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Short Communication

Synthesis and structure of dithiagermocane containing a spiro eight-membered ring

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Abstract

The title compounds were synthesized from $[Ge(OH)_2\{RN(CH_2CH_2O)_2\}]$ (R = H or CH_3) and the corresponding ligands in refluxed methanol. Both compounds have distorted tetrahedral geometry around the coordinated sphere. Distortion may be attributed to the formation of the two eight-membered chelating rings and to the interaction between Ge and the free oxygens or sulfurs of the ligands.

Introduction

The hypervalent species of germanium has attracted much attention recently [1–5]. In previous reports [2, 3], we have published the syntheses and crystal structures of a trigonal bipyramidal germanium complex, dihydroxo(2,2′-iminodiethoxo)germanium(IV) and an octahedral complex, diaquabis(glycolato-*O,O″*)-germanium(IV). In continuation of our research on the coordination chemistry of germanium, we here report the eight-membered ring complexes, bis(2,2′-thiodiethanethiolato-*S,S″*)germanium(IV) (**1**), a new method for the preparation of bis(2,2′-oxydiethanethiolato-*S,S″*)germanium(IV) (**2**) which was first synthesized by Backer and Stienstra [6] from germanium tetrachloride in ethanol with the presence of sodium and the comparison between their X-ray crystal structures.

Experimental

General

All chemicals were commercially available and were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a JEOL EX400 (400 MHz) spectrometer. Mass spectra were obtained on a JEOL-D300 instrument.

Synthesis

$[Ge(S(CH_2)_2S(CH_2)_2S)_2]$ (1)

$HS(CH_2)_2S(CH_2)_2SH$ (**5**) (1.31 ml, 10 mmol) was added dropwise to a solution of $[Ge(OH)_2\{HN(CH_2CH_2O)_2\}]$ (**3**) [2] (1.05 g, 5 mmol) in methanol (500 ml) and the mixture was refluxed for 3 h. After the mixture had stood at room temperature for 72 h, the precipitate was filtered and recrystallized from methanol (yield 45%). A similar result was obtained when $[Ge(OH)_2\{CH_3N(CH_2CH_2O)_2\}]$ (**4**) was used as the starting material. ^1H NMR ($CDCl_3$, δ (ppm)): 3.1

TABLE 1. Selected crystallographic data of **1** and **2**

	1	**2**
Formula	$C_8H_{16}GeS_6$	$C_8H_{16}GeO_2S_4$
Molecular weight	377.16	345.04
Space group	$Pca2_1$	$P2_1/c$
Crystal system	orthorhombic	monoclinic
Crystal size (mm)	0.35×0.40×0.50	0.45×0.50×0.55
Cell dimensions		
a (Å)	12.167(1)	15.824(2)
b (Å)	11.495(1)	7.411(1)
c (Å)	10.3928(6)	23.303(7)
β (°)		94.99(2)
V (Å^3)	1453.4(2)	2722(1)
Z	4	8
D_{calc} (g/cm^3)	1.72	1.68
μ (mm^{-1})	2.88	2.79
Radiation (Å)	Mo Kα	Mo Kα
Diffractometer	CAD4	CAD4
Scan technique	$\theta/2\theta$	$\theta/2\theta$
Scan speed (°/min)	1.27–8.24	1.83–8.24
2θ Range (°)	$2<2\theta<50$	$2<2\theta<50$
Reflections measured	1402	4898
Unique reflections	1357	4777
Observed reflections	1262 ($>2\sigma$)	3319 ($>2\sigma$)
Temperature (K)	298	298
Absorption correction	experimental Ψ rotation	experimental Ψ rotation
Min. and max. transmission	0.876, 0.999	0.807, 1.000
Program	NRCVAX package [7]	NRCVAX package [7]
R; R_w (%)	3.9; 3.9	3.0; 2.2
Weight	$1/\sigma^2$	$1/\sigma^2$
Parameters refined	136	272
Δ/σ	0.004	0.001
Peaks in last D map (e/Å^3)	−0.96–0.37	−0.48–0.30

