

## The First Example of Ammonium Selenothioates: Isolation and Characterization

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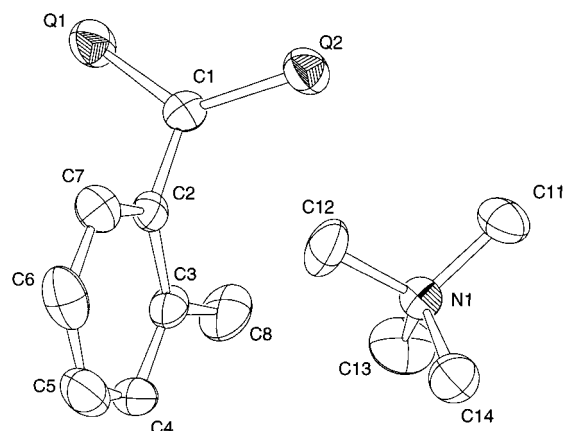
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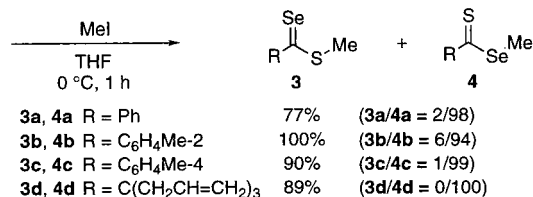
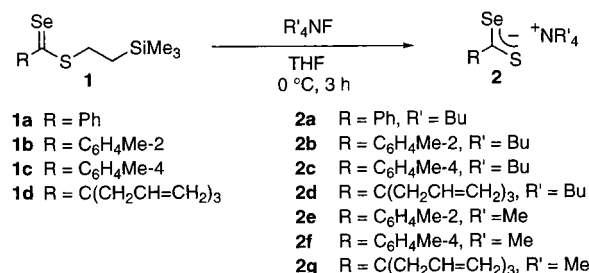
Dithioic acids and their salts have been extensively studied for over 50 years.<sup>1</sup> In contrast, their selenium counterparts, i.e., selenothioic acids and their salts, have been totally ignored,<sup>2</sup> but are nonetheless fundamentally important classes of compounds not only for the syntheses of a variety of selenothioates but also for probing the electronic properties of heavy atom-containing conjugate ions.<sup>3,4</sup> Our recent studies in the area of heavy chalcogenocarboxylic acids<sup>5a</sup> and their metal salts<sup>5b–e</sup> have encouraged us to explore the synthesis of selenothioic acid salts, and we report here the first successful isolation and characterization of ammonium selenothioates.

Selenothioic acid *S*-2-trimethylsilylethyl esters **1**<sup>6</sup> were chosen as a precursor of ammonium selenothioates. The high affinity of a fluorine atom toward a silicon atom enabled us to obtain ammonium salts **2** (Scheme 1). For example, the ester **1a** was treated with a THF solution of tetrabutylammonium fluoride for 3 h at 0 °C. The reaction mixture gradually turned from deep purple to green. Upon subsequent concentration and washing of the residue with hexane, this gave the desired ammonium selenothioate **2a** nearly quantitatively with a purity higher than 90% on the basis of NMR spectra (vide infra). To ensure the efficient formation of ammonium selenothioate **2a**, it was further reacted with methyl iodide to give *S*- or *Se*-methyl selenothioate **3a** and **4a** (**3a/4a** = 2/98) in 77% yield. Similar reactions of **1b–d** proceeded smoothly to form ammonium selenothioates **2b–d** as green to purple oils with high efficiency.<sup>7</sup> The methylation of



**Figure 1.** ORTEP drawing of **2e**. Hydrogen atoms are omitted for clarity. The atoms Q1 and Q2 represent selenium or sulfur atom. Selected bond lengths (Å): Q1–C1, 1.787(4); Q2–C1, 1.757(9); C1–C2, 1.486(5). Selected bond angles (deg): Q1–C1–Q2, 126.4(2); Q1–C1–C2, 117.1(3), Q2–C1–C2 116.5(3).

