New Chalcogenotelluroxides from 5*H*,7*H*-Dibenzo[*b*,*g*][1,5]tellurazocine and Related Hypervalent Azatelluranes. The First Molecular Structure of a Selenotelluroxide

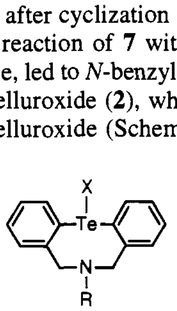
Hisashi Fujihara,*[†] Toshinori Uehara,[‡] and
Naomichi Furukawa*[‡]

Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305, Japan
Environmental Science Research Institute
Kinki University, Kowakae, Higashi-Osaka 577, Japan

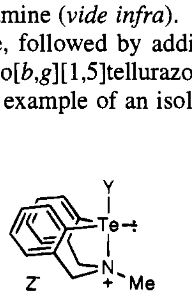
Received March 20, 1995

The chemistry of compounds having a double bond between two chalcogen atoms has been a subject of growing interest. Although thiosulfoxides ($R_2S{=}S$) have been suggested as reactive intermediates in reactions of organosulfur compounds, there is no report concerning the isolation of stable alkyl- and/or aryl-substituted thiosulfoxides,[1] In contrast, the chemistry of their analogous compounds containing heavier group 16 elements, e.g., chalcogenotelluroxides ($R_2Te{=}S$, $R_2Te{=}Se$) has received much less attention.[2,3] Recently, we have shown that the reactive species generated on the heteroatoms of cyclic compounds involving multiheteroatoms were stabilized by a transannular participation of the second heteroatoms.[4] We now report the preparation, first crystal structure, and reactivities of novel thio- and selenotelluroxides (**1** and **2**) of 5*H*,7*H*-dibenzo-[*b*,*g*][1,5]tellurazocine, stabilized by the transannular participation of the tertiary amine, and related new hypervalent azatelluranes derived from **1**.

When a tellurane, bis(2-bromomethylphenyl)tellurium dibromide (**7**),[5] was treated with methylamine, followed by addition of Na_2S to reduce the bromine of the dibromotelluride, surprisingly, the sulfur-substituted telluroxide **1** was obtained instead of *N*-methyl-5*H*,7*H*-dibenzo[*b*,*g*][1,5]tellurazocine (**3**) (Scheme 1).[6,7] It has been reported that diaryl dihalotellurides (Ar_2TeHal_2) were reduced to the corresponding diaryl tellurides (Ar_2Te) upon treatment with Na_2S or Na_2Se.[3] Actually, the dibromotelluride **7** reacted with Na_2S to afford 5*H*,7*H*-dibenzo-[*b*,*g*][1,5]tellurathiocin.[5] Thiotelluroxide **1** may be formed via an intermediary formation of a bromoammoniotellurane of **3** derived after cyclization of **7** with the amine (*vide infra*). The similar reaction of **7** with benzylamine, followed by addition of Na_2Se, led to *N*-benzyl-5*H*,7*H*-dibenzo[*b*,*g*][1,5]tellurazocine selenotelluroxide (**2**), which is the first example of an isolable selenotelluroxide (Scheme 1).[6,7]

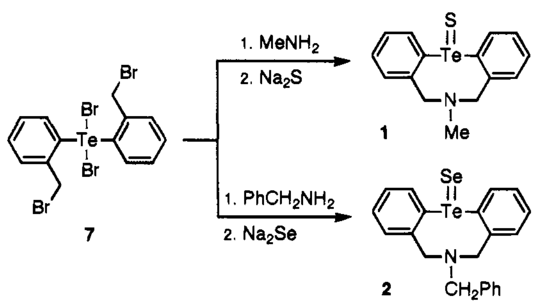


3 X = electron pair, R = Me
4 X = O, R = Me
8 X = electron pair, R = CH_2Ph
9 X = S, R = CH_2Ph



5 Y = Cl, Z = PF_6
6 Y = SMe, Z = TfO

Scheme 1



The crystal structure of the selenotelluroxide **2** was determined by X-ray diffraction analysis,[8,9] As clearly shown in Figure 1, the selenium atom in **2** is bound to the tellurium atom, The Te−Se bond length [2,445(1) Å] of **2** is shorter than a Te−Se single bond (2.54 Å), which shows significant double bond character in the Te=Se moiety.[10] The conformation of the eight-membered ring is boat. There is a short transannular Te···N contact of 2.620 Å, which is remarkably shorter than the sum of the van der Waals radii (3.70 Å). The angle of Se−Te···N is 163,9°, and the C(1)−Te−C(2) bond angle is 102,9°, Thus, the configuration about the tellurium atom is distorted pseudo-trigonal-bipyramidal geometry, The X-ray data suggest that the Te=Se moiety of **2** is considered to be stabilized by the transannular participation of the nitrogen atom.

