

The Crystal Structure of $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$

YNGVE HERMODSSON

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$ 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:

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

The structure consists of discrete tetramethylammonium ions and solvated chloride ions. Each anion is octahedrally surrounded by six SeOCl_2 molecules, two of which are shared by an adjacent octahedron. One of these molecules, with a $\text{Cl}^- \cdots \text{Se}$ distance of 4.02 \AA, is much more remote than the other five, which have $\text{Cl}^- \cdots \text{Se}$ distances ranging between 2.93 \AA and 3.09 \AA.

In a study concerning the coordination in complexes of the strongly ionizing non-aqueous solvent seleninyldichloride, SeOCl_2 , the structures of two molecular addition compounds, $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ and $\text{SbCl}_5 \cdot \text{SeOCl}_2$, 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 SeOCl_2 molecule and the chloride ion in solutions, since the reaction $\text{SeOCl}_2 = \text{SeOCl}^+ (\text{solvent}) + \text{Cl}^- (\text{solvent})$ occurs according to the self-ionization theory.

In the system $(\text{CH}_3)_4\text{NCl} - \text{SeOCl}_2$ three intermediate phases occur:³ $(\text{CH}_3)_4\text{NCl} \cdot 2\text{SeOCl}_2$, $(\text{CH}_3)_4\text{NCl} \cdot 3\text{SeOCl}_2$, and $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$. 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 $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$ was undertaken from three-dimensional single-crystal diffraction data.

EXPERIMENTAL

The solid solvate $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$ was prepared by cooling a heated mixture of $(\text{CH}_3)_4\text{NCl}$ 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 $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$ were made in thin-walled glass capillaries according to a method described in a previous paper.³ The melting point of the crystals, $+45^\circ\text{C}$, was in close

agreement with the value $+45^\circ$ to $+47^\circ\text{C}$ previously reported.³ 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 $0 \leq l \leq 11$ were recorded with $\text{CuK}\alpha$ 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:

$$\begin{aligned} a &= 15.540 \pm 0.025 \text{ \AA} \\ b &= 10.845 \pm 0.010 \text{ \AA} \\ c &= 16.550 \pm 0.015 \text{ \AA} \\ \beta &= 95^\circ 32' \pm 5' \end{aligned}$$

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 ($a = 4.913 \text{ \AA}$, $c = 5.405 \text{ \AA}$ for α -quartz, $\lambda(\text{CuK}\alpha_1) = 1.54051 \text{ \AA}$, $\lambda(\text{CuK}\alpha_2) = 1.54433 \text{ \AA}$, $\lambda(\text{CuK}\beta_1) = 1.39217 \text{ \AA}$. 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 $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$ per unit cell is $2.25 \text{ g}\cdot\text{cm}^{-3}$ in agreement with the density observed, $2.22 \text{ g}\cdot\text{cm}^{-3}$. 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.⁵ 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 $(F_o - F_{se} - F_{cl})$ 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 Åsbrink *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 Trueblood¹⁰ 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 $(F_o - F_c)$ and F_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	x	y	z	$B \text{ \AA}^2$	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B) \text{ \AA}^2$
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
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	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
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	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.

Interval $\sin \theta$	Number of reflexions	$\overline{wA^2}$ (normalized)	Interval F_o	Number of reflexions	$\overline{wA^2}$ (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	212	0.97

maximum and minimum values of the difference Fourier were less than one half of the carbon peaks in the F_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

