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Synthesis and Structure of Novel Haloselenurane−Lewis Acid Complexes

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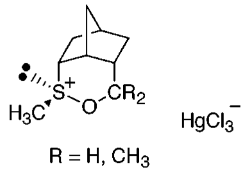
Inorganic hypervalent chalocogen(IV) halides react with Lewis acids to give complexes such as SCl_4SbCl_5, $SeCl_4SbCl_5$, and $TeCl_3FAsF_5$. The structure of these inorganic complexes has been investigated mainly by means of vibrational spectra and X-ray crystallographic analyses.[1] The presence of secondary covalent interaction between the cations and the anions was observed, and it will be more appropriate to describe the structure of some complexes as "chalcogen(IV) halide−Lewis acid complex" rather than "chalcogenoium cation−anion salt". X-ray crystallographic analyses of the complexes revealed that the strength of the interaction between cationic fragment and anionic fragment increases in the series S < Se < Te.[1h] Compared to these inorganic complexes, the structure of the complexes formed by the reaction of organic halochalcogenuranes and Lewis acids has been studied to a much lesser extent.[2,3] Glass et al. prepared sulfoxonium salts such as **1** and the ionic structure of **1** was confirmed by an X-ray crystallographic analysis.[2] The distances between S and Cl were 3.25 and 4.08 Å, and the values are comparable to or larger than the sum of van der Waals radii of the two elements (3.55 Å).[4] Secondary interaction between the sulfur atom and chlorine atom is therefore negligible. In this paper we report the synthesis and structure of novel haloselenurane−Lewis acid complexes.



Alkoxysulfonium cation (**1**)

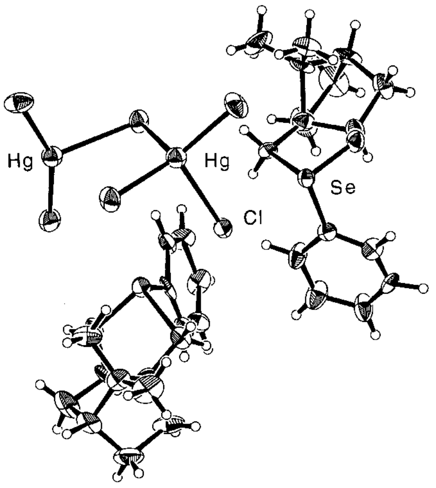
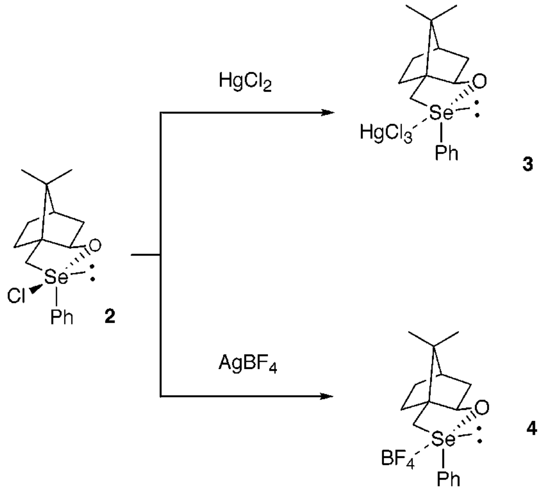


Figure 1. ORTEP drawing of the compound **3** with 30% thermal ellipsoids.

Scheme 1



Chloroselenurane **2**[5] reacted with $HgCl_2$ to give a new compound (**3**), which was characterized as **2**·$HgCl_2$ (Scheme 1).[6] A crystal of **3** which was suitable for X-ray crystallographic analysis was obtained by recrystallization from CH_2Cl_2−hexane. The structure of **3**[7] is shown in Figure 1, and it is compared with that of the parent chloroselenurane **2**.[5] Selected bond lengths and angles are summarized in Table 1.

Compound **3** is a chlorine-bridged dimer. The shortest distances of Se−Cl in each fragment were 2.835(7) and

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(6) Experimental procedure: To the solution of chlorooxaphenylselenurane[5] (**2**, 36 mg, 0.11 mmol) in anhydrous CH_2Cl_2 (4 mL) was added $HgCl_2$ (29 mg, 0.11 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at 0 °C to room temperature overnight. Evaporation of the solvent gave optically pure alkoxyselenonium salt **3** as colorless crystals (60 mg) in 93% yield. See Supporting Information for the spectral data.

