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First Isolation and Crystal Structure of Heavier Chalcogenenium Cations (RSe^+, RTe^+) Stabilized by Two Neighboring Amino Groups

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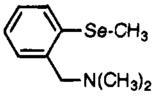
There has been much interest in the preparation and property of chalcogenenium cations (RX^+: X = S, Se, Te) over the last several decades.[1,2] Although a number of studies for sulfenium ions (RS^+) have been reported, there is no report concerning the actual structure of the sulfenium ions.[1] In contrast, the chemistry of their analogous species of heavier group 16 elements, e.g., selenenium and tellurenium cations (RSe^+, RTe^+), has received much less attention.[2] Recently, we have described that either the reaction of *N*-methyl-5*H*,7*H*-dibenzo[*b*,*g*][1,5]selenazocine with *tert*-butyl hypochlorite (*t*-BuOCl) or the reaction of *N*-benzyl-1,11-(methanoaminomethano)-5*H*,7*H*-dibenzo[*b*,*g*][1,5]selenazocine with *N*-bromosuccinimide gave the hypervalent selenuranes containing a transannular Se−N bond.[3] We have now found that the reaction of a linear selenide, 2,6-bis[(dimethylamino)methyl]phenyl methyl selenide (**1**), with *t*-BuOCl gave the *Se*-demethylated product, i.e., the selenenium cation, without formation of the corresponding selenoxide, in which its novel *Se*-dealkylation was induced by the neighboring group participation of the two nitrogen atoms. This paper presents the preparation, crystal structure, and properties of the first selenenium and tellurenium cations stabilized by two intramolecular amino groups.

Generally, the reactions of phenyl methyl selenide (PhSeMe) and 2-[(dimethylamino)methyl]phenyl methyl selenide (**5**) with *t*-BuOCl gave the corresponding selenoxides [PhSe(O)Me and **6**] in good yields. *t*-BuOCl is widely used as an oxidant for the conversion of selenides into selenoxides.[2] Surprisingly, however, treatment of a selenide having two amino ligands, 2,6-bis[(dimethylamino)methyl]phenyl methyl selenide (**1**), with *t*-BuOCl in anhydrous MeOH at 0 °C gave the *Se*-demethylated product, the selenenium cation (**2**), which was converted into the PF_6^- salt upon treatment with KPF_6 (Scheme 1).[4] Thus, the result indicates that the selenide **1** underwent *Se*-dealkylation (i.e., cleavage of a C−Se bond) to form the selenenium cation **2** on reaction with *t*-BuOCl, although the reaction of normal alkyl-substituted selenides with *t*-BuOCl led to the selenoxides. This is the first example of a remarkably stable selenenium cation salt.



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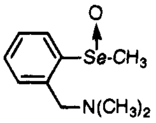

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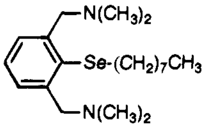

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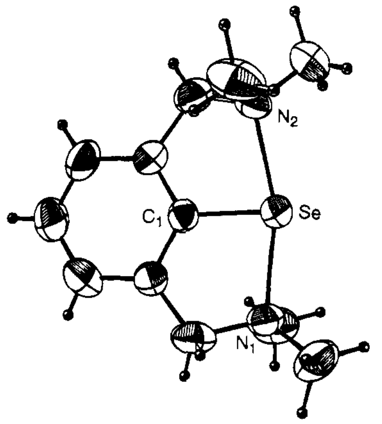
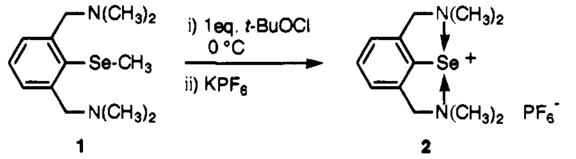


Figure 1. Crystal structure of selenenium salt **2**. Selected bond lengths (Å) and angles (deg): Se−N(1) 2.180(7), Se−N(2) 2.154(7), Se−C(1) 1.874(8), N(1)−Se−N(2) 161.9(3), N(1)−Se−C(1) 81.0(3), N(2)−Se−C(1) 80.9(3).

Scheme 1



The selenenium cation **2** in solution was characterized by spectroscopic means.[5,6] The proton and carbon-13 absorptions due to the methyl group in selenide **1** were not present in the spectra of **2**. The ^{77}Se NMR spectrum of **2** in CD_3CN shows a singlet peak at δ 1208, shifted downfield from the resonance (^{77}Se δ 90; q, J_{Se-H} = 12 Hz) of selenide **1**.[6,7] Its remarkable low-field ^{77}Se chemical shift is characteristic of cationic species.[2] The ^{31}P NMR spectrum of the PF_6^- anion of **2** in CD_3CN shows a phosphorus absorption at δ −144.8 (sept, J_{P-F} = 707 Hz), in the region of ionic PF_6^-.