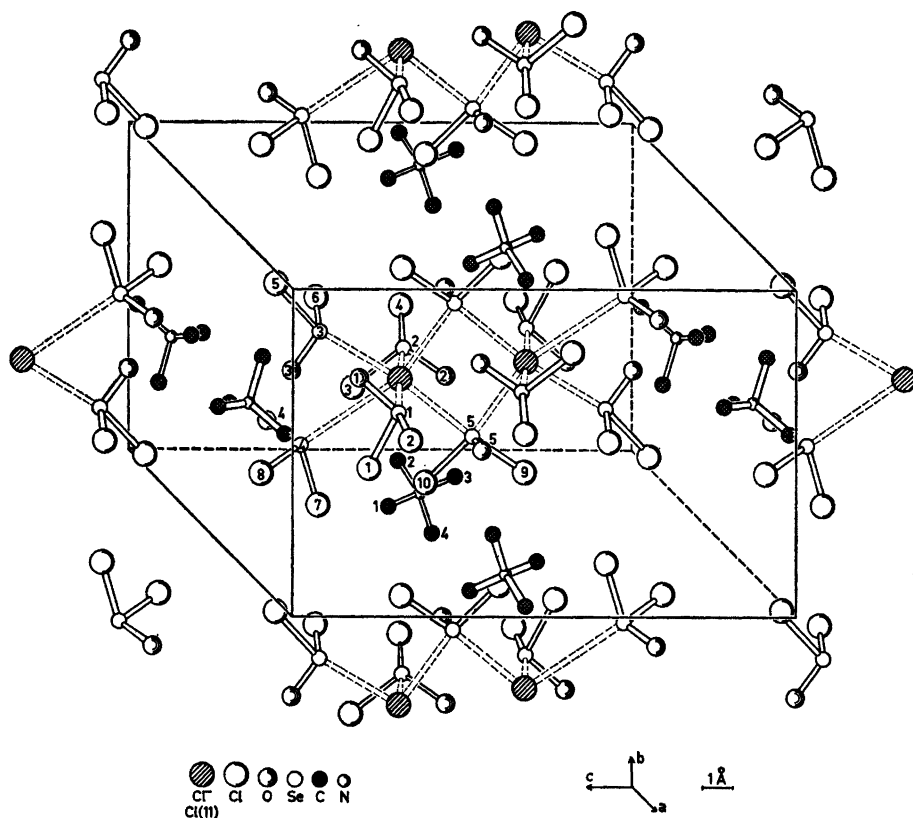


Fig. 1. The crystal structure of $(\text{CH}_3)_4\text{NCl}\cdot 5\text{SeOCl}_2$. For clarity only parts of the cell content are shown. The glide plane operation has been omitted. Double dashed lines indicate weak ion-dipole interactions.

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 tetramethylammonium 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 $\text{SeOCl}_2:\text{Cl}^-$ ratio of 5:1, two of these molecules are common to an adjacent $\text{Cl}(\text{SeOCl}_2)_6^-$ octahedron. In the resulting binuclear complex ion $\text{Cl}_2(\text{SeOCl}_2)_{10}^{2-}$, the two halves are related by a symmetry center (Fig. 2). This picture of an ion-solvent dipole interaction is consistent with the $\text{Se}\cdots\text{Cl}^-$ distances. Five of these distances are rather short (Fig. 2), being about midway between that for the sum of normal covalent

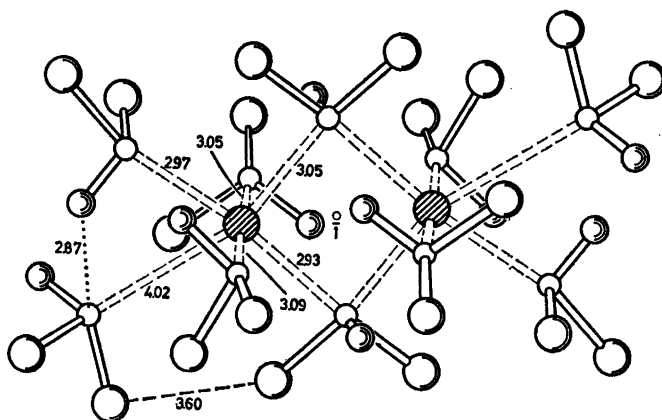


Fig. 2. The arrangement of SeOCl_2 molecules around chloride ions in $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$. The orientation and notation of the atoms is the same as in Fig. 1.

radii (2.2 Å), and the normal van der Waals distance (3.8 Å). The sixth distance, $\text{Se}(4) \cdots \text{Cl}^-$, 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 $\text{C} \cdots \text{Cl}$ distance is 3.65 Å and the shortest $\text{C} \cdots \text{O}$ 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.* $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. In this case the $\text{Li}^+ - \text{H}_2\text{O}$ chains¹⁵ are analogous to the $\text{Cl}^- - \text{SeOCl}_2$ 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 $\text{KF} \cdot 4\text{SbF}_3$ ¹⁶ in view of the large difference between the two types of $\text{Sb}-\text{F}$ distances (2.0 and 2.9 Å).

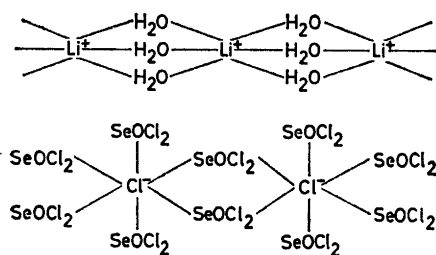


Fig. 3. Comparison of ion-solvent interactions in $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ and $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$.