(7) Crystallographic data for **3**: MF = $C_{16}H_{21}Cl_3HgOSe$, MW = 615.25, monoclinic; $a = 10.545(3)$, $b = 13.937(3)$, $c = 13.379(3)$ Å, $\beta = 90.77(2)°$, $V = 1966.2(6)$ Å^3, space group $P2_1$, $Z = 4$, $D_c = 2.078$ g/cm^3. Data collection was done using Mo Kα radiation ($\mu = 101.1$ cm^{-1}) with a rotating anode diffractometer (50 kv, 120 mA). A total of 4566 reflections were collected, of which 2179 reflections with $I_o > 3\sigma(I_o)$ were used in the refinement. After applying the empirical absorption correction using the DIFABS method, the final R factor was 0.045 (R_w = 0.057). The final difference peaks were $\rho_{max} = 1.70$ and $\rho_{min} = -1.41$ e/Å^3.

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Table 1. Bond Distances, Angles, and ^{77}Se NMR Spectroscopic Data for 2−5

	2[a]	**3**	**4**	**5**[a]
Se−Cl (Å)	2.587(2)	2.835(7), 2.977(7)	*b*	*c*
Se−O (Å)	1.838(5)	1.78(2), 1.83(2)	1.780(5)	*c*
O−Se−X (deg) (X = Cl, or F)	174.1(2)	174.0(6), 169.3(6)	172.4(2)	*c*
^{77}Se NMR (ppm)[d]	901	990	1081[e]	853[e]

[a] Reference 5. [b] The length of the Se−F bond is 2.566(4) Å. [c] Data not available. [d] Referenced to Me_2Se (281 ppm). [e] No coupling was observed between selenium and fluorine. See also ref 13.

2.977(7) Å. As expected, the distances are longer than the distance of Se−Cl [2.587(2) Å] in **2**. The difference is obviously caused by the coordination of the chlorine atom with $HgCl_2$. However, these values are significantly shorter than the sum of van der Waals radii (3.80 Å)[4] of Se and Cl, indicating some covalent character of the Se−Cl bond.[8]

There are few other structural differences between **2** and **3**. For example, there is no essential difference between the bond angle of O−Se−Cl in **2** and the bond angles in **3**. Moreover, the distance of Se−O is 1.838(5) Å in **2**, whereas the distances are 1.78(2) and 1.83(2) Å in **3**. This small difference indicates the limited cationic character of the selenoxonium moiety.[9] On the basis of these results, we describe the crystal structure of **3** as a "haloselenurane−Lewis acid complex" rather than a "selenonium cation−anion salt". The result we obtained is in sharp contrast to the result obtained by Glass et al., who reported the isolation of a sulfoxonium cation **1** by the reaction of a chlorosulfurane with $HgCl_2$.[2] It may be possible to explain the difference of the structures in terms of the softness of the selenium cation.

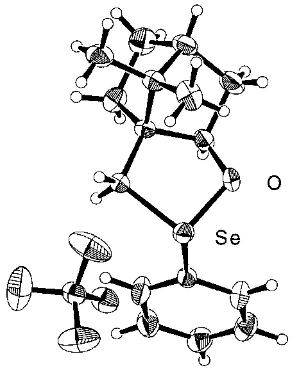

Figure 2. ORTEP drawing of the compound **4** with 30% thermal ellipsoids.

We also prepared a fluoroselenurane−BF_3 complex (**4**) from **2** and $AgBF_4$.[10] The structure of **4** was also analyzed by X-ray crystallography, as shown in Figure 2.[11] The structure of **4** was compared with other selenuranes (Table 1). Though we expected that a free selenoxonium cation would be isolated, a covalent interaction between selenium atom and fluorine atom was observed: the distance of Se−F is 2.566(4) Å, which is much smaller than the sum of the van der Waals radii (3.37 Å)[4] of the two elements. This compound is also a haloselenurane−Lewis acid complex.

