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 (26) The root-mean-square thermal displacements of  $u(2) = 0.304$  (10) Å and  $u(3) = 0.404$  (8) Å obtained from the anisotropic refinement of the bridging D atom are directed 91 (2) and 92 (1)°, respectively, with respect to the Cr–Cr line.  
 (27) In the  $[\text{Et}_4\text{N}]^+$  salt, the Cr–H–Cr bond angle is 158.9 (6)° and the two independent Cr–H internuclear separations are 1.707 (21) and 1.737 (19) Å.  
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## The Nature of Triphenylselenonium Chloride. Crystal and Molecular Structure of the Monohydrate: $(\text{C}_6\text{H}_5)_3\text{SeCl}\cdot\text{H}_2\text{O}$

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Triphenylselenonium chloride hydrate  $((\text{C}_6\text{H}_5)_3\text{SeCl}\cdot\text{H}_2\text{O})$ , previously reported to be anhydrous, has been synthesized and investigated via a full three-dimensional X-ray structural analysis. The salt crystallizes in the noncentrosymmetric orthorhombic space group  $Pna2_1$  with  $a = 10.974$  (2) Å,  $b = 10.444$  (4) Å, and  $c = 14.493$  (4) Å (22 °C);  $V = 1661.1$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd}} = 1.454$  g/cm<sup>3</sup>, and  $d_{\text{obsd}} = 1.46$  (2) g/cm<sup>3</sup>. Diffraction data were collected with a Syntex P2<sub>1</sub> diffractometer using graphite-monochromated Mo K $\alpha$  radiation. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares methods using 2001 symmetry-independent reflections. Anisotropic thermal motion was assumed for all nonhydrogen atoms. The resulting discrepancy indices are  $R_F = 0.037$  and  $R_{wF} = 0.029$ . The structure consists of triphenylselenonium cations, chloride ions, and water molecules linked by a secondary bonding scheme involving shorter than van der Waals Se–Cl (3.530 (2) Å) and Se–O (3.147 (4) Å) distances. The salt is monomeric (Se–Se: 7.414 (2) Å) with five-coordinate selenium and has a packing arrangement different from that of the six-coordinate, dimeric dihydrate,  $(\text{C}_6\text{H}_5)_3\text{SeCl}\cdot 2\text{H}_2\text{O}$ . Enantiomorphs of the triphenylselenonium ion alternate along a hydrogen-bonded water–chlorine chain that runs parallel to  $a$  at  $y = 1/4, z = 0$  and  $y = 3/4, z = 1/2$ . The spatial arrangement of the five-coordination sites in the monohydrate is nearly identical with that in the dihydrate providing strong evidence that the Se–Cl and Se–O interactions are directed, albeit weak, chemical bonds. Additionally, shorter Se–Cl and Se–O distances are observed in the monohydrate, consistent with the lower coordination number for selenium. These salts constitute the first examples of two distinctly different group 6 onium-salt compounds that possess directly comparable secondary interactions. Calculated X-ray powder patterns are provided for identification and comparison of the monohydrate and dihydrate which constitute the only two characterized forms of  $(\text{C}_6\text{H}_5)_3\text{SeCl}$ . Numerous attempts to obtain the anhydrous salt by slow, open-air solvent evaporation resulted in the formation of only hydrated or solvated crystals. Discussion on the crystallization and characterization of the salt is given, and the existence of an anhydrous form under ordinary conditions is questioned. Triphenylselenonium chloride demonstrates a high propensity for water.

### Introduction

Secondary bonding has been shown to play a central role in the structures of the triorganoselenonium and triorganotelluronium salts.<sup>2–4</sup> Recently, Lee and Titus reported the X-ray structure of triphenylselenonium chloride dihydrate,  $(\text{C}_6\text{H}_5)_3\text{SeCl}\cdot 2\text{H}_2\text{O}$ , and showed that both water molecules and chloride ion formed a contiguous part of the structure by being involved in a secondary bonding scheme with the selenium atom.<sup>5</sup> The compound is dimeric (Se–Se: 4.762 (8) Å) with bridging chloride ions and one water molecule contributing to form six-coordinate selenium. Since 1929, the dihydrate and a so-called “anhydrous” compound have constituted the only known forms of triphenylselenonium chloride.<sup>6</sup>

In an early X-ray study of the “anhydrous” form, McCullough and Marsh were able to determine the atomic positional parameters of the selenium and chlorine atoms.<sup>7</sup> In this form the shortest Se–Cl distance (3.67 Å)<sup>8</sup> is approximately equal to the sum of the respective van der Waals radii, 3.65 Å, which suggests the absence of secondary bonding between selenium and chlorine.<sup>9</sup> Furthermore, the shortest Se–Se distance (7.51 Å) rules out a dimeric structure and suggests that selenium is three-coordinate which would be unlikely in view of the potential donor capacity of the chloride ion.<sup>10</sup> To resolve this situation, we determined the complete X-ray structure of triphenylselenonium chloride.

