bonds \\ Cl(1) - Se(1) - Cl(2) \\ Cl(1) - Se(1) - O(1) \\ Cl(2) - Se(1) - O(1) \end{array}$	Angle (°) 94.8 ± 0.4 103.7 ± 0.8 102.2 ± 0.8
$\begin{array}{l} {\rm Se}(2) - {\rm Cl}(3) \\ {\rm Se}(2) - {\rm Cl}(4) \\ {\rm Se}(2) - {\rm O}(2) \end{array}$	$\begin{array}{c} 2.196 \pm 0.010 \\ 2.196 \pm 0.010 \\ 1.573 \pm 0.021 \end{array}$	$\begin{array}{c} {\rm Cl}(3) - {\rm Se}(2) - {\rm Cl}(4) \\ {\rm Cl}(3) - {\rm Se}(2) - {\rm O}(2) \\ {\rm Cl}(4) - {\rm Se}(2) - {\rm O}(2) \end{array}$	$\begin{array}{c} 95.8 \pm 0.4 \\ 104.3 \pm 0.8 \\ 102.4 \pm 0.8 \end{array}$
Se(3) - Cl(5) Se(3) - Cl(6) Se(3) - O(3)	$\begin{array}{c} \textbf{2.215} \pm 0.009 \\ \textbf{2.204} \pm 0.009 \\ \textbf{1.579} \pm 0.021 \end{array}$	Cl(5) - Se(3) - Cl(6) Cl(5) - Se(3) - O(3) Cl(6) - Se(3) - O(3)	$\begin{array}{c} 95.7 \pm 0.3 \\ 101.6 \pm 0.8 \\ 103.8 \pm 0.8 \end{array}$
$\begin{array}{l} {\rm Se}(4) - {\rm Cl}(7) \\ {\rm Se}(4) - {\rm Cl}(8) \\ {\rm Se}(4) - {\rm O}(4) \end{array}$	$\begin{array}{c} 2.169 \pm 0.010 \\ 2.166 \pm 0.011 \\ 1.568 \pm 0.025 \end{array}$	Cl(7) - Se(4) - Cl(8) Cl(7) - Se(4) - O(4) Cl(8) - Se(4) - O(4)	$\begin{array}{c} 95.6 \pm 0.4 \\ 103.7 \pm 0.9 \\ 101.3 \pm 1.0 \end{array}$
$\begin{array}{l} {\rm Se}(5) - {\rm Cl}(9) \\ {\rm Se}(5) - {\rm Cl}(10) \\ {\rm Se}(5) - {\rm O}(5) \end{array}$	$egin{array}{l} 2.238\ \pm\ 0.009\ 2.219\ \pm\ 0.008\ 1.617\ \pm\ 0.018 \end{array}$	Cl(9) - Se(5) - Cl(10) Cl(9) - Se(5) - O(5) Cl(10) - Se(5) - O(5)	$\begin{array}{c} 93.3 \ \pm \ 0.3 \\ 103.6 \ \pm \ 0.7 \\ 102.3 \ \pm \ 0.7 \end{array}$
Mean values	Se-Cl = 2.198 Se-O = 1.586	Cl-Se-Cl = 95.0 Cl-Se-O = 102.9	

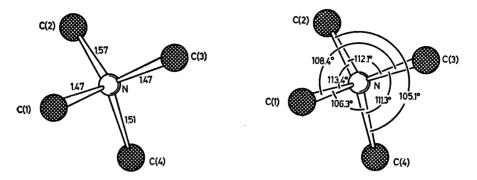


Fig. 4. Bond distances and bond angles within the tetramethylammonium ion.

the non-bridging oxygen atoms. The π -bond order for these Se—O bonds in the last compound has been calculated by Mijlhoff ¹⁸ to be 0.78. In this connection it may be of interest to mention that the Se—O distances for the bridging oxygen atoms in SeO₃ are closer to the reported Se—O values in SnCl₄·2SeOCl₂ and SbCl₅·SeOCl₂. According to the picture of SeOCl₂ molecules bound only by weak ion-dipole interaction it is not inconceivable that the molecular dimensions in solid SeOCl₂, the detailed structure of which is unknown, should be rather close to those reported here.

The tetramethylammonium ion forms an almost regular tetrahedron (Table 5, Fig. 4), the average value of the C—N bond distances is 1.51 Å. The deviations of the individual C—N—C bond angles from the ideal tetrahedral value are insignificant. The mean bond angle of 109.4° is close to the tetrahedral value. The average values are furthermore in agreement with those reported for other tetramethylammonium compounds, e.g. in $[(CH_3)_4N]_2ZnCl_4$, ¹⁹ 1.55 Å and 109.4°, and in $(CH_3)_4NClO_4$, ²⁰ 1.47 Å and 109.4°.