### Scheme 1



(1) For reviews of dithioic acids and their salts, see: (a) Scheithauer, S.; Mayer, R. In *Topics in Sulfur Chemistry*; Senning, A., Ed.; Georg Thieme Publishers: Stuttgart, Germany, 1979; Vol. 4. (b) Mayer, R.; Scheithauer, S. In *Methoden der Organischen Chemie*; Falbe, J., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1985; Band E5, Teil 2, p 891. (c) Kato, S.; Murai T. In *Supplement B: The Chemistry of Acid Derivatives*; Patai, S., Ed.; John Wiley & Sons: New York, 1992; Vol. 2, p 803. (d) Murai, T.; Kato, S. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 5, p 545.

(2) Very recently, Nakayama et al. have reported the formation of inner salts involving selenothiocarboxylate and diselenocarboxylate groups; see: (a) Nakayama, J.; Akiyama, I.; Sugihara, Y.; Nishio, T. *J. Am. Chem. Soc.* **1998**, *120*, 10027. (b) Nakayama, J.; Akiyama, I.; Sugihara, Y. *Phosphorus Sulfur and Silicon* **1998**, *136*, 137, 138, 569.

(3) Several types of heavy atom-containing allylic anions have been theoretically studied, see: (a) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 9287. (b) M6, O.; Y6nez, M.; Decouzon, M.; Gal, J.-F.; Maria, P.-C.; Guillemin, J.-C. *J. Am. Chem. Soc.* **1999**, *121*, 4653.

(4) Increasing attention has been paid to theoretical studies on selenoic acids and their heavy isologues; see: (a) Jemmis, E. D.; Giju, K. T.; Leszczynski, J. *J. Phys. Chem. A* **1997**, *101*, 7389. (b) Remko, M.; Rode, B. M. *J. Phys. Chem. A* **1999**, *103*, 431. (c) Gonz6lez, A. I.; M6, O.; Y6nez, M. *J. Phys. Chem. A* **1999**, *103*, 1662.

(5) (a) Kato, S.; Kawahara, Y.; Kageyama, H.; Yamada, R.; Niyomura, O.; Murai, T.; Kanda, T. *J. Am. Chem. Soc.* **1996**, *118*, 1262. (b) Kawahara, Y.; Kato, S.; Kanda, T.; Murai, T.; Ebihara, M. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3507. (c) Kato, S.; Kitaoka, N.; Niyomura, O.; Kitoh, Y.; Kanda, T.; Ebihara, M. *Inorg. Chem.* **1999**, *38*, 496. (d) Niyomura, O.; Kato, S.; Kanda, T. *Inorg. Chem.* **1999**, *38*, 507. (e) Kato, S.; Niyomura, O.; Nakaiida, S.; Kawahara, Y.; Kanda, T.; Yamada, R.; Hori, S. *Inorg. Chem.* **1999**, *38*, 519 and references therein.

(6) The esters **1** were prepared according to the literature, see: (a) Murai, T.; Ogino, Y.; Mizutani, T.; Kanda, T.; Kato, S. *J. Org. Chem.* **1995**, *60*, 2942. (b) Murai, T.; Takada, H.; Kakami, K.; Fujii, M.; Maeda, M.; Kato, S. *Tetrahedron* **1997**, *53*, 12237.

**2b–d** took place at their selenium atoms almost exclusively to give esters **4** as deep blue oils in high yields. The use of tetramethylammonium fluoride gave ammonium salts **2e–g** as green to purple solids.

The tetramethylammonium selenothioate **2e** adopts a monomeric structure, as evidenced by X-ray crystallography,<sup>8,9</sup> and its molecular structure is shown in Figure 1. For **2e**, two independent molecules were present in one asymmetric unit and their average data are shown. The selenothiocarboxyl unit in **2e** has a completely trigonal-planar geometry. The dihedral angle formed by the selenothiocarboxyl unit and the phenyl plane is almost a right angle (99.4(4)°).

The structure of **2** in solution was investigated by NMR spectroscopy. The results are shown in Table 1 along with those

(7) Although the ammonium selenothioates **2** were sensitive toward water and oxygen, they were easily handled under an inert atmosphere at room temperature.

(8) Crystal data of **2e**: C<sub>12</sub>H<sub>10</sub>NSSe, FW = 288.31, monoclinic, space group P2<sub>1</sub>/n, a = 14.233(3) Å, b = 9.036(5) Å, c = 21.565(4) Å, β = 92.92(2)°, V = 2769(1) Å<sup>3</sup>, Z = 8, D<sub>calc</sub> = 1.383 g·cm<sup>-3</sup>, temperature 193 K, R = 0.040, R<sub>w</sub> = 0.034, 3671 reflections (I > 3σ(I)), 271 parameters.

