Sterically Protected Dipotassium Germanedithiolate

Tsuyoshi Matsumoto and Kazuyuki Tatsumi*
Research Center for Materials Science, and Department of Chemistry, Graduate School of Science, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8602

(Received July 5, 2001; CL-010628)

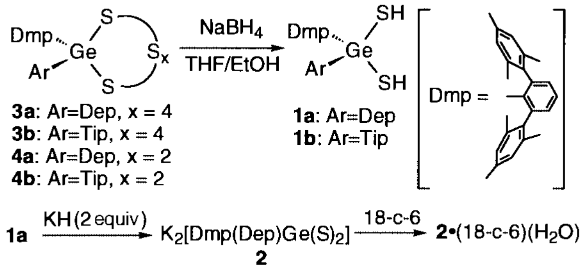
The germanedithiols Dmp(Ar)Ge(SH)$_2$ [Dmp=2,6-dimesitylphenyl; Ar = Dep (2,6-diethylphenyl) **1a**, Tip (2,4,6-triisopropylphenyl) **1b**] were synthesized by the reduction of hexathiagermepanes Dmp(Ar)GeS$_6$ and tetrathiagermolanes Dmp(Ar)GeS$_4$ with NaBH$_4$. The treatment of **1a** with 2 equiv of potassium hydride afforded the dipotassium germanedithiolate **2**.

Although organogermanium compounds have attracted attention as potential functional materials,[1] the chemistry of chalcogen containing germanium compounds is not well investigated. Compounds having two or more Ge–SH functions are useful precursor of heterocycles containing germanium, and in fact dithiagermatitanacycles and their zirconium analogue were synthesized by Steudel[2] and Ando.[3]

The structural properties of organogermanethiols have not been well studied and X-ray crystallographic data are limited to Cy$_3$GeSH (Cy = cyclohexyl).[4] In addition, no structural data on their thiolato anions have been reported.

The synthetic route to germanethiol is limited to the following two methods; (1) reaction of elemental sulfur with hydrogermanes; (2) nucleophilic substitution of the halogermanes by H$_2$S in the presence of amines.[1,3,5] We previously reported the synthesis of hexathiagermepanes **3a**,**b** and tetrathiagermolanes **4a**,**b** via sulfurization of dihydrogermanes, Dmp(Ar)GeH$_2$ [Dmp=2,6-dimesitylphenyl, Ar = Dep (2,6-diethylphenyl), Tip (2,4,6-triisopropylphenyl)].[6] We sensed that the polysulfides could be good precursors for the synthesis of Ge–SH function. Reported in this paper is the successful isolation of the dimercaptogermanes, Dmp(Ar)Ge(SH)$_2$ **1**, from reduction of the polysulfides **3** and **4** (Scheme 1).

Scheme 1.



The treatment of **3a** with LiAlH$_4$ in THF at r.t. turned out to give dihydrogermane, Dmp(Dep)GeH$_2$, quantitatively. In contrast, reduction with NaBH$_4$ in THF generated dimercaptogermane **1a**, although the reaction proceeded very slowly due to low solubility of NaBH$_4$ in THF. Upon warming the reaction system up to 40 °C, partial reduction of Ge–S bonds occurred to give an unseparable mixture of Dmp(Dep)Ge(SH)H and **1a**.[7] The addition of a small amout of ethanol to the THF solution at r.t. worked effectively to afford **1a** in 83 and 79% yields from **3a** and **4a**, respectively. A similar reduction of the mixture of **3b** and **4b** also gave **1b** in 82% yield.[8]

In ^{1}H NMR spectra the singlet peaks attributable to GeSH were observed at 0.52 (**1a**) and 0.63 ppm (**1b**).[9] The Raman spectra of **1a** shows two S–H stretching bands at 2564 and 2552 cm^{-1}, which are shifted to 1863 and 1854 cm^{-1} for Dmp(Dep)Ge(SD)$_2$.[10] Similar S–H stretching bands were observed at 2583, 2563 cm^{-1} for **1b**. The relatively strong Ge–S stretching bands appear at 383.3 and 370.0 cm^{-1} for **1a** and 384.5 and 370.1 cm^{-1} for **1b**, which are similar to the value reported for Me$_3$GeSMe, 385 cm^{-1}.[1,11]

The structure of **1a** is shown in Figure 1.[12] The Ge–S bond lengths are 2.2388(9) and 2.2283(8) Å, which are slightly shorter compared with that of Cy$_3$GeSH [2.253(2) Å] reported earlier.[4] The intramolecular S(1)–S(2) separation is 3.408(1) Å and no significant intermolecular contact was observed between the mercapto groups.