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TABLE 2. Fractional atomic parameters and equivalent isotropical thermoparameters of **1** and **2**

	x	y	z	B_{iso}[a]
1				
Ge	0.48678(7)	0.2450(1)	0.42125	2.20(5)
S(1)	0.3523(2)	0.3725(2)	0.3884(3)	3.0(1)
S(2)	0.4760(3)	0.3149(3)	0.0984(4)	4.0(2)
S(3)	0.6490(2)	0.3265(3)	0.3756(4)	3.8(2)
S(4)	0.4814(3)	0.0758(2)	0.3162(3)	3.0(1)
S(5)	0.2623(3)	0.1187(3)	0.5129(4)	3.4(1)
S(6)	0.5154(2)	0.2208(2)	0.6295(3)	3.2(1)
C(1)	0.416(1)	0.4804(9)	0.281(1)	3.8(6)
C(2)	0.411(1)	0.450(1)	0.147(1)	4.4(7)
C(3)	0.622(1)	0.350(1)	0.109(1)	4.8(7)
C(4)	0.681(1)	0.282(1)	0.212(1)	4.8(7)
C(5)	0.4415(9)	−0.0235(8)	0.444(1)	3.7(6)
C(6)	0.319(1)	−0.0228(9)	0.464(1)	3.3(5)
C(7)	0.3049(9)	0.135(1)	0.676(1)	3.6(6)
C(8)	0.3805(9)	0.2381(9)	0.699(1)	3.3(5)
2				
Ge	0.37534(3)	0.27817(7)	0.12217(2)	2.28(2)
S(1)	0.46363(7)	0.4024(2)	0.19011(5)	3.08(5)
S(2)	0.26067(7)	0.4429(2)	0.09840(5)	3.53(6)
S(3)	0.33666(7)	−0.0033(2)	0.13891(5)	3.30(6)
S(4)	0.43297(7)	0.3120(2)	0.03940(5)	3.25(6)
C(1)	0.3910(3)	0.5193(6)	0.2337(2)	3.2(2)
C(2)	0.3350(3)	0.3924(7)	0.2635(2)	3.5(2)
C(3)	0.2030(3)	0.3857(7)	0.2052(2)	3.6(2)
C(4)	0.1832(2)	0.3463(7)	0.1421(2)	3.8(2)
C(5)	0.4052(3)	−0.1309(6)	0.0951(2)	3.4(2)
C(6)	0.4950(3)	−0.1353(6)	0.1209(2)	3.9(3)
C(7)	0.5707(3)	0.0942(6)	0.0751(2)	3.5(2)
C(8)	0.5462(2)	0.2850(7)	0.0602(2)	3.3(2)
O(1)	0.2800(2)	0.2933(4)	0.2236(1)	3.1(1)
O(2)	0.5319(2)	0.0395(4)	0.1249(1)	3.3(1)
GE′	0.87995(3)	0.27128(7)	0.11649(2)	2.52(2)
S(1′)	0.86755(8)	−0.0125(2)	0.14469(5)	3.90(7)
S(2′)	0.96892(7)	0.3010(2)	0.04841(5)	3.37(6)
S(3′)	0.76055(7)	0.4115(2)	0.08643(5)	3.19(5)
S(4′)	0.95780(7)	0.4239(2)	0.18372(6)	3.99(6)
C(1′)	0.8841(3)	−0.1357(6)	0.0795(2)	4.2(3)
C(2′)	0.8123(3)	−0.1108(7)	0.0333(2)	4.7(3)
C(3′)	0.8600(3)	0.1153(7)	−0.0296(2)	4.2(3)
C(4′)	0.8988(3)	0.2962(7)	−0.0171(2)	3.7(2)
C(5′)	0.7316(3)	0.5253(6)	0.1502(2)	3.5(2)
C(6′)	0.7100(3)	0.3982(7)	0.1974(2)	3.7(2)
C(7′)	0.8359(3)	0.3808(7)	0.2610(2)	4.0(3)
C(8′)	0.9262(3)	0.3334(7)	0.2509(2)	4.1(2)
O(1′)	0.8065(2)	0.0711(5)	0.0144(1)	4.0(2)
O(2′)	0.7815(2)	0.2934(4)	0.2179(1)	3.3(2)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

(t, 8H, $GeSCH_2$), 3.0 (t, 8H, SCH_2). ^{13}C NMR ($CDCl_3$, δ): 39.4 ($GeSCH_2$), 31.5 (SCH_2). Mass spectrum (m/z): 377 (M^+).

[Ge(S(CH$_2$)$_2$O(CH$_2$)$_2$S)$_2$)] (2)

The same procedure for the preparation of **1** was followed, but the ligand was $HS(CH_2)_2O(CH_2)_2SH$ (**6**). The crude product was recrystallized from chloroform (yield 70%). ^1H NMR ($CDCl_3$, δ (ppm)): 3.7 (t, 8H, SCH_2), 3.0 (t, 8H, OCH_2). ^{13}C NMR ($CDCl_3$, δ): 72.6 (SCH_2), 32.5 (OCH_2). Mass spectrum (m/z): 345 (M^+).