[†] Kinki University.

[‡] University of Tsukuba.

(1) (a) Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978. (b) Kutney, G. W.; Turnbull, K. *Chem. Rev.* **1982**, *82*, 333−357. (c) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 8, pp 403−415. (d) Oae, S. *Organic Sulfur Chemistry: Structure and Mechanism*; CRC Press: Boca Raton, FL, 1991.

(2) (a) Hereinafter, the term thiotelluroxides and selenotelluroxides are used for the $R_2Te{=}S$ and $R_2Te{=}Se$ moieties. (b) No clear-cut example of the isolation of selenotelluroxide has been hitherto known. (c) The formation of tellurosulfide containing Te−S bond has been proposed: Detty, M. R.; Murray, B. J. *J. Org. Chem.* **1982**, *47*, 1146−1148.

(3) (a) *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, Chapters 3, 6 and 14, and 1987; Vol. 2. The term tellurane has been used for tetracoordinate tellurium(IV) compounds. (b) Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordon and Breach Science: New York, 1974.

(4) Fujihara, H.; Mima, H.; Erata, T.; Furukawa, N. *J. Am. Chem. Soc.* **1992**, *114*, 3117−3118.

(5) Fujihara, H.; Takaguchi, Y.; Chiu, J.-J.; Erata, T.; Furukawa, N. *Chem. Lett.* **1992**, 151−154.

(6) The preparation, physical properties, and spectral data for **1−6**, **8**, and ^{15}N-labeled thiotelluroxide (**9**-^{15}N) are described in the supplementary material.

(7) NMR data. **1** ($CDCl_3$): ^1H δ 2.63 (s, 3 H, NCH_3), 3.89, 3.98 (ABq, J = 15 Hz, 4 H, CH_2), 7.10−7.13 (m, 2 H, ArH), 7.36−7.42 (m, 2 H, ArH), 7.48−7.54 (m, 2 H, ArH), 8.61−8.64 (m, 2 H, ArH); ^{13}C δ 41.6, 59.0, 123.8, 126.6, 130.0, 130.7, 131.8, 139.1. **2** ($CDCl_3$): ^1H δ 3.76, 4.09 (ABq, J = 15 Hz, 4 H, CH_2), 3.94 (s, 2 H, CH_2), 7.09−7.13 (m, 2 H, ArH), 7.33−7.36 (m, 2 H, ArH), 7.41−7.53 (m, 7 H, ArH), 8.65−8.68 (m, 2 H, ArH); ^{13}C δ 53.8, 55.6, 117.4, 126.8, 128.3, 128.6, 130.0, 130.5, 130.8, 132.6, 133.3, 138.4. **3** ($CDCl_3$): ^1H δ 2.31 (s, 3 H, NCH_3), 3.76 (s, 4 H, CH_2), 7.03−7.09 (m, 2 H, ArH), 7.20−7.22 (m, 4 H, ArH), 7.65−7.68 (m, 2 H, ArH); ^{13}C δ 42.0, 58.8, 120.4, 127.85, 127.9, 132.0, 134.4, 140.8; ^{125}Te δ 582. **4** ($CDCl_3$): ^1H δ 2.67 (s, 3 H, NCH_3), 3.93, 3.99 (ABq, J = 15.2 Hz, 4 H, CH_2), 7.15−7.18 (m, 2 H, ArH), 7.35−7.40 (m, 2 H, ArH), 7.47−7.52 (m, 2 H, ArH), 8.24−8.27 (m, 2 H, ArH); ^{13}C δ 42.3, 59.9, 126.6, 129.8, 130.7, 131.2, 131.3, 140.1; ^{125}Te δ 1170. **5** (CD_3CN): ^1H δ 3.09 (s, 3 H, NCH_3), 4.56 (s, 4 H, CH_2), 7.52−7.56 (m, 2 H, ArH), 7.67−7.73 (m, 4 H, ArH), 8.18−8.24 (m, 2 H, ArH); ^{13}C δ 44.4, 62.9, 124.6, 128.4, 131.7, 132.8, 133.6, 141.8; ^{31}P δ −145.0 (sept, J_{PF} = 707 Hz; relative to H_3PO_4), in the region of ionic PF_6^-. **6** ($CDCl_3$): ^1H δ 2.70 (s, 3 H, SCH_3), 2.91 (s, 3 H, NCH_3), 4.19, 4.38 (ABq, J = 15.5 Hz, 4 H, CH_2), 7.35−7.39 (m, 2 H, ArH), 7.51−7.59 (m, 4 H, ArH), 8.20−8.26 (m, 2 H, ArH); ^{13}C δ 12.1, 41.8, 59.4, 119.3, 128.5, 130.7, 132.6, 132.7, 140.3; ^{19}F δ 83.5 (s, relative to C_6F_6), in the region of ionic $CF_3SO_3^-$.