An analysis of the individual bond lengths and bond angles in the five SeOCl_2 molecules shows no significant differences between distances of the same type with the possible exception of the $\text{Se}(5)-\text{Cl}(9)$ 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: $\text{Se}-\text{Cl}$ 2.198 Å, $\text{Se}-\text{O}$ 1.586 Å, $\text{Cl}-\text{Se}-\text{Cl}$ 95.0°, and $\text{Cl}-\text{Se}-\text{O}$ 102.9°. In comparison with the dimensions found in the molecular complexes $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ ¹ and $\text{SbCl}_5 \cdot \text{SeOCl}_2$ ² these values differ significantly, which is to be expected in view of the weaker bonding of the SeOCl_2 groups in the present structure. Thus the $\text{Se}-\text{Cl}$ 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 $\text{Se}-\text{O}$ bond length, 1.586 Å, suggests a more pronounced double bond character in $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$. This also agrees with the increase in the $\text{Cl}-\text{Se}-\text{O}$ angle. Nearly the same $\text{Se}-\text{O}$ distance, 1.59 Å, has been found in $\text{SeOCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ¹⁷ and in the tetragonal form of SeO_3 ,¹⁸ 1.54 Å and 1.56 Å for

Table 4. Bond distances and bond angles with standard deviations within the five SeOCl_2 molecules in $(\text{CH}_3)_4\text{NCl} \cdot 5\text{SeOCl}_2$.

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

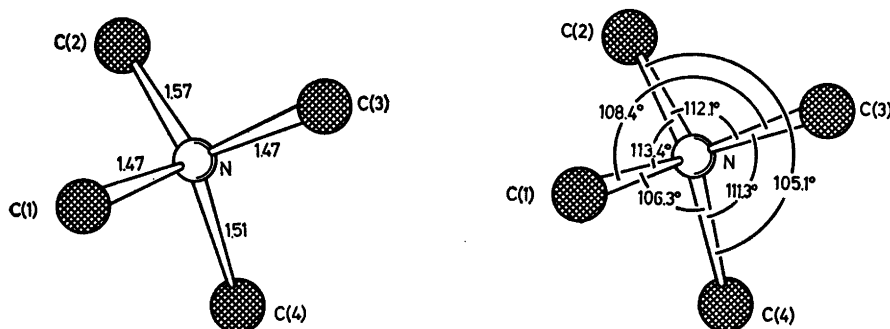


Fig. 4. Bond distances and bond angles within the tetramethylammonium ion.

the non-bridging oxygen atoms. The π -bond order for these Se—O bonds in the last compound has been calculated by Mijlhoff¹⁸ 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 SeO_3 are closer to the reported Se—O values in $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ and $\text{SbCl}_5 \cdot \text{SeOCl}_2$. According to the picture of SeOCl_2 molecules bound only by weak ion-dipole interaction it is not inconceivable that the molecular dimensions in solid SeOCl_2 , 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 $[(\text{CH}_3)_4\text{N}]_2\text{ZnCl}_4$,¹⁹ 1.55 Å and 109.4° , and in $(\text{CH}_3)_4\text{NClO}_4$,²⁰ 1.47 Å and 109.4° .

Another feature of the structure worth mentioning is the occurrence of an interaction between different SeOCl_2 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 $\text{N}(\text{CH}_3)_4^+$ ion.

Bond	Distance (Å)	Bonds	Angle (°)
N—C(1)	1.47 ± 0.04	C(1)—N—C(2)	113.4 ± 2.6
N—C(2)	1.57 ± 0.05	C(1)—N—C(3)	108.4 ± 2.7
N—C(3)	1.47 ± 0.06	C(1)—N—C(4)	106.3 ± 2.4
N—C(4)	1.51 ± 0.05	C(2)—N—C(3)	112.1 ± 2.9
Mean value	1.51	C(2)—N—C(4)	105.1 ± 2.5
		C(3)—N—C(4)	111.3 ± 2.9
		Mean value	109.4

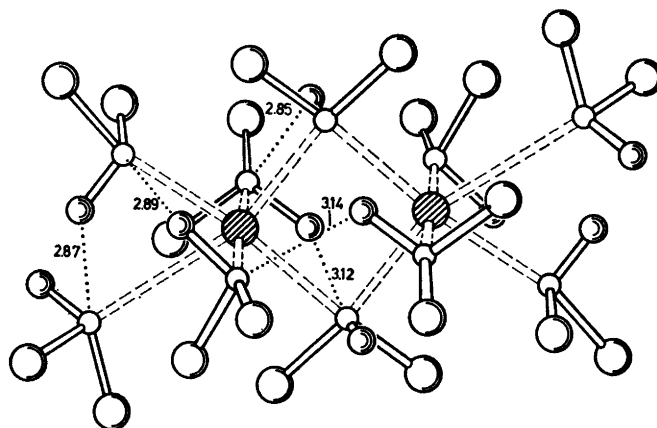


Fig. 5. The Se...O linking in $(\text{CH}_3)_4\text{NCl}\cdot 5\text{SeOCl}_2$. The orientation and notation of the atoms is the same as in Fig. 1.