The crystal structure of the selenenium cation **2** was determined by X-ray diffraction analysis.[8] The X-ray data reveals no interaction at all between the counteranion and countercation (Figure 1).[9] There are short intramolecular Se···N contacts of 2.154 and 2.180 Å, which are remarkably shorter than the sum of the van der Waals radii (3.5 Å) of the two elements. Normally, the bond length of the covalent bond of

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(1) *Topics in Sulfur Chemistry*; Senning, A., Ed.; Georg Thieme: Stuttgart, 1976.

(2) (a) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1; 1987; Vol. 2. (b) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, 1986. (c) Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordon and Breach Science: New York, 1974.

(3) Fujihara, H.; Mima, H.; Ikemori, M.; Furukawa, N. *J. Am. Chem. Soc.* **1991**, *113*, 6337−6338. Fujihara, H.; Mima, H.; Erata, T.; Furukawa, N. *J. Am. Chem. Soc.* **1993**, *115*, 9826−9827.

(4) The preparation, physical properties, and spectral data of **1**−**4** are described in the supporting information.

(5) NMR data. **1** ($CDCl_3$): ^{1}H δ 2.09 (s, 3H, $SeCH_3$), 2.26 (s, 12H, CH_3), 3.73 (s, 4H, CH_2), 7.22−7.30 (m, 1H, ArH), 7.34−7.39 (m, 2H, ArH); ^{13}C δ 9.7, 45.3, 64.7, 127.8, 128.4, 133.7, 143.3; ^{77}Se δ 90.0 (q, J_{Se-H} = 12 Hz). **2** (CD_3CN): ^{1}H δ 2.82 (s, 12H, CH_3), 4.04 (s, 4H, CH_2), 7.25−7.31 (m, 2H, ArH), 7.32−7.40 (m, 1H, ArH); ^{13}C δ 49.0, 64.4, 126.5, 129.0, 133.7, 133.8; ^{77}Se δ 1208.3 (s); ^{31}P δ −144.8 (sept, J_{P-F} = 707 Hz) (relative to H_3PO_4). **3** ($CDCl_3$): ^{1}H δ 0.85 (t, 3H, CH_3), 1.24−1.40 (m, 2H, CH_2), 1.56−1.69 (m, 2H, CH_2), 2.20 (s, 12H, NCH_3), 2.55 (t, 2H, CH_2), 3.60 (s, 4H, CH_2), 7.16−7.24 (m, 1H, ArH), 7.26−7.32 (m, 2H, ArH); ^{13}C δ 9.1, 13.4, 25.2, 33.8, 44.7, 68.5, 122.9, 127.2, 127.4, 144.9; ^{125}Te δ 287.2 (m). **4** (CD_3CN): ^{1}H δ 2.97 (s, 12H, CH_3), 4.03 (s, 4H, CH_2), 7.30−7.43 (m, 3H, ArH); ^{13}C δ 50.6, 67.2, 125.4, 127.1, 129.9, 138.5; ^{125}Te δ 1949.8 (s); ^{31}P δ −144.9 (sept, J_{P-F} = 707 Hz).

(6) The ^{77}Se chemical shift is relative to Me_2Se. The ^{125}Te chemical shift is relative to Me_2Te.

(7) The ^{77}Se chemical shift of phenylselenenyl bromide (PhSeBr) is δ 867.[2]

(8) Crystal data for **2**: $C_{12}H_{19}N_2SePF_6$, monoclinic, space group $P2_{1/c}$, a = 9.254(2) Å, b = 9.856(1) Å, c = 18.328(2) Å, β = 93.65(1)°, V = 1668.3 Å^3, Z = 4, D = 1.65 g/cm^3, Mo Kα radiation (λ = 0.710 73 Å), CAD4 diffractometer, 1736 with $I > 3\sigma(I)$. The structure was solved by direct methods and refined anisotropically by full-matrix least squares using the MolEN program package. The final R value was 0.053.

(9) The crystal structure of PhSeBr shows a covalent bond between Se and Br.[2a]

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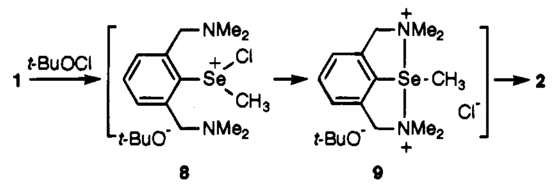
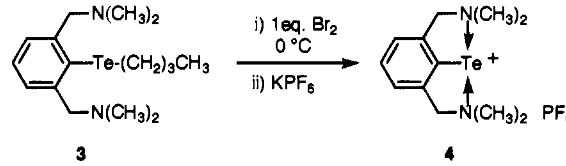
Scheme 2



Scheme 3



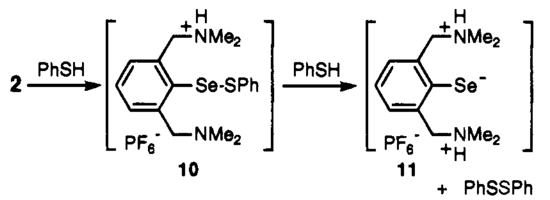
Se–N is 1.87 Å. The angle of N···Se···N is 161.9°, which is strongly distorted from a linear arrangement. The X-ray data suggest that the selenenium cation **2** is considered to be stabilized by the neighboring-group participation of the two nitrogen atoms.

