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## Comparison of the Chemical Bonding in (Eind)<sub>2</sub>Ge=E (E = O and S): Synthesis and Characterization of Germanethione Bearing Bulky Eind Groups

Naoko Fujita,<sup>1</sup> Liangchun Li,<sup>2,†</sup> Nicolas Lentz,<sup>1,3</sup> Shigeaki Konaka,<sup>1</sup> Airi Kuroda,<sup>1</sup> Ryoma Ohno,<sup>1</sup> Naoki Hayakawa,<sup>1</sup> Kohei Tamao,<sup>2</sup> David Madec,<sup>3</sup> Tsuyoshi Kato,<sup>3</sup> Alfredo Rosas-Sanchez,<sup>4</sup> Daisuke Hashizume,<sup>4</sup> and Tsukasa Matsuo\*<sup>1,2</sup>

<sup>1</sup>Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

<sup>2</sup>Functional Elemento-Organic Chemistry Unit, RIKEN Advanced Science Institute, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

<sup>3</sup>Université de Toulouse, UPS, and CNRS, LHFA UMR 5069, 31062 Toulouse, France

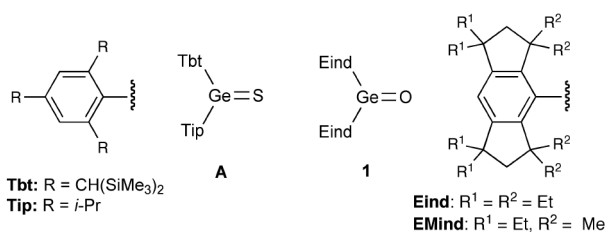
<sup>4</sup>RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

E-mail: t-matsuo@apch.kindai.ac.jp

A new diarylgermanethione, (Eind)<sub>2</sub>Ge=S, supported by the fused-ring bulky Eind groups (Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl) has been obtained as yellow-orange crystals by the direct reaction between the diarylgermylene, (Eind)<sub