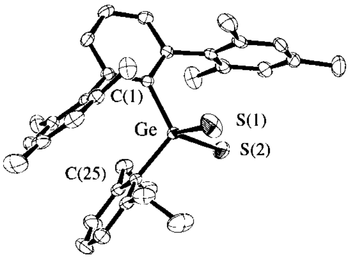


Figure 1. Structure of Dmp(Dep)Ge(SH)$_2$ **1a.** Selected bond lengths (Å) and bond angles (deg): Ge-S(1) 2.2388(9), Ge-S(2) 2.2283(8), Ge-C(1) 1.982(2), Ge-C(25) 1.979(2), S(1)-Ge-S(2) 99.44(4), S(1)-Ge-C(1) 109.36(7), S(1)-Ge-C(25) 116.46(8), S(2)-Ge-C(1) 112.76(7), S(2)-Ge-C(25) 104.39(7), C(1)-Ge-C(25) 113.52(9).

The dipotassium germanedithiolate, K$_2$[Dmp(Dep)Ge(S)$_2$] **2**, was prepared by addition of 2 equiv of potassium hydride to a THF solution of **1a**. The Raman spectra of the potassium salt in solid show a broad band at 400.1 cm^{-1} for the Ge–S vibration, which is slightly shifted to higher frequency compared with **1a**. This shift indicates a partial Ge–S double bond character arising from the resonance form shown in Scheme 2, although weak interactions between potassium cations and the sulfur atoms may exist.

The compound **2** was crystallized from toluene in the presence of 18-crown-6. The resulting colorless crystals were subjected to X-ray analysis, and the salt was formulated as [**2**(18-c-6)(H$_2$O)].[12]

The crystal structure is shown in Figure 2, where K(2) is coordinated by H$_2$O[O(7)], S(1), S(2), and S(1*). Thus [**2**(18-c-6)(H$_2$O)] is crystallized in a dimeric form. Another potassium cation K(1) is coordinated by S(2) and 18-c-6. The Ge–S

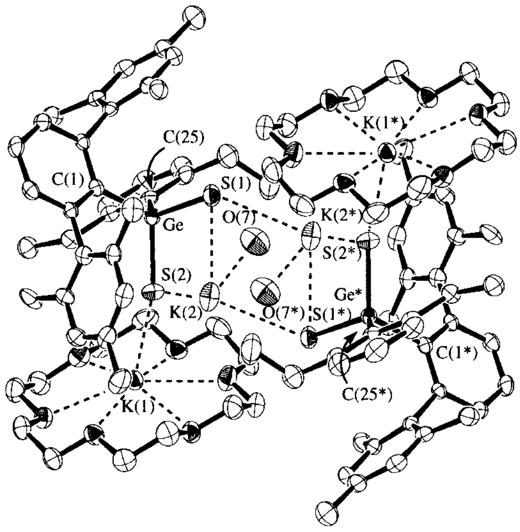
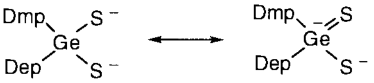


Figure 2. Structure of potassium dithiolate **2**(18-c-6)(H_2O). Selected bond lengths (Å) and bond angles (deg): Ge-S(1) 2.195(1), Ge-S(2) 2.199(1), Ge-C(1) 2.043(4), Ge-C(25) 2.016(4), S(1)-K(2) 3.230(2), S(2)-K(2) 3.058(2), S(2)-K(1) 3.118(2), S(1)-K(2*) 3.134(1), O(7)–S(1) 3.431(5) Å, O(7)–S(2*) 3.338(4), S(1)-Ge-S(2) 107.20(4), S(1)-Ge-C(1) 105.40(10), S(1)-Ge-C(25) 119.0(1), S(2)-Ge-C(1) 116.54(10), S(2)-Ge-C(25) 102.6(1), C(1)-Ge-C(25) 106.7(1), Ge-S(1)-K(2) 86.63(4), S(1)-K(2)-S(2) 68.38(4), Ge-S(2)-K(2) 90.98(4).

Scheme 2.



bond distances are 2.195(1) and 2.199(1) Å, which are shortest among the reported Ge–S single bonds.[1,13] The shortening of the Ge–S bonds by 0.03–0.04 Å on going from **1a** to [**2**(18-c-6)(H_2O)] supports contribution of the resonance form shown in Scheme 2,[14] although the Ge–S distances are considerably longer than Ge=S distances.[15] The K–S distances range from 3.058(2) to 3.230(2) Å, showing that the interactions are weak.

Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

1 P. Riviere, M. R.–Baudet, and J. Satgé in "Comprehensive Organometallic Chemistry II," ed. by E. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon Press, New York (1995), Vol. 2, pp137–216, and references cited therein.