### Experimental Section

**Crystal Preparation and Data.** Crude triphenylselenonium chloride was obtained from ROC/RIC Corp., Sun Valley, Calif. Several grams were purified by extracting an aqueous solution three times with reagent grade benzene and passing it down a column containing purified Dowex 1-X8 (100–200 mesh) ion-exchange resin. The re-

sulting clear, colorless solution was vacuum evaporated at about 60 °C until crystals appeared. The solution was then cooled and filtered to remove the crystallized salt which was subsequently dried in a vacuum desiccator. Crystals suitable for X-ray diffraction studies were obtained by slow, open evaporation of a 60:40 v/v mixture of methylene chloride and ethyl acetate containing about 5 wt %  $(\text{C}_6\text{H}_5)_3\text{SeCl}$ . The solvent mixture was dried with anhydrous  $\text{MgSO}_4$  before use. During evaporation, the room temperature was 23 °C and the relative humidity about 60%.

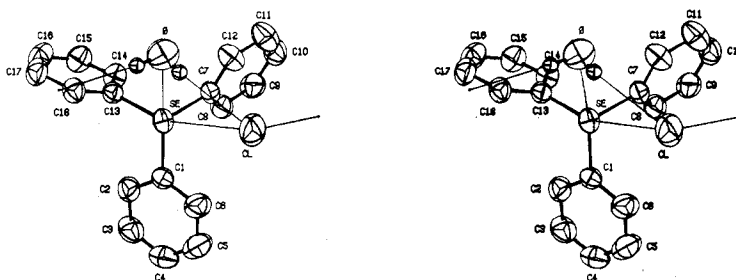
Preliminary precession photographs showed extinctions ( $0kl, k + l \neq 2n; h0l, h \neq 2n$ ) consistent with the orthorhombic space groups  $Pnam$  and  $Pna2_1$ . Accurate cell dimensions were calculated by using a least-squares procedure to fit the orientation angles of 15 randomly chosen reflections measured on a Syntex P2<sub>1</sub> diffractometer. The density, 1.46 (2) g/cm<sup>3</sup>, was measured by flotation in a mixture of hexane and  $\text{CCl}_4$  and was consistent with 4 formula units/unit cell. The noncentrosymmetric space group  $Pna2_1$  was assumed since mirror or inversion center symmetry was unlikely for  $(\text{C}_6\text{H}_5)_3\text{SeCl}$ . This assignment was later confirmed by the Patterson map and by the successful refinement of the structure. Crystal data are as follows:  $a = 10.974$  (2) Å,  $b = 10.444$  (4) Å,  $c = 14.493$  (4) Å,  $V = 1661.1$  (8) Å<sup>3</sup>, and  $Z = 4$ . The space group and cell dimensions appeared identical with those reported for anhydrous  $(\text{C}_6\text{H}_5)_3\text{SeCl}$ .<sup>7</sup> Better agreement between the observed and calculated densities, however, was obtained by assuming the presence of one water molecule:  $d_{\text{calcd}}((\text{C}_6\text{H}_5)_3\text{SeCl}\cdot\text{H}_2\text{O}) = 1.454$  g/cm<sup>3</sup> vs.  $d_{\text{calcd}}((\text{C}_6\text{H}_5)_3\text{SeCl}) = 1.382$  g/cm<sup>3</sup>. Subsequent electron density maps and thermal gravimetric data confirmed the presence and amount of  $\text{H}_2\text{O}$ . The linear absorption coefficient,  $\mu(\text{Mo K}\alpha)$  ( $\lambda = 0.710688$  Å), and  $F(000)$  for  $(\text{C}_6\text{H}_5)_3\text{SeCl}\cdot\text{H}_2\text{O}$  (mol wt 363.75) are 27.0 cm<sup>-1</sup> and 736, respectively.

X-ray powder diffraction patterns were calculated by using Clark, Smith, and Johnson's POWDS.<sup>11</sup> Atomic positional and thermal parameters (anisotropic for nonhydrogen and isotropic for hydrogen atoms) of all atoms were used in the calculation of the patterns. Parameters for the four water-hydrogen atoms in the dihydrate are

Table I. Positional ( $\times 10^4$ ) and Thermal Parameters ( $\text{\AA}^2$ ) for Atoms in  $(\text{C}_6\text{H}_5)_3\text{SeCl}\cdot\text{H}_2\text{O}^{a,b}$ 