(8) Crystal data for **2**: $C_{21}H_{19}NSeTe$, monoclinic, space group, $P2_1$, a = 10.015(1), b = 10.497(1), and c = 18.001(1) Å, β = 95.91(26)°, V = 1882.2 Å^3, Z = 4, D = 1.74 g/cm^3, Mo Kα radiation (λ = 0.710 73 Å), CAD4 diffractometer, 3181 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 0.029.

(9) According to the X-ray analysis of **2**, there are two independent selenotelluroxides, A and B, in the crystals. The X-ray data of crystal A are described in the text. The length of the Te-Se bond is equal in crystals A and B.

(10) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.

0002-7863/95/1517-6388$09.00/0

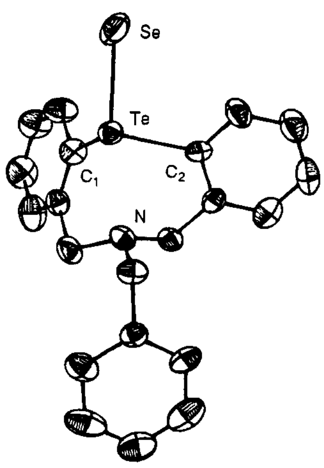
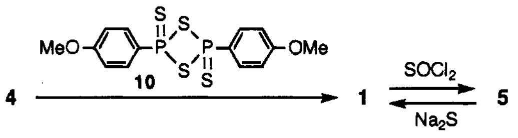


Figure 1. Crystal structure of selenotelluroxide **2**. Selected bond lengths (Å) and angles (deg): Te−Se 2.445(1), Te−C(1) 2.155(9), Te−C(2) 2.150(8), C(1)−Te−C(2) 102.9(3), Se−Te−C(1) 100.5(2), Se−Te−C(2) 98.0(2).

The thio- and selenotelluroxides (**1** and **2**) were characterized by the following spectroscopic and chemical means.[7,11−14] The ^{77}Se NMR spectrum of selenotelluroxide **2** in $CDCl_3$ shows a resonance at δ −164, while its ^{125}Te chemical shift is δ 979, shifted downfield from the resonance (^{125}Te δ 586) of *N*-benzyl-5*H*,7*H*-dibenzo[*b*,*g*][1,5]tellurazocine (**8**).[6,15] Both proton-decoupled ^{77}Se and ^{125}Te NMR spectra of **2** give a large ^{77}Se−^{125}Te coupling constant of $J = 577$ Hz. The ^{125}Te chemical shift of thiotelluroxide **1** in $CDCl_3$ is δ 1029.

Desulfurization reaction of **1** with 1 equiv of $(Et_2N)_3P$ resulted in the formation of the tellurazocine **3** (96%) and $(Et_2N)_3P{=}S$ (99%).[6,7] Treatment of **3** first with *t*-BuOCl, followed by alkaline hydrolysis, gave exclusively the corresponding telluroxide (**4**) (81%).[6,7] It is of particular interest that the telluroxide **4** was converted into the thiotelluroxide **1** upon treatment with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson reagent, **10**) (Scheme 2); in contrast, the similar reaction of bis(2-methylphenyl)telluroxide with Lawesson reagent gave the corresponding telluride as a reduction product.[16]

Scheme 2



The thiotelluroxide **1** can be reacted with thionyl chloride, $SOCl_2$, to give a new chloro-substituted ammoniotellurane (**5**) (84%), which is consistent with the product formed from the reaction of telluroxide **4** with $SOCl_2$.[6,7,11] The ^{125}Te NMR spectrum of **5** in CD_3CN shows a single peak at δ 1146, as is characteristic of a tellurane,[3a] *Te*-Chloroammoniotellurane **5** exists solely as a single conformer, boat form, from −50 to +120 °C, as evidenced from the variable-temperature ^{1}H NMR spectral data. *Te*-Chloroammoniotellurane **5** was converted quantitatively into the thiotelluroxide **1** upon treatment with Na_2S,[6] i.e., **1** arises presumably by an attack of Na_2S on tellurium without reduction of halotellurane **5**. This result suggests that the reaction from **7** to **1** likely proceeds through an intermediate of a *Te*-bromoammoniotellurane of **3** formed by a transannular participation of the nitrogen atom.