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 $\text{C}_6\text{H}_5\text{SeO}_2\text{H}$ ²³ (3.17 Å). No further intermolecular interactions within the $\text{Cl}_2(\text{SeOCl}_2)_{10}^{2-}$ 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, $\text{CH}_3\cdots\text{Cl}$, and $\text{CH}_3\cdots\text{O}$ 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 $\text{CH}_3\cdots\text{O}$ 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 $(\text{CH}_3)_4\text{NClO}_4$ a $\text{CH}_3\cdots\text{O}$ distance of 3.04 Å has been found.²⁰

Table 6. Short intermolecular distances within a $\text{Cl}_2(\text{SeOCl}_2)_{10}^{2-}$ 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	Se(3)...O(1)	2.891 ± 0.021
Se(3)...Cl(9)A	3.443 ± 0.009	Se(4)...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 $\text{Cl}_2(\text{SeOCl}_2)_2^{2-}$ 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:	x	$1+y$	z
C:	$1-x$	$-y$	$1-z$
D:	$1-x$	$1-y$	$2-z$
E:	$1/2+x$	$1/2-y$	$1/2+z$
F:	$1/2-x$	$1/2+y$	$3/2-z$
G:	$1/2-x$	$y-1/2$	$3/2-z$
H:	$3/2-x$	$y-1/2$	$3/2-z$
I:	$x-1/2$	$1/2-y$	$z-1/2$

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

$\sigma(\text{Cl}\cdots\text{Cl}) = \pm 0.02 \text{ \AA}$	$\sigma(\text{Cl}\cdots\text{O}) = \pm 0.03 \text{ \AA}$
---	--

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	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 $(\text{CH}_3)_4\text{NCl}$ in similar solvents. In the solvent POCl_3 , with a rather low dielectric constant, Baaz and Gutmann²⁵ have reported the value of 5.44 Å for $(\text{C}_2\text{H}_5)_4\text{NCl}$. 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.

Acknowledgements. The author wishes to express his gratitude to the head of the institute, Prof. G. Hägg, for all the facilities placed at his disposal and to Prof. I. Lindqvist for his unfailing interest in this investigation.

This work has been sponsored by grants from the *Air Force Office of Scientific Research*, OAR, through its European Office under contract No. AF 61(052)-43 and the *Swedish Natural Science Research Council*. These grants are gratefully acknowledged. Facilities for the use of electronic computers were given by the *Computer Division of the National Swedish Office for Administrative Rationalization and Economy*.

REFERENCES

1. Hermodsson, Y. *Acta Cryst.* **13** (1960) 656.
2. Hermodsson, Y. *Acta Chem. Scand.* **21** (1967) 1313.
3. Agerman, M., Andersson, L.-H., Lindqvist, I. and Zackrisson, M. *Acta Chem. Scand.* **12** (1958) 477.
4. Buerger, M. J. *X-Ray Crystallography*, Wiley, New York 1949, p. 377.
5. Lundström, T. and Klimecki, V. *J. Sci. Instr.* **38** (1961) 424.
6. Åsbrink, S., Blomqvist, G. and Westman, S. *Arkiv Kemi* **14** (1959) 545.
7. Westman, S., Blomqvist, G. and Åsbrink, S. *Arkiv Kemi* **14** (1959) 535.
8. Åsbrink, S. and Brändén, 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 Crystallographic 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, I. J. 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.
17. Lindqvist, I. and Nahrungbauer, G. *Acta Cryst.* **12** (1959) 638.
18. 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.
22. Wells, A. F. and Bailey, M. *J. Chem. Soc.* **1949** 1282.
23. Bryden, J. H. and McCullough, J. D. *Acta Cryst.* **7** (1954) 833.
24. Wartenberg, E. W. *Proc. 8. I.C.C.C. Wien* 1964, p. 325.
25. Baaz, M. and Gutmann, V. *Monatsh.* **90** (1959) 256.

Received February 9, 1967.