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
Se	3354.7 (3)	5113.0 (3)	1/2	3.38 (1)	3.52 (1)	3.64 (1)	0.29 (1)	0.16 (2)	0.54 (2)
Cl	1466 (1)	7105 (2)	3648 (1)	5.23 (5)	11.75 (11)	4.81 (5)	2.28 (6)	1.10 (5)	1.40 (6)
C(1)	3105 (3)	3394 (3)	4527 (2)	3.8 (2)	3.8 (1)	3.2 (1)	0.0 (1)	0.4 (1)	0.1 (1)
C(2)	3906 (4)	2427 (4)	4722 (3)	4.3 (2)	4.3 (2)	5.9 (2)	0.4 (1)	0.3 (2)	0.3 (2)
C(3)	3679 (4)	1224 (4)	4313 (4)	6.0 (2)	3.8 (2)	7.1 (3)	0.6 (2)	0.6 (2)	0.4 (2)
C(4)	2715 (5)	1034 (4)	3751 (3)	7.1 (2)	4.7 (2)	5.1 (2)	0.7 (2)	1.2 (2)	1.3 (2)
C(5)	1928 (4)	2040 (5)	3570 (4)	6.7 (2)	7.4 (3)	5.8 (2)	1.1 (2)	1.6 (2)	1.2 (2)
C(6)	2127 (4)	3249 (4)	3949 (3)	6.2 (2)	5.8 (2)	4.5 (2)	0.6 (2)	1.1 (2)	0.4 (2)
C(7)	2011 (3)	5235 (3)	5848 (3)	3.1 (1)	3.9 (2)	3.6 (2)	0.6 (1)	0.2 (1)	0.0 (1)
C(8)	1643 (4)	6444 (4)	6047 (3)	4.2 (2)	4.3 (2)	5.4 (2)	0.4 (1)	0.7 (2)	0.4 (2)
C(9)	658 (5)	6616 (5)	6644 (3)	4.7 (2)	6.1 (2)	5.6 (2)	1.5 (2)	0.9 (2)	0.8 (2)
C(10)	79 (4)	5588 (5)	7010 (3)	4.2 (2)	8.0 (3)	4.5 (2)	0.4 (2)	0.8 (2)	0.6 (2)
C(11)	480 (4)	4340 (5)	6814 (4)	6.5 (2)	6.5 (2)	5.0 (2)	1.7 (2)	1.4 (2)	0.2 (2)
C(12)	1435 (3)	4171 (4)	6210 (3)	5.8 (2)	4.7 (2)	4.4 (2)	1.2 (2)	0.9 (2)	0.1 (2)
C(13)	4696 (3)	4839 (3)	5841 (3)	3.3 (1)	3.1 (1)	3.8 (1)	0.1 (1)	0.0 (1)	0.1 (1)
C(14)	5825 (3)	5246 (3)	5514 (3)	4.3 (2)	4.8 (2)	4.2 (2)	0.4 (1)	0.1 (2)	0.9 (2)
C(15)	6838 (3)	5092 (4)	6072 (4)	5.4 (2)	5.8 (2)	4.3 (2)	0.2 (2)	0.6 (2)	0.9 (2)
C(16)	6717 (4)	4500 (4)	6935 (4)	4.9 (2)	5.0 (2)	6.4 (3)	0.2 (2)	1.8 (2)	0.5 (2)
C(17)	5575 (4)	4137 (4)	7239 (3)	3.5 (2)	5.0 (2)	6.5 (2)	0.8 (1)	0.2 (2)	0.1 (2)
C(18)	4555 (3)	4296 (4)	6705 (3)	3.8 (2)	3.9 (2)	4.6 (2)	0.2 (1)	0.6 (1)	0.3 (1)
O	3880 (4)	8052 (4)	4735 (3)	6.3 (2)	6.1 (2)	8.3 (3)	0.8 (1)	0.1 (2)	1.2 (2)
HO(1) <sup>c</sup>	348 (6)	805 (7)	430 (5)	6.9 <sup>d</sup>					
HO(2) <sup>c</sup>	456 (6)	811 (6)	432 (4)	6.9 <sup>d</sup>					

<sup>a</sup> In this and subsequent tables the estimated standard deviations of the least significant figures are given in parentheses. <sup>b</sup> The form of the anisotropic thermal ellipsoid is  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ ; the  $B_{ij}$  are related to the dimensionless  $\beta_{ij}$  employed during refinement as  $B_{ij} = 4\beta_{ij}/a^*a^*a^*$ . <sup>c</sup> Hydrogen positional parameters  $\times 10^3$ . <sup>d</sup> Isotropic temperature factor,  $B$ , in the expression  $\exp[-B(\sin^2 \theta)/\lambda^2]$ .

Figure 1. Stereoscopic view of  $(\text{C}_6\text{H}_5)_3\text{SeCl}\cdot\text{H}_2\text{O}$ .

not available.<sup>12</sup> The scattering factors used in calculating the powder patterns were those of Cromer and Mann,<sup>13</sup> and an anomalous dispersion correction for the heavy atoms was applied.<sup>14</sup>

Thermal data (DSC and TGA) were obtained on a Du Pont 900 differential thermal analyzer. Powder patterns were obtained with a scintillation counter GE X-ray diffractometer.

**Intensity Data Collection.** Several well-formed crystals were ground into spheres. One with a 0.32-mm diameter was mounted on a Syntex P2<sub>1</sub> diffractometer for data collection. A  $\theta$ - $2\theta$  scan technique was used, following the procedure described earlier.<sup>15</sup> A total of 2001 symmetry-independent reflections were collected within a  $2\theta(\text{max})$  of  $55^\circ$  by using graphite-monochromated Mo  $K\alpha$  radiation. Of these, 1617 had intensities greater than  $3\sigma$ . The intensities of three standard reflections were monitored throughout the data collection after every 97 reflections. All showed a slight decrease in intensity over the data collection period giving an overall root-mean-square drop of 1.6%. The intensities were scaled accordingly. A spherical absorption correction was made by using Bond's table,<sup>16</sup> and the Lorentz-polarization correction was applied.