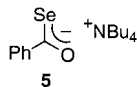
(9) The position of the sulfur and selenium atoms is disordered. The selenium or sulfur atom appeared at the position [Q(1)] or at the position [Q(2)] shown in Figure 1. The occupancy of the selenium atom is 0.8 in [Q(1)] and 0.2 in [Q(2)], respectively, and the reverse results are obtained for the sulfur atom.

**Table 1.** Typical Spectroscopic Properties of Compounds **1**, **2**, and **4**

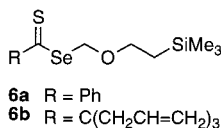
compd	<sup>13</sup> C NMR <sup>a</sup> δ [ppm]	<sup>77</sup> Se NMR <sup>a</sup> δ [ppm]	<sup>1</sup> J <sub>Se-C</sub> <sup>b</sup> [Hz]	UV/vis <sup>c</sup> n-π* λ <sub>max</sub> [nm] (log ε)
<b>1a</b>	233.3	1599.0	221.1	605 (2.21)
<b>1b</b>	237.2	1669.7	222.3	589 (2.11)
<b>1c</b>	232.6	1555.1	220.4	603 (2.23)
<b>1d</b>	251.9	1536.3	225.2	580 (2.30)
<b>2a</b>	254.3	1205.0	209.6	587 (2.29)
<b>2b</b>	260.6	1262.4	207.7	561 (2.29)
<b>2c</b>	254.1	1177.7	201.8	597 (2.05)
<b>2d</b>	273.8	1105.6	208.7	583 (1.99)
<b>2e</b>	262.9	1256.6	<i>d</i>	[547] <sup>e</sup>
<b>2f</b>	257.1	1175.6	<i>d</i>	[567, sh] <sup>e</sup>
<b>2g</b>	275.3	1110.4	208.7	577 (1.92), [579] <sup>e</sup>
<b>4a</b>	233.3	710.9	158.9	514 (2.27)
<b>4b</b>	238.4	764.6	162.8	503 (2.06)
<b>4c</b>	232.5	696.6	158.0	514 (2.21)
<b>4d</b>	252.4	746.6	169.7	490 (2.18)

<sup>a</sup> CDCl<sub>3</sub> was used as a solvent for **1** and **4**, whereas THF-*d*<sub>8</sub> and CD<sub>3</sub>CN were used for **2**. <sup>b</sup> Coupling constants were determined in the <sup>13</sup>C NMR spectra. <sup>c</sup> THF was used as a solvent. <sup>d</sup> The coupling was not observed because of the low solubility. <sup>e</sup> The UV-vis spectra were measured in the solid state.

of *S*-esters **1** and *Se*-esters **4**. In <sup>13</sup>C NMR spectra, the signals of the carbonyl carbon atom of aromatic esters **1a–c** and **4a–c** were observed at 235.0 ± 2.5 ppm. On the other hand, those of **2** were shifted to a lower field by about 26 ppm. In the <sup>77</sup>Se NMR spectra, the signals of **2** were observed midway between those of **1** and **4**, but they were still in the range of those of selenocarbonyl groups.<sup>10</sup> The coupling constants between the carbon and selenium atoms of **2** were larger than 200 Hz. For comparison, the coupling constant in ammonium selenobenzoate **5**<sup>11</sup> was also measured to be 192.1 Hz. Furthermore, two typical types of couplings for

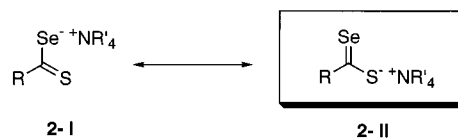
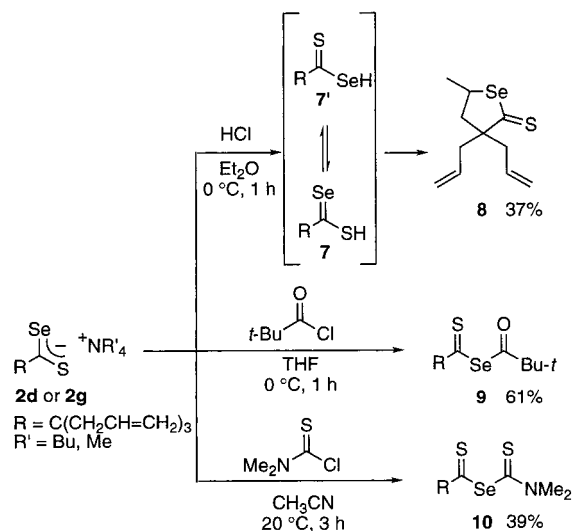