Another feature of the structure worth mentioning is the occurrence of an interaction between different SeOCl₂ molecules through Se···O contacts. The five Se···O distances are 3.14, 2.85, 2.89, 2.87, and 3.12 Å (Fig. 5, Table 6), which is considerably less than corresponding van der Waals distances (3.4 Å). This seleninyl-bridging may be a further case of an intermolecular bonding between solvent molecules of the same type as has been reported in solid

Table 5. Bond distances and bond angles with standard deviations within the N(CH₃)₄⁺ ion.

Bond	Distance (Å)	${f Bonds}$	Angle (°)
N-C(1) N-C(2)	$1.47 \pm 0.04 \\ 1.57 + 0.05$	C(1) - N - C(2) C(1) - N - C(3)	113.4 ± 2.6 $108.4 + 2.7$
N-C(3)	1.47 ± 0.06	C(1)-N-C(4)	$106.3~\pm~2.4$
N-C(4)	1.51 ± 0.05	$C(2)-N-C(3) \ C(2)-N-C(4)$	$112.1 \pm 2.9 \\ 105.1 \pm 2.5$
Mean value	1.51	C(3)-N-C(4)	$\frac{111.3 \pm 2.9}{100.4}$
		Mean value	109.4

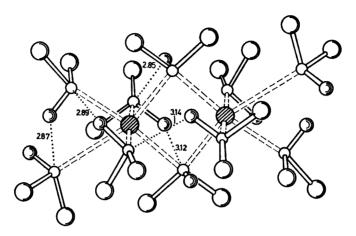


Fig. 5. The Se...O linking in (CH₃)₄NCl-5SeOCl₂. The orientation and notation of the atoms is the same as in Fig. 1.

 $POCl_3^{24}$ Similar short distances have been found in SeO_2^{21} (2.63, 3.00, and 3.00 Å), in $H_2SeO_3^{22}$ (3.00, 3.08, and 3.09 Å) and in $C_6H_5SeO_2H^{23}$ (3.17 Å). No further intermolecular interactions within the $Cl_2(SeOCl_2)_{10}^{2-}$ unit seem to occur. Table 6 gives all such distances, which are less than the appropriate sum of respective van der Waals radii.

The interionic packing involves Cl···Cl, Cl···O, CH₃···Cl, and CH₃···O contacts. The observed distances are listed in Tables 7 and 8 and may be compared with the corresponding sum of the van der Waals radii 3.6, 3.2, 3.8, and 3.4 Å, respectively. The smallest Cl···Cl distance is 3.40 Å and similar short intermolecular contacts have been found in other compounds. The shortness of some CH₃···O distances (3.26 and 3.38 Å) may be due to a movement of the hydrogen atoms out of the line of the contact through rotation about the C–N bond. In $(CH_3)_4NClO_4$ a CH_3 ···O distance of 3.04 Å has been found.²⁰

Table 6. Short intermolecular distances within a Cl₂(SeOCl₂)₁₀²⁻ unit. Only distances shorter than the corresponding van der Waals distances are included.

Contact	Distance (Å)	Contact	Distance (Å)
Se(1)Cl(11)	3.091 ± 0.008	Se(1)O(2)A	3.140 ± 0.021
Se(2)Cl(6)	3.601 + 0.010	Se(2)O(5)A	2.852 ± 0.018
Se(2)Cl(11)	3.052 + 0.008	$\mathbf{Se(3)}\mathbf{O(1)}$	2.891 ± 0.021
Se(3)Cl(9)A	3.443 + 0.009	$\mathbf{Se}(4)\mathbf{O}(3)$	2.868 ± 0.021
Se(3)Cl(11)	$2.972 \ -0.008$	Se(5)O(2)	3.122 ± 0.019
Se(4)Cl(1)	3.794 + 0.011	, , , , ,	
Se(4)Cl(3)	3.653 ± 0.011	Se(1)Se(3)	3.938 ± 0.006
Se(5)Cl(11)	2.928 + 0.007	Se(2)Se(5)A	3.907 ± 0.005
Se(5)Cl(11)A	3.051 + 0.007	, , , , ,	
, , , , , , , , , , , , , , , , , , , ,		Cl(7)Cl(10)	3.598 ± 0.013
		Cl(10)Cl(11)	3.564 ± 0.010

A denotes a molecule with the atomic coordinates in 1-x, 1-y, 1-z.