These NMR and X-ray data clearly indicate the selenenium cation **2**, which may be formed in the following mechanism. The selenium of **1** reacts with chlorine of *t*-BuOCl to form the selenonium cation **8**, which subsequently is converted into a hypercoordinate selenium species **9** by the neighboring-group participation of two amino nitrogens. Finally, the chloride anion attacks the methyl carbon atom on selenium of **9** to generate **2** and methyl chloride (Scheme 2). Actually, an alkyl chloride, *n*-octyl chloride, was obtained in the reaction of the octyl analogue of **1**, 2,6-bis[(dimethylamino)methyl]phenyl *n*-octyl selenide (**7**), with *t*-BuOCl. This is a novel dealkylation promoted by the neighboring-group participation of two nitrogen atoms. This dealkylation reaction was also observed in the reaction of the selenides **1** and **7** with Br_2, which resulted in the formation of the selenenium salt **2**.

Similar reaction of a telluride, 2,6-bis[(dimethylamino)methyl]-phenyl *n*-butyl telluride (**3**), with Br_2 (1 equiv) afforded the first isolable tellurenium cation (**4**) (Scheme 3).[4,5] The ^{125}Te NMR spectrum of **4** in CD_3CN shows a significant downfield shift at δ 1950 from the peak (δ 287) of telluride **3**.

Interestingly, benzenethiol (PhSH, 2 equiv) was oxidized quantitatively to diphenyl disulfide (PhSSPh) on treatment with selenenium cation **2** under an Ar atmosphere at room temperature; during the reaction, solutions of **2** and PhSH were followed by ^{77}Se NMR spectroscopy. The ^{77}Se NMR spectrum indicates that the Se peak (δ 1208) of **2** is changed to high field at δ 6, which suggests the formation of species **11**, and then the absorption of δ 6 is again changed to the peak of selenenium cation **2** after addition of air to the reaction mixture solutions. After the usual workup, the selenenium cation **2** was recovered quantitatively. This redox reaction may proceed as follows (Scheme 4).[10] The thiol attacks the selenium atom of **2** to form the intermediary selenosulfide (**10**), which converts into the selenolate anion (**11**) by reaction of a second thiol. The selenolate anion formed is oxidized to the selenenium cation **2** by oxygen. This result suggests that the selenenium cation **2** may become the selenocysteine model system in glutathione peroxidase.[11]

Scheme 4



On the other hand, on treatment of selenenium salt **2** with methyl triflate ($MeOSO_2CF_3$) in anhydrous CH_2Cl_2 under an Ar atmosphere at room temperature for 24 h, none of the *N*-methylated ammonium salt and the *Se*-methylated selenide was obtained, and **2** was recovered. Analogously, **2** did not react with olefins (norbornene, stilbene) and phenylacetylene. It was reported that phenylselenenyl halides or pseudohalides (PhSeX: X = Cl, Br, OSO_2CF_3) reacted with such olefins to give the addition products.[2] These reactivities of **2** cannot be explained at the present time. Further studies for the characterization of the selenenium and tellurenium cations are in progress.[12]

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Supporting Information Available: Preparation and physical and spectral data of **1**–**4** and tables of positional parameters, bond distances and angles, and torsional angles for the X-ray analysis of **2** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(10) An electron transfer pathway between **2** and benzenethiol seems to be difficult, since the reduction potential of **2** is −1.87 V (*vs* Ag/0.01 M $AgNO_3$) and the oxidation potential of the thiol is 0.20 V (*vs* Ag/0.01 M $AgNO_3$).

(11) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *116*, 2557–2561 and references cited therein.

(12) One reviewer pointed out the possibility of an anionic selenium ate complex for compound **2**, which is conceivable. However, the selenenium cation **2** would be supported by the following results. (i) Treatment of compound **2** with methyl triflate gave none of the products, while Martin and co-workers found that an anionic sulfur ate complex reacted with CH_3-OSO_2F to afford the *S*-methylated product.[13a] (ii) the ^{77}Se peak in the ^{77}Se NMR spectrum of **2** appeared at a remarkable low field, which indicates the cationic property of selenium. (iii) van Koten and co-workers reported a tin analog of **2**, that is, a triorganotin cation with a 2,6-bis[(dimethyl-amino)methyl]phenyl ligand.[13b]

(13) (a) Lau, P. H. W.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7077–7078. (b) Koten, G. van; Jastrzebski, J. T. B. H.; Noltes, J. G.; Spek, A. L.; Schoone, J. C. *J. Organomet. Chem.* **1978**, *148*, 233–245.