**Structure Determination and Refinement.** The structure was determined by using the heavy-atom technique. Selenium and chlorine positions were determined from the Patterson map. Other nonhydrogen atom positions were found from subsequent electron density maps. Although all hydrogen atoms could be located in a difference electron density map, only those of the water molecule were taken from it. Hydrogens on the phenyl rings were placed at theoretical positions by using a C-H distance of 0.95 Å after Churchill.<sup>17</sup>

Structure factors were calculated by using Cromer's atomic scattering factor tables.<sup>13</sup> The structure was refined by using the full-matrix least-squares procedure and all 2001 reflections. The weighting scheme was that described earlier<sup>15</sup> and is based on counting statistics. All nonhydrogen atoms were assigned anisotropic thermal parameters.

All hydrogens were assigned a fixed isotropic thermal parameter, 110% of that of the attached atom. During refinement, the only hydrogen parameters varied were the positional parameters of the hydrogens of the water molecule.

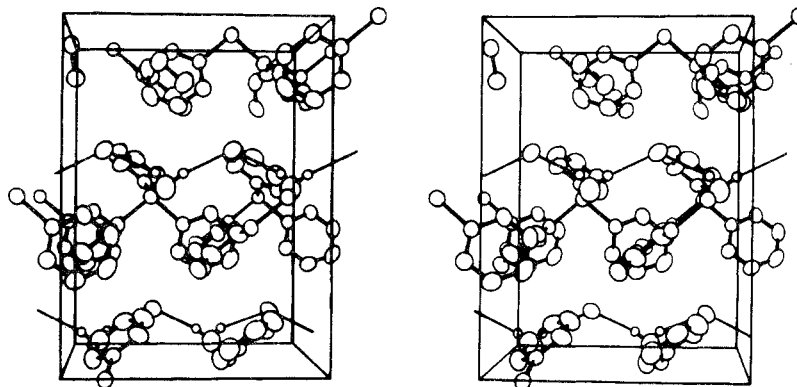
Toward the end of the refinement, the anomalous dispersion correction<sup>18</sup> was made and the original structure and that of its enantiomorph were refined in parallel. With the anomalous dispersion correction, these structures refined to  $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.044$  and  $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.038$  for the original structure and  $R = 0.038$  and  $R_w = 0.029$  for the enantiomer with use of all reflections. The enantiomer was therefore taken as the structure more consistent with the data set and was further refined until the shifts in parameters were less than or equal to  $0.05\sigma$ . Final discrepancy indices were  $R = 0.037$  and  $R_w = 0.029$  for all 2001 reflections and  $R = 0.025$  and  $R_w = 0.027$  for the 1617 reflections with intensities  $> 3\sigma$ .

The final positional and thermal parameters for atoms in the structure are given in Table I. The observed and calculated structure factors are available as supplementary material.

## Results and Discussion

Triphenylselenonium chloride, previously reported to be anhydrous,<sup>7</sup> is the monohydrated species,  $(\text{C}_6\text{H}_5)_3\text{SeCl}\cdot\text{H}_2\text{O}$ . Interatomic distances and angles are given in Tables II and III, and stereoscopic views of the compound and its crystal packing arrangement are given in Figures 1 and 2, respectively.

The compound is monomeric and predominantly ionic but has shorter than van der Waals Se-Cl and Se-O distances (3.530 (2) vs. 3.65 Å and 3.147 (4) vs. 3.42 Å, respectively). These distances together with the spatial arrangements of the chlorine and oxygen atoms suggest that these atoms are in-



**Figure 2.** Stereoscopic view of the packing arrangement for  $(C_6H_5)_3SeCl \cdot H_2O$ . Positive  $x$  runs from right to left, positive  $y$  toward viewer, and positive  $z$  from bottom to top.

**Table II.** Interatomic Distances (Å) in  $(C_6H_5)_3SeCl \cdot H_2O$

Se-C(1)	1.941 (4)	C(4)-C(5)	1.385 (7)
Se-C(7)	1.924 (4)	C(5)-C(6)	1.395 (7)
Se-C(13)	1.932 (4)	C(6)-C(1)	1.370 (6)
Se-O	3.147 (4)	C(7)-C(8)	1.383 (5)
Se-Cl	3.530 (2)	C(8)-C(9)	1.376 (6)
Se-Se'	7.414 (2) <sup>a</sup>	C(9)-C(10)	1.405 (7)
Cl-O	3.237 (4)	C(10)-C(11)	1.356 (7)
Cl-O'	3.250 (4) <sup>a</sup>	C(11)-C(12)	1.397 (6)
O-HO(1)	0.77 (6)	C(12)-C(7)	1.356 (5)
O-HO(2)	0.96 (6)	C(13)-C(14)	1.382 (5)
Cl-HO(2')	2.32 (6) <sup>a</sup>	C(14)-C(15)	1.371 (5)
Cl-HO(1)	2.60 (6)	C(15)-C(16)	1.381 (6)
Cl-HO(2)	3.68 (6)	C(16)-C(17)	1.389 (7)
C(1)-C(2)	1.369 (4)	C(17)-C(18)	1.388 (6)
C(2)-C(3)	1.412 (6)	C(18)-C(13)	1.394 (5)
C(3)-C(4)	1.349 (7)		

<sup>a</sup> Primed atoms at  $[x - 1/2, 1.5 - y, z]$ .