Table 7. Intermolecular distances less than 4.0 Å between the $\text{Cl}_2(\text{SeOCl}_2)_{10}^{2-}$ units. Distances are given between the reference molecule of which the atomic coordinates are given in Table 1, and surrounding molecules designated as follows:

B: C: D: E: F: G: H: I:	$x \\ 1-x \\ 1-x \\ 1/2+x \\ 1/2-x \\ 1/2-x \\ 3/2-x \\ x-1/2$	1+y $-y$ $1-y$ $1/2-y$ $1/2+y$ $y-1/2$ $y-1/2$ $1/2-y$	$ \begin{array}{c} z \\ -z \\ 2-z \\ 1/2+z \\ 3/2-z \\ 3/2-z \\ 3/2-z \\ z-1/2 \end{array} $
Contact	Distance (Å)	Contact	Distance (Å)
Cl(1)Cl(2)H	3.69	Cl(5)Cl(8)D	3.83
Cl(2)Cl(5)H	3.87	Cl(7)Cl(9)C	3.75
Cl(2)Cl(9)E	3.91	Cl(9)Cl(10)C	3.75
Cl(3)Cl(6)G	3.40	` ' ` '	
Cl(4)Cl(8)F	3.78	Cl(1)O(1)H	3.74
Cl(4)Cl(8)I	3.67	Cl(4)O(4)F	3.58
Cl(5)Cl(7)B	3.76	Cl(6)O(4)F	3.38
$\sigma(\text{Cl} \cdots \text{Cl}) = \pm 0$	0.02 Å	$\sigma(\text{Cl}\text{O}) = \pm 0$.03 Å

Table 8. Closest chlorine and oxygen atoms to the carbon atoms. For the symbols A etc. see Tables 6 and 7.

C(1)Cl(7)B	3.65 Å
C(2)Cl(8)I	3.70
C(3)Cl(9)	3.92
C(4)Cl(4)	3.74
C(1)O(4)F	3.38
C(2)O(3)G	3.38
C(3)O(1)I	$\bf 3.62$
C(4)O(5)A	3.26

It should be of considerable interest to compare the distance between the tetramethylammonium ion and the chloride ion found in this structure with the distance of closest approach between this cation and anion in solutions of seleninyldichloride. Such information enables predictions to be made about solute-solvent interactions existing in solutions. On account of the high dielectric constant of this solvent, it seems likely that the magnitude of this ion-pairing should be small. A high dielectric constant diminishes the electric field of an ion more rapidly than a solvent with a low dielectric constant. Unfortunately, no such data are at present available for similar solutes in $SeOCl_2$, or for solutions of $(CH_3)_4NCl$ in similar solvents. In the solvent $POCl_3$, with a rather low dielectric constant, Baaz and Gutmann ²⁵ have reported the value of 5.44 Å for $(C_2H_5)_4NCl$. In view of this result the closest distances of 6.87, 6.91, 7.04, 7.12, 7.41, and 7.77 Å between ions of opposite sign observed in the present compound are reasonable.

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REFERENCES

- Hermodsson, Y. Acta Cryst. 13 (1960) 656.
 Hermodsson, Y. Acta Chem. Scand. 21 (1967) 1313.
 Agerman, M., Andersson, L-H., Lindqvist, I. and Zackrisson, M. Acta Chem. Scand. 12 (1958) 477.

Buerger, M. J. X-Ray Crystallography, Wiley, New York 1949, p. 377.
 Lundström, T. and Klimecki, V. J. Sci. Instr. 38 (1961) 424.
 Asbrink, S., Blomqvist, G. and Westman, S. Arkiv Kemi 14 (1959) 545.
 Westman, S., Blomqvist, G. and Asbrink, S. Arkiv Kemi 14 (1959) 535.

- 8. Åsbrink, S. and Brandén, C.-I. IUCr World List of Crystallographic Computer Programs, No. 6023 FACIT.
- 9. Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. Computing Methods and the Phase Problem in X-ray Crystal Analysis, Pergamon, Oxford 1961, p. 32.

 10. Gantzel, P. K., Sparks, R. A. and Trueblood, K. N. IUCr World List of Crystallo-

graphic Computer Programs, No. 384 IBM 7090.

11. Liminga, R. and Olovsson, I. Acta Polytech. Scand. Math. Computing Mach. Ser. 10

(1964).

12. Thomas, L. H. and Umeda, K. J. Chem. Phys. 26 (1957) 293.

13. Tomiie, Y. and Stam, C. H. Acta Cryst. 11 (1958) 126.

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

15. West, C. D. Z. Krist. 88 (1934) 198.

- 16. Byström, A. and Wilhelmi, K-A. Arkiv Kemi 3 (1951) 17.
- Lindqvist, I. and Nahringbauer, G. Acta Cryst. 12 (1959) 638.
 Mijlhoff, F. C. Acta Cryst. 18 (1965) 795.

19. Morosin, B. and Lingafelter, E. C. Acta Cryst. 12 (1959) 611.

20. McCullough, J. D. Acta Cryst. 17 (1964) 1067.

- 21. McCullough, J. D. J. Am. Chem. Soc. 59 (1937) 789.
- Wells, A. F. and Bailey, M. J. Chem. Soc. 1949 1282.
 Bryden, J. H. and McCullough, J. D. Acta Cryst. 7 (1954) 833.
 Wartenberg, E. W. Proc. 8. I.C.C.C. Wien 1964, p. 325.
- 25. Baaz, M. and Gutmann, V. Monatsh. 90 (1959) 256.

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