carbon–selenium single and double bonds (<sup>1</sup>J<sub>C–Se</sub> = 175.75 Hz, <sup>1</sup>J<sub>C=Se</sub> = 224.7 Hz) were observed in diselenobenzoic acid methyl ester (PhC(Se)SeMe). The absorptions of **2** that are probably due to n–π\* transitions are substantially red-shifted compared to those of **4** and rather close to those of **1** in the UV-vis spectra. Accordingly, the contribution of the resonance form **2-II**, where the electrons of selenothiocarboxyl groups reside on the sulfur atom, to the resonance hybrid **2** appears to be more important than that of resonance form **2-I**, and the carbon–selenium bond of **2** possesses a double-bond character (Scheme 2). These properties may depend on a subtle balance between the stability of a carbon–selenium or carbon–sulfur bond and the electronegativity of both atoms, although further studies are needed. To confirm that the electronic properties of ammonium selenothioates were independent of the starting esters, *Se*-esters **6** were reacted with a THF solution of tetrabutylammonium fluoride to give ammonium salts **2a** and **2d**. They exhibited exactly the same



(10) (a) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Am. Chem. Soc.* **1981**, *103*, 7055. (b) Peng, J.; Barr, M. E.; Ashburn, D. A.; Odom, J. D.; Dunlap, R. B.; Silks, L. A. *J. Org. Chem.* **1994**, *59*, 4977. (c) Duddeck, H. *Prog. NMR Spectrosc.* **1995**, *27*, 1. (d) Klapötke, T. M.; Broschag, M. *Compilation of Reported <sup>77</sup>Se NMR Chemical Shifts*; John Wiley & Sons: New York, 1996.

(11) The ammonium selenobenzoate **5** was prepared from *O*-2-trimethylsilylethyl selenobenzoate in a similar way to that in Scheme 1.

**Scheme 2****Scheme 3**

spectra as those of **2a** and **2d** obtained from **1a** and **1d**. The UV-vis spectra of **2e–g** measured in the solid state were also close to those of **2a–d** and **2g** in solution. These results have implied that the electrons of selenothiocarboxyl groups of **2** reside on the sulfur atom even in the solid state.

The results of the reactivity tests carried out with ammonium salts **2** are shown in Scheme 3. When the ammonium salt **2d** was treated with hydrochloric acid in Et<sub>2</sub>O, the mixture immediately changed from green to blue. It then turned reddish to orange within 1 h to give selenothioic acid **7** and/or **7'**.<sup>12</sup> The acylation and thiocarbonylation of ammonium selenothioate **2g** successfully gave rare examples of heavy congeners of acid anhydrides **9** and **10** with high selectivity.<sup>13</sup> In these reactions no products derived from the acylation at the sulfur atom of **2g** were observed.

In summary, we have demonstrated the first example of ammonium selenothioates and their electronic properties and reactivity. Further efforts to examine their applications as a new type of heavy atom-containing conjugate anion are currently in progress.

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**Supporting Information Available:** Experimental procedures, compound characterization data for **1–10**, tables of crystallographic data including atomic positional and thermal parameters for **2e** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) The following spectroscopic data of a blue solution derived from ammonium selenothioate **2g** and Et<sub>2</sub>O solution of HCl at –78 °C have supported the formation of selenothioic acid **7**. A broad signal at δ 8.36 in the <sup>1</sup>H NMR spectrum may be ascribed to the signal of the acidic proton of **7**, and the carbonyl carbon atom of **7** was observed at δ 251.4 in the <sup>13</sup>C NMR spectrum at –20 °C, although the selenium atom of **7** was not detected in the <sup>77</sup>Se NMR spectrum probably because of the rapid tautomerization between **7** and **7'**. The absorption that could be ascribed to n–π\* transitions of **7** was detected at 603 nm in the UV-vis spectrum.

(13) To the best of our knowledge, no examples of acid anhydride derivatives bearing a selenothiocarboxyl group are known.