**Table III.** Interatomic Angles (Deg) in  $(C_6H_5)_3SeCl \cdot H_2O$

C(1)-Se-C(7)	100.3 (1)	C(18)-C(13)-Se	114.7 (3)
C(7)-Se-C(13)	101.0 (2)	O-HO(1)-Cl''	147 (7) <sup>a</sup>
C(13)-Se-C(7)	101.1 (1)	O-HO(2)-Cl''	164 (5) <sup>a</sup>
C(1)-Se-Cl	105.4 (1)	C(2)-C(1)-C(6)	123.2 (4)
C(7)-Se-Cl	82.3 (1)	C(3)-C(2)-C(1)	117.2 (4)
C(13)-Se-Cl	152.2 (1)	C(4)-C(3)-C(2)	121.5 (4)
C(1)-Se-O	152.2 (1)	C(5)-C(4)-C(3)	119.4 (4)
C(7)-Se-O	98.8 (1)	C(6)-C(5)-C(4)	121.0 (4)
C(13)-Se-O	94.7 (1)	C(1)-C(6)-C(5)	117.6 (4)
O-Se-Cl	57.7 (1)	C(8)-C(7)-C(6)	122.1 (4)
Cl-O-Cl''	117.6 (1) <sup>a</sup>	C(9)-C(8)-C(7)	119.1 (4)
Se-O-Cl	67.1 (1)	C(10)-C(9)-C(8)	119.1 (4)
HO(1)-Cl-HO(2')	131 (2) <sup>a</sup>	C(11)-C(10)-C(9)	120.6 (4)
HO(1)-O-HO(2)	86 (6)	C(12)-C(11)-C(10)	120.2 (4)
HO(1)-O-Se	90 (6)	C(7)-C(12)-C(11)	118.9 (4)
HO(2)-O-Se	106 (6)	C(14)-C(13)-C(12)	122.2 (3)
C(2)-C(1)-Se	121.3 (3)	C(15)-C(14)-C(13)	118.0 (3)
C(6)-C(1)-Se	115.4 (3)	C(16)-C(15)-C(14)	121.8 (4)
C(8)-C(7)-Se	122.7 (3)	C(17)-C(16)-C(15)	119.3 (4)
C(12)-C(7)-Se	115.2 (3)	C(18)-C(17)-C(16)	120.4 (4)
C(14)-C(13)-Se	123.2 (3)	C(13)-C(18)-C(17)	118.2 (4)

<sup>a</sup> Primed atom at  $[x - 1/2, 1.5 - y, z]$ ; doubly primed atoms at  $[1/2 + x, 1/2 - y, z]$ .

involved in a secondary bonding scheme with selenium as found in the six-coordinate dihydrate,<sup>5</sup> and in other triorgano-chalcogenonium salts.<sup>2-4,19,20</sup> In the present structure the chlorine and oxygen atoms serve to give selenium a five-coordinate environment consistent with the trend that, in triorganoselenonium salts containing potentially coordinating species, selenium has a coordination number consistent with the stoichiometry of the compound.<sup>21</sup> In the corresponding triorganotelluronium salts, tellurium exceeds its stoichiometric coordination number.<sup>3</sup> Accompanying the increase in coordi-

**Table IV.** Summary Comparison of Distances and Angles in  $(C_6H_5)_3SeCl \cdot H_2O$  and  $(C_6H_5)_3SeCl \cdot 2H_2O$

$(C_6H_5)_3SeCl \cdot H_2O$		$(C_6H_5)_3SeCl \cdot 2H_2O$ <sup>a</sup>	
Distances, Å			
Se-Se'	7.414 (2) <sup>b</sup>	Se-Se'	4.762 (8)
Se-O	3.147 (4)	Se-O(1)	3.238 (13)
Se-Cl	3.530 (2)	Se-Cl'	3.616 (4)
Cl-O	3.237 (4)	Cl-O(1)'	3.164 (10)
Cl-O'	3.250 (4) <sup>b</sup>	Cl-O(2)''	3.231 (13)
Se-C (mean)	1.932 (5)	Se-C (mean)	1.93 (1)
Angles, Deg			
C(1)-Se-C(7)	100.3 (1)	C(31)-Se-C(21)	99.9 (7)
C(1)-Se-C(13)	101.1 (1)	C(31)-Se-C(11)	101.7 (4)
C(7)-Se-C(13)	101.0 (2)	C(21)-Se-C(11)	99.5 (5)
Cl-Se-C(1)	105.4 (1)	Cl'-Se-C(31)	104.9 (4)
Cl-Se-C(7)	82.3 (1)	Cl'-Se-C(21)	87.3 (3)
Cl-Se-C(13)	152.2 (1)	Cl'-Se-C(11)	150.9 (3)
O-Se-C(1)	152.2 (1)	O(1)-Se-C(31)	158.9 (3)
O-Se-C(7)	98.8 (1)	O(1)-Se-C(21)	85.3 (5)
O-Se-C(13)	94.7 (1)	O(1)-Se-C(11)	97.5 (4)
Cl-Se-O	57.7 (1)	Cl'-Se-O(1)	54.6 (2)