2 J. Albertsen and R. Steudel, *J. Organomet. Chem.*, **424**, 153 (1992).

3 N. Choi, S. Morino, S. Sugi, and W. Ando, *Bull. Chem. Soc. Jpn.*, **69**, 1613 (1996).

4 F. Brisse, F. Bélanger-Gariépy, B. Zacharie, Y. Gareau, and K. Steliou, *New J. Chem.*, **7**, 391 (1983).

5 Y. Cai and B. P. Roberts, *Tetrahedron Lett.*, **42**. 763 (2001).

6 T. Matsumoto, Y. Matsui, Y. Nakaya, and K. Tatsumi, *Chem. Lett.*, **2001**, 60.

7 The generation of Dmp(Dep)Ge(SH)H was confirmed by ^{1}H NMR (δ 6.03 ppm Ge*H*, $CDCl_3$) and EI-MS [*m/z* 554 (M^+)].

8 **1a**: colorless crystals; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.52 (s, 2H), 1.03 (t, *J* = 7.6 Hz, 6H), 1.97 (s, 12H), 2.27 (s, 6H), 2.30 (br m, 4H), 6.74 (s, 4H), 6.82 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H). Anal. Calcd for $C_{34}H_{40}GeS_2$: C, 69.76; H, 6.89; S, 10.95%. Found: C, 69.65; H, 6.94; S, 10.32%. **1b**: colorless crystals; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.63 (s, 2H), 0.85 (d, *J* = 6.9 Hz, 6H), 1.01 (d, *J* = 6.9 Hz, 6H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.93 (br s, 12H), 2.30 (s, 6H), 2.81 (sept, *J* = 6.9 Hz, 1H), 3.10 (sept, *J* = 6.9 Hz, 2H), 6.81 (br s, 2H), 6.83 (s, 4H), 7.01 (br s, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H). Anal. Calcd for $C_{39}H_{50}GeS_2$: C, 71.45; H, 7.69; S, 9.78%. Found: C, 71.10; H, 7.90; S, 9.72%.

9 ^{1}H NMR of dimesitylgermanedithiol was reported at δ 0.90 ppm (GeSH) in C_6D_6. See ref 4.

10 The S–H stretching band of $(CF_3)_3GeSH$ was reported to shift from 2592 to 1862 cm^{-1} by deuteration. R. Eujen and F. E. Laufs, *Z. Anorg. Allg. Chem.*, **561**, 82 (1988).

11 D. F. van de Vondel, E. V. van den Berghe, and G. P. van der Kelen, *J. Organomet. Chem.*, **23**, 105 (1970).

12 The data collection was made with a Rigaku-AFC7 diffractometer equipped with an MSC/ADSC Quantum1 CCD detector. Crystal data for **1a**: $C_{34}H_{40}GeS_2$, M_r = 585.40, triclinic, space group $P\bar{1}$, a = 8.9817(5), b = 11.966(2), c = 15.694(2) Å, α = 68.505(3), β = 75.288(1), γ = 77.806(1)°, V = 1504.8(2) Å^3, Z = 2, D_{calc} = 1.292 g/cm^3, T = 193 K, μ(Mo Kα) = 47.74 cm^{-1}, R = 0.051, R_w = 0.054, GOF = 1.26, 334 variables, 6720 unique reflections [$I > 0\sigma(I)$]. For **2**: $C_{46}H_{64}GeS_2O_7K_2$, M_r = 943.91, triclinic, space group $P\bar{1}$, a = 11.5609(7), b = 12.667(1), c = 18.099(2) Å, α = 101.999(4), β = 102.149(1), γ = 108.640(1)°, V = 2344.4(4) Å^3, Z = 2, D_{calc} = 1.337 g/cm^3, T = 193 K, μ(Mo Kα) = 47.74 cm^{-1}, R = 0.080, R_w = 0.081, GOF = 1.02, 523 variables, 10066 unique reflections [$I > 0\sigma(I)$].

13 K. M. Baines and W. G. Stibbs, *Coord. Chem. Rev.*, **145**, 157 (1995).

14 A similar shortening of the Si–S bonds was observed for the silanethiol Ph_3SiSH [2.151(1) and 2.150(1) Å] and its sodium salt $NaPh_3SiS(H_2O)_3$ [2.079(1) Å]. W. Wojnowski, K. Peters, E.-M. Peters, and H. G. von Schnering, *Z. Kristallogr.* **174**, 297 (1986).

15 T. Matsumoto, N. Tokitoh, and R. Okazaki, *J. Am. Chem. Soc.*, **121**, 8811 (1999), and references cited therein.