The selective *S*-methylation of thiotelluroxide **1** with 1 equiv of methyl triflate (MeOTf, Tf = CF_3SO_2) afforded a novel *Te*-(methylthio)ammoniotellurane (**6**) in 85% yield.[6,7] The tellurane structure of **6** is supported by the ^{125}Te chemical shift of δ 1014.[3a] The tellurane **6** exists solely as a single conformer from −50 to +100 °C, as evidenced from its dynamic ^{1}H NMR spectrum; i.e., the conformation of **6** was fixed as the boat form by a transannular bond between the tellurido and amino groups. The tellurane **6** consists of two unsymmetrical apical ligands, such as thio and ammonio groups, and two equatorial carbon ligands. Normally, telluranes have two symmetrical electronegative groups such as oxygen atoms or halogen atoms at the apical positions, although the chemistry of telluranes is noticeably underdeveloped compared with that of hypervalent organosulfur compounds.[3,17]

In summary, the transannular Te••N interaction of new heterocycles can produce the first stable heavier chalcogenotelluroxides which can convert into the ammoniotelluranes as new types of hypervalent organotellurium compounds.

Acknowledgment. This work was supported in part by Grant No. 06640677 from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: Preparation details and physical and spectral data for **1**−**6**, **8**, and **9**-^{15}N; 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.

JA950901L

---

(11) (a) The X-ray analysis of **1** or **5** showed the boat conformation and the existence of the transannular interaction or bond formation between Te and N atoms; however, the fine structure could not be determined. Nevertheless, the X-ray analyses have been performed several times. (b) The Cl^- salt of **5** was converted to its PF_6^- salt on treatment with NH_4PF_6.

(12) The conformation of **1** or **2** can be assigned to the boat form according to the ^{1}H NMR spectrum. (a) Gellatly, R. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1976**, 913−925. (b) Brieaddy, L. E.; Hurlbert, B. S.; Mehta, N. B. *J. Org. Chem.* **1981**, *46*, 1630−1634 and references cited therein.

(13) (a) The existence of transannular Te••N interaction is supported by NMR studies; i.e., the ^{1}H-decoupled ^{15}N NMR spectrum of 40% ^{15}N-enriched thiotelluroxide (**9**-^{15}N)[6] of *N*-benzyltellurazocine in $CDCl_3$ exhibits one resonance at δ 43.1 which shows ^{125}Te satellite peaks due to the ^{15}N−^{125}Te coupling ($J_{NTe} = 37$ Hz).[13b,c] While the ^{15}N NMR spectrum of the tellurazocine **8**-^{15}N in $CDCl_3$ shows a resonance at δ 36.3, both ^{1}H-decoupled ^{15}N and ^{125}Te NMR spectra of **8**-^{15}N reveal none of the ^{15}N−^{125}Te coupling. (b) ^{15}N chemical shifts were measured by using CH_3CN as an external reference (δ 239.5) and were evaluated from a $^{15}NH_3$ external standard.[13c] (c) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; John Wiley & Sons: New York, 1979.

(14) Reviewers pointed out the possibility of the dipolar form of **1** and **2**, but the relative importance of $R_2Te{=}X$ and $R_2Te^+{-}X^-$ (X = S, Se) is difficult to assess at the present time. Such a problem in $R_2Te{=}O$ has not previously been described specifically.[3] Similarly, the same problem for $R_3P{=}Y$ (Y = S, Se) is still controversial.[3]

(15) ^{125}Te chemical shift is relative to Me_2Te. ^{77}Se chemical shift is relative to Me_2Se.

(16) (a) Sulfoxides were reduced to the sulfides on treatment with the Lawesson reagent, in which thiosulfoxides ($R_2S{=}S$) have been proposed as intermediates: Rasmussen, J. B.; Jorgensen, K. A.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 307 and refs 1b,c. (b) Although Lawesson reagent is well known to be capable of effecting carbonyl−thiocarbonyl exchange,[16c] Lawesson reagent acts as a reductant toward normal sulfoxides, selenoxides, and telluroxides. (c) Cava, M. P.; Levinson, M. I. *Tetrahedron* **1985**, *41*, 5061−5087.

(17) For a review, see: Hayes, R. A.; Martin, J. C. Sulfurane Chemistry. In *Organic Sulfur Chemistry, Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; Chapter 8.