<sup>a</sup> Atom notation is that given in ref 5; doubly primed atom is at  $[1/2 - x, 1/2 + y, 1/2 - z]$ . <sup>b</sup> Se' and O' in monohydrate at  $[x - 1/2, 1.5 - y, z]$ .

nation number is a decrease in the C-(group 6)-C angle.

The triphenylselenonium cation is trigonal pyramidal and nearly identical with that in the four-coordinate thiocyanate<sup>2</sup> and six-coordinate dihydrate.<sup>5</sup> The mean<sup>22</sup> Se-C distance is 1.932 (5) Å and the mean C-Se-C angle 100.8 (3)°. The distance of the selenium atom from the trigonal plane formed by the three bonded carbon atoms is also identical at 0.88 Å. Despite these similarities in structural parameters, the triphenylselenonium cations in the three compounds are not superimposable due to differences in conformation as reflected by the differences in the dihedral angles between the phenyl ring planes (vide infra). The volatile nature of the phenyl groups in the  $(C_6H_5)_3Se^+$  ion allows for a versatility in packing analogous to that observed for the  $(C_6H_5)_3Te^+$  ion.<sup>3</sup> Conformational flexibility has been noted in other ions such as  $(C_6H_5)_4P^+$  and  $(C_6H_5)_4As^+$  but apparently not in  $B(C_6H_5)_4^{23}$

A comparison of interatomic distances and angles between the monohydrate and dihydrate is given in Table IV. In both compounds, selenium has a very distorted octahedral environment. In the monohydrate, one site is vacant. Despite differences in coordination number and in packing arrangement between the two structures, the spatial arrangements of the chlorine atom and coordinated water molecule in the two structures are essentially identical. The Se-O and Se-Cl vectors in both structures make angles between 35 and 45° with respect to the pseudo-threefold axis passing through sel-

Table V. Unit Cell Data Comparison of the Monohydrate and Dihydrate

(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SeCl·H <sub>2</sub> O	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SeCl·2H <sub>2</sub> O <sup>5</sup>
space group: <i>Pna</i> 2 <sub>1</sub>	space group: <i>C2/c</i>
<i>a</i> = 10.974 (2) Å	<i>a</i> = 12.798 (3) Å
<i>b</i> = 10.444 (4) Å	<i>b</i> = 13.802 (1) Å
<i>c</i> = 14.493 (4) Å	<i>c</i> = 19.933 (34) Å
<i>V</i> = 1661 Å <sup>3</sup>	<i>β</i> = 90.0 (1) <sup>o</sup>
<i>Z</i> = 4	<i>V</i> = 3521 Å <sup>3</sup>
<i>d</i> <sub>calcd</sub> = 1.454 g/cm <sup>3</sup>	<i>Z</i> = 8
	<i>d</i> <sub>calcd</sub> = 1.440 g/cm <sup>3</sup>

enium in the direction of the sum of the three Se–C vectors. The dimeric dihydrate, therefore, may be viewed as consisting of two units of monohydrate related by a twofold axis and positioned such that the chloride ions are within secondary binding distance to both selenium atoms to give each a six-coordinate environment. These salts provide the first instance of two distinctly different group 6 onium-salt compounds that possess directly comparable secondary interactions. The fact that the relative orientation of the Se–Cl and Se–O vectors with respect to the cation is essentially the same in both structures, despite their differences, provides strong support that the secondary interactions are directed, albeit weak, chemical bonds. Furthermore, a significant shortening (7–21σ) of the Se–Cl and Se–O distances is observed in the monohydrate consistent with its lower coordination number and with the nonsharing of the chlorine atom.<sup>24</sup> We note that packing efficiencies appear to be about the same for both compounds and that the shorter distances are consistent with the slight increase in density (1% at comparable temperatures) in going from the dihydrate to the monohydrate (Table V). The formula-unit volume difference, Δ(*V*/*Z*), between the monohydrate and dihydrate is 25 Å<sup>3</sup> and is in reasonably good agreement with the volume of one water molecule (32 Å<sup>3</sup>) as found in ice I (hexagonal, loose pack) at –20 °C.<sup>25</sup>

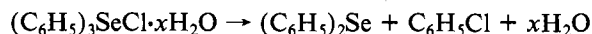
Bond distances and angles within the three crystallographically independent phenyl rings appear normal and are listed in Tables II and III. The mean values of the 18 independent phenyl C–C distances and the C–C–C angles are 1.381 (4) Å and 120.0 (4)<sup>o</sup>, respectively. The rings are planar with no carbon atom deviating more than 0.009 Å from the least-squares plane of its respective phenyl ring. Dihedral angles between the phenyl groups containing carbon atoms 1 and 7, 1 and 13, and 7 and 13 are 14.1, 50.9, and 75.8<sup>o</sup>, respectively.