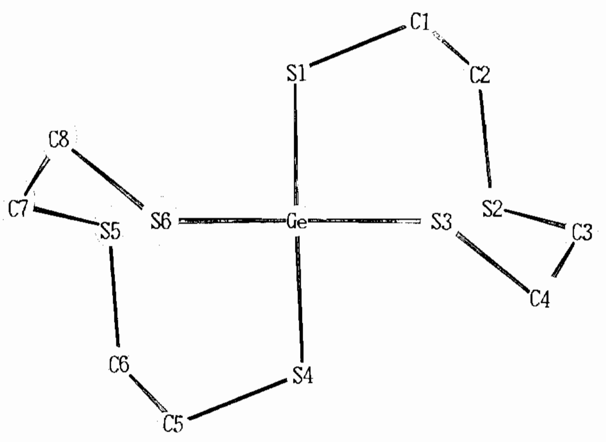


Fig. 1. Molecular structure of compound **1** (H atoms omitted).

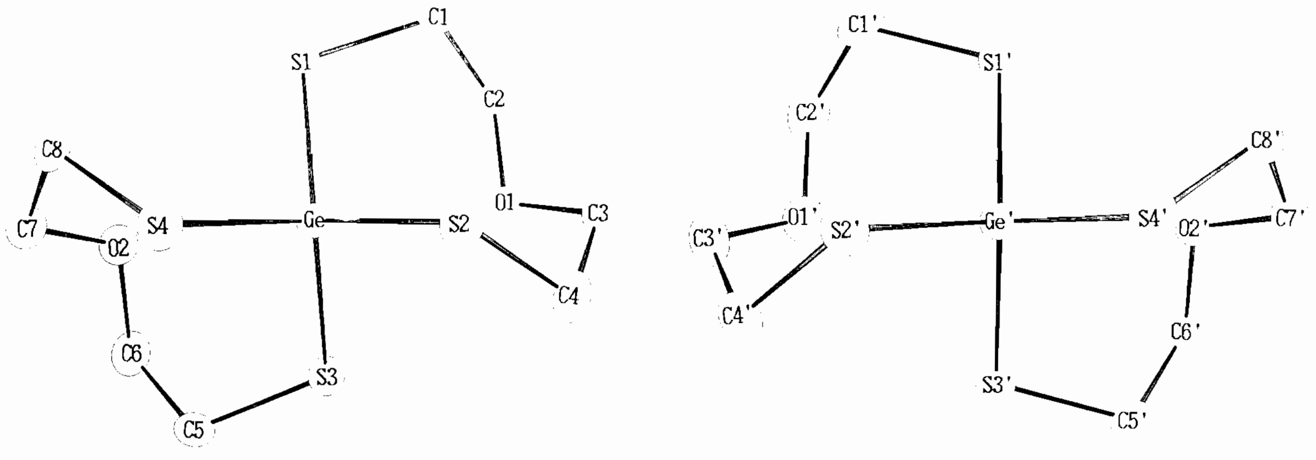
X-ray structure analysis of 1 and 2

Single crystals of **1** and **2** were obtained by evaporation from CH_3OH and $CHCl_3$ solutions, respectively. Structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically and isotropical hydrogen atoms were included in structure factor calculation but not refined. Table 1 summarizes crystallographic data for **1** and **2**; the fractional atomic coordinates are listed in Table 2. Molecular structures of **1** and **2** are given in Figs. 1 and 2, respectively.

Results and discussion

The title compounds, **1** and **2**, were synthesized from **3** (or **4**) and the corresponding ligands, **5** or **6**, in a 1:2 molar ratio in refluxed methanol. The mixed ligand complexes, $[Ge\{RN(CH_2CH_2O)_2\}(SCH_2CH_2XCH_2CH_2S)]$ ($R=H$ or CH_3, $X=O$ or S) resulted from substitution of hydroxyl groups by **5** or **6**, are expected as reaction intermediates. However, further substitution of diethanol moieties also occurred and led the products to the spirocyclic compounds **1** and **2**.