It is less likely that **3** and **4** completely dissociate in solution. Though the ^{77}Se NMR chemical shift of the haloselenurane−Lewis acid complexes (δ 990 for **3** and δ 1081 ppm for **4**) in $CDCl_3$ appeared at lower field compared to the chemical shift of chloro- or fluoroselenurane (δ 901 for **2**, and δ 853 ppm for **5**), it is apparently affected by the anionic moiety of the complex (Table 1). The result indicates that the complexes have limited cationic character even in solution ($CDCl_3$).[12,13]

In summary, we prepared haloselenurane−Lewis acid complexes and examined the structure by means of X-ray crystallographic analyses and ^{77}Se NMR spectroscopy. The structure of the complexes was significantly different from that of a chlorosulfurane−$HgCl_2$ complex, probably due to the softness of the selenium atom. A covalent interaction between the cationic chalcogenium fragment and the anionic fragment exists even in solution. The present results will be helpful to understand the structural preference of the chalcogen compounds.

Supporting Information Available: Experimental procedures, spectral data, and crystallographic data for compounds **3** and **4** (70 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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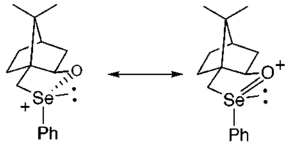
(8) The anionic fragment of **3** is also a dimeric structure. A similar structure has been observed for an alkoxysulfonium salt (ref 2).

(9) If the selenium atom becomes more cationic, the positive charge would delocalize as shown below. In this case, the length of the Se−O bond would become shorter due to the increased double bond character of the Se−O bond. We observed this phenomenon in some cases (Zhang, J.; Saito, S.; Koizumi, T. unpublished results).



(10) Experimental procedure: To the solution of chlorooxaphenylselenurane[5] (**2**, 79 mg, 0.23 mmol) in anhydrous CH_2Cl_2 (6 mL) was added silver tetraflouroborate (45 mg, 0.23 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was then stirred at room temperature for 20 min, while the precipitation of AgCl deposited. Filtration of AgCl and evaporation of the solvent gave optically pure alkoxyselenonium salt **4** as crystals (83 mg) in 91% yield. The product was further purified by crystallization from hexane and CH_2Cl_2. See Supporting Information for the spectral data.

(11) Crystallographic data for **4**: MF = $C_{16}H_{21}BF_4OSe$, MW = 395.10, orthorombic; a = 11.351(3), b = 13.786(2), c = 10.795(3) Å, V = 1689.3(6) Å^3, space group $P2_12_12_1$, Z = 4, D_c = 1.55 g/cm^3. Data collection was done using Mo Kα radiation (μ= 22.6 cm^{-1}) with a rotating anode diffractometer (50 kv, 120 mA). A total of 2305 reflections was collected, of which 1316 reflections with $I_o > 3\sigma(I_o)$ were used in the refinement. The final R factor was 0.035 (R_w = 0.037). The final difference peaks were $\rho_{max} = 0.31$ and $\rho_{min} = -0.28$ e/Å^3. See Supporting Information for further details of the crystal structures.

(12) On the basis of the present study, it is likely that the ^{77}Se NMR chemical shift of the free selenoxonium cation is at the lowest field, and we were not able to exclude the possibility that the complex **4** is completely dissociated in solution. On the other hand, the ^{77}Se NMR chemical shifts of **2**, **3**, and **5** are different from that of **4**, and they are obviously affected by the anionic fragment. Therefore, we concluded that **2** and **5** are haloselenuranes, **3** is a haloselenurane−Lewis acid complex, and they are not free selenoxonium cations. We assume that the complex **4** does not completely dissociate since the length of the Se−F bond is relatively short (Table 1).

(13) It is noteworthy that the copuling between the selenium atom and the fluorine atom was not observed (Table 1). We assume that a fast intermolecular exchange process of the fluorine atom takes place in a solution of **4** or **5** in $CDCl_3$. Wynne et al. prapared arylselenium trifluorides and observed a similar phenomenon. See: Maxwell, W. M.; Wynne, K. J. *Inorg. Chem.* **1981**, *20*, 1707−1712.