Packing within the crystal (Figure 2) is dominated by a presumably hydrogen-bonded water–chlorine chain along *y* = 1/4, *z* = 0 and *y* = 3/4, *z* = 1/2. The Cl–O–Cl angle is 117.6<sup>o</sup>, and the shortest Cl–O distances are comparable to the sum of the respective van der Waals radii. Enantiomorphs of the triphenylselenonium cation alternate along the water–chlorine chain. This arrangement of atoms differs drastically from that of the dihydrate which, with the incorporation of an additional water molecule, has four-membered water clusters separating layers of dimers. In both compounds only one water molecule coordinates to the selenium atom.

During numerous attempts to obtain anhydrous or nonsolvated triphenylselenonium chloride by slow, open-air solvent evaporation, we observed the formation of only hydrated or solvated crystals. The monohydrate formed under low-moisture conditions while the dihydrate formed in the presence of larger amounts of water. Often, mixtures of both were obtained. The use of elemental analyses and Karl Fischer determinations to identify and distinguish the hydrates most often led to inconclusive results. To facilitate identification of the salts, we calculated the X-ray powder patterns of both hydrates on the basis of the crystallographic cell constants and structural data reported herein and elsewhere.<sup>5,12</sup> The calculated *d* spacings, 2θ values, and intensities (*I*) are reported in Table

VI. The diffraction patterns observed for both compounds were identical with those calculated. Accordingly, the patterns may be used to unequivocally identify or characterize either salt or a mixture of the salts.

Thermal gravimetric analyses show that mass loss, presumably water, occurs for both compounds before 100 °C and continues until the decomposition of the compound. Catastrophic mass loss (about 90%) occurs for both compounds upon slow heating between 235 and 255 °C where decomposition to diphenyl selenide and chlorobenzene takes place.<sup>6a</sup> In contrast to the monohydrate, which appears to have no sharply defined melting point, the dihydrate has a sharp melting point (decomposition) at 232 °C (capillary, DSC, TGA). This melting point can sometimes serve as a spot-check for the dihydrate if other species, including other solvents,<sup>26</sup> are not present. Both compounds decompose slowly in solution over extended periods, presumably due to the irreversibility of the reaction



To date, the existence of only hydrated forms of (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SeCl (monohydrate and dihydrate<sup>5</sup>) has been demonstrated. Anhydrous (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SeCl has not been characterized. Leicester noted that the dihydrate completely dehydrates at 100 °C.<sup>6</sup> We observed that gentle heating of the dihydrate at 100 °C forms a white crystalline powder whose diffraction pattern differs from that of either hydrate.<sup>29</sup> Recrystallization of the powder from methyl ethyl ketone<sup>26</sup> leads to the formation of the monohydrate or dihydrate. Exposure of the powder to room temperature and moisture for several days results in the formation of the dihydrate. Clearly, triphenylselenonium chloride possesses a large propensity for water, and gain or loss of this water involves lattice changes in the crystal. Characterization studies of the various compounds formed is sometimes complicated by the presence of other solvents of crystallization and by the slow decomposition of the compound over extended periods in solution.

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**Registry No.** (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SeCl·H<sub>2</sub>O, 71648-10-7; (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SeCl·2H<sub>2</sub>O, 63057-97-6.

**Supplementary Material Available:** A listing of the observed and calculated structure factors and Table VI, calculated powder diffraction patterns for (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SeCl·H<sub>2</sub>O and (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SeCl·2H<sub>2</sub>O (15 pages). Ordering information is given on any current masthead page.

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## Copper Thiolate Cluster Compounds. X-ray Structure and Properties of Pentathallium(I) $\mu_8$ -Chloro-dodecakis( $\alpha$ -mercaptoisobutyrate)octacuprate(I)hexacuprate(II) Hydrate, $Tl_5[Cu^{II}_6Cu^I_8(SC(CH_3)_2COO)_{12}Cl] \cdot \sim 12H_2O$