There are two independent molecules in the unit cell of compound **2** and both molecules have a similar structure related with a pseudo-mirror plane as shown in Fig. 2. The selective bond lengths and angles are listed in Table 3. The molecule consists of a central Ge atom bonded to four sulfur atoms of the two bidentate ligands and the coordination around the metal is a distorted tetrahedron. Distortion from the tetrahedral geometry is largely due to the formation of the two eight-membered rings (bite angles, 113.57(5) and 113.63(5) for **2**; 112.56(5) and 112.97(6)° for **2′**) and to the interaction between the central metal and the two oxygen atoms of the two ligands (Ge–O distances,



2

2'

Fig. 2. Molecular structure of compound **2** (H atoms omitted).

TABLE 3. Selective bond lengths (Å) and angles (°) of **1** and **2**

	1	**2**
Ge–S(1)	2.223(3)	2.218(1)
Ge–S(2)		2.217(1)
Ge–S(3)	2.236(3)	2.218(1)
Ge–S(4)	2.231(3)	2.218(1)
Ge–S(6)	2.210(3)	
Ge′–S(1′)		2.217(2)
Ge′–S(2′)		2.222(1)
Ge′–S(3′)		2.216(1)
Ge′–S(4′)		2.217(1)
S(1)–Ge–S(2)		113.63(5)
S(1)–Ge–S(3)	110.0(1)	115.53(5)
S(1)–Ge–S(4)	118.5(1)	107.02(5)
S(1)–Ge–S(6)	110.5(1)	
S(2)–Ge–S(3)		109.23(5)
S(2)–Ge–S(4)		96.32(5)
S(3)–Ge–S(4)	106.7(1)	113.57(5)
S(3)–Ge–S(6)	97.0(1)	
S(4)–Ge–S(6)	112.0(1)	
S(1′)–Ge′–S(2′)		112.56(5)
S(1′)–Ge′–S(3′)		116.32(5)
S(1′)–Ge′–S(4′)		109.42(6)
S(2′)–Ge′–S(3′)		107.68(5)
S(2′)–Ge′–S(4′)		96.11(5)
S(3′)–Ge′–S(4′)		112.97(6)

2.914(3) and 3.040(3) Å for **2**; 2.946(3) and 2.955(3) Å for **2′**) [8, 9]. Owing to the Ge---O interaction and the four atoms, S(2), S(4), O(1) and O(2), almost lying in the same plane, the S2–Ge–S4 angles (96.32(5)° for **2**, 96.11(5)° for **2′**) largely deviate from those of the typical tetrahedral geometry (109.5°).

The structure of compound **1** (Fig. 1) around the coordinated sphere is also a distorted tetrahedron and is similar to compound **2** with comparable bond lengths and angles (Table 3). The four atoms, S(2), S(3), S(5) and S(6), also lie in a pseudo-equatorial plane, but the difference between the two Ge---S distances (3.453(3) and 3.237(3) Å) [10–12] is larger than those in compound **2**.

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References

1 V. F. Mironov, T. K. Gar, N. Y. Khromova and O. D. Frid, *Zh. Obshch. Khim.*, *56* (1986) 638.

2 H.-C. Chiang, S.-M. Lin and C.-H. Ueng, *Acta Crystallogr., Sect. C*, *48* (1992) 991.

3 H.-C. Chiang, M.-H. Wang and C.-H. Ueng, *Acta Crystallogr., Sect. C*, *49* (1993) 244.

4 S. N. Gurkova, A. I. Gusev, V. A. Sharapov, N. V. Alekseev, T. K. Gar and N. J. Chromova, *J. Organomet. Chem.*, *268* (1984) 119.

5 N. A. Viktorov, S. N. Gurkova, A. I. Gusev, T. K. Gar and V. F. Mironov, *Metalloorg. Khim.*, *1* (1988) 715.

6 H. J. Backer and F. Stienstra, *Recl. Trav. Chim. Pays-Bas*, *52* (1933) 1033.

7 A. C. Larson, F. L. Lee, Y. Le Page, M. Webster, J.-P. Charland and E. J. Gabe, *NRCVAX*, crystal structure system, 1990.

8 J. E. Drake, A. G. Mislankar and M. L. Y. Wong, *Inorg. Chem.*, *30* (1991) 2174.

9 J. E. Drake, A. B. Sarkar and M. L. Y. Wong, *Inorg. Chem.*, *29* (1990) 785.

10 R. K. Chadha, J. E. Drake and A. B. Sarkar, *Inorg. Chem.*, *25* (1986) 2201.

11 R. K. Chadha, J. E. Drake and A. B. Sarkar, *Inorg. Chim. Acta*, *143* (1988) 31.

12 M. Drager, *Chem. Ber.*, *108* (1975) 1723.