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Crystalline derivatives of a  $Cu^I, Cu^{II}$  cluster complex of  $\alpha$ -mercaptoisobutyric acid ( $H_2MIBA$ ) were obtained with  $Co(NH_3)_6^{3+}$  and  $Tl^+$  as counterions. The structure of the  $Tl^+$  derivative was determined by X-ray diffraction. The compound  $Tl_5[Cu^{II}_6Cu^I_8(SC(CH_3)_2COO)_{12}Cl] \cdot nH_2O$  crystallizes in the space group  $C2/c$  with  $a = 18.339$  (2) Å,  $b = 21.114$  (2) Å,  $c = 24.858$  (3) Å,  $\beta = 101.77$  (2)°,  $V = 9423$  (2) Å<sup>3</sup>,  $d_m = 2.52$  (1) g cm<sup>-3</sup>, and  $d_x = 2.52$  g cm<sup>-3</sup> for  $n = 12$  and  $Z = 4$ . The intensities of 5771 independent reflections were measured by counter methods by using Mo  $K\alpha$  radiation ( $\theta_{max} = 22^\circ$ ). The structure was solved by direct phasing and refined by full-matrix least-squares methods. The final residual for 3908 reflections with  $I > \sigma(I)$  and  $(\sin \theta)/\lambda > 0.09$  Å<sup>-1</sup> was 0.19. The structure consists of ordered cluster anions interlinked by Tl-O bonds. The  $Tl^+$  ions and the water molecules in the structure are disordered. The  $[Cu_{14}(MIBA)_{12}Cl]^{5-}$  clusters consist of a chloride ion at the center of a cube of eight  $Cu^I$  atoms, which is inscribed into an icosahedron of 12 sulfur atoms. The sulfur atoms form bridges between two  $Cu^I$  atoms and one  $Cu^{II}$  atom. The six  $Cu^{II}$  atoms in the structure form an octahedron in such an orientation that there is a  $Cu^{II}$  atom centered above each of the six faces of the  $Cu^I_8$  cube. The  $Cu^I$  atoms are trigonally coordinated by three sulfur atoms. The  $Cu^{II}$  atoms are bound to two sulfur and two oxygen atoms of cis-bidentate-chelating  $H_2MIBA$  ligands. The structural and spectral parameters of the  $Cu$ -MIBA complex are compared with those of other copper thiolate complexes. The strong absorption in the visible spectra of the  $Cu$ -MIBA complex (485 nm,  $\epsilon$  21 000 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>) and related compounds has previously been assigned to a  $S \rightarrow Cu^{II}(d_{x^2-y^2})$  charge-transfer transition. An alternative assignment to a  $S(3p) \rightarrow Cu^I(4s, 4p)$  transition is discussed.

### Introduction

The reaction between  $Cu^{II}$  and thiols often leads to the formation of intensely colored reddish brown or purple products. Klotz et al.<sup>1</sup> first described this phenomenon for a number of thiol ligands and characterized them as mixed-valence  $Cu^I, Cu^{II}$  complexes. Structural investigations of these complexes were hampered for many years by instability, irreproducible analytical results, and lack of crystals.

All thiols which are able to form such colored complexes contain, apart from the thiol group, one or more potentially metal-binding substituents (e.g.,  $COO^-$  or  $NH_2$  groups) in a position suitable for the formation of a five-membered chelate ring.<sup>2</sup> When the carbon atom adjacent to the sulfur atom has two alkyl substituents, the colored  $Cu$  complex tends to be exceptionally stable.<sup>3</sup> The presence of halide ions is essential for the formation of this class of exceptionally stable colored complexes. Examples of such ligands are (i) penicillamine<sup>3-7</sup> ( $H_2Pen^8$ ), (ii)  $\beta, \beta$ -dimethylcysteamine<sup>9</sup> (HDMC<sup>8</sup>), and (iii)  $\alpha$ -mercaptoisobutyric acid<sup>4,5,6</sup> ( $H_2MIBA^8$ ). The copper complexes with D-penicillamine and  $\beta, \beta$ -dimethylcysteamine have

been crystallized and their structures have been solved.<sup>7,9</sup> The complex ions are mixed-valence cluster anions of composition  $[Cu^{II}_6Cu^I_8L_{12}Cl]^z$ , where  $z = 5-$  for  $L = D$ -penicillamine and  $z = 7-$  for  $L = \beta, \beta$ -dimethylcysteamine. It has been postulated<sup>7</sup> that the copper-mercaptoisobutyric acid complex is a similar mixed-valence cluster  $[Cu^{II}_6Cu^I_8(MIBA)_{12}Cl]^{5-}$ , with cis-bidentate  $Cu^{II}S_2O_2$  coordination instead of the  $Cu^{II}S_2N_2$  coordination found in the  $H_2Pen$  and HDMC compounds. This hypothesis is proved to be correct by the present work.

### Experimental Section

**Materials.** Mercaptoisobutyric acid was prepared as described by Biilmann.<sup>10</sup> All other reagents and solvents were of reagent grade quality.

**Preparations.** The crude sodium salt of the complex was prepared by adding a solution of  $H_2MIBA$  (80 mg, 0.67 mmol) in 15 mL of 0.2 M sodium acetate buffer to a solution of  $CuCl_2 \cdot 2H_2O$  (85 mg, 0.5 mmol) in 2 mL of water. The dark brown solution thus obtained was treated with 35 mL of alcohol and 125 mL of ether. A dark brown oily layer separated out. The almost colorless supernatant was removed and discarded. Addition of 15 mL of alcohol to the brown residue resulted in the precipitation of a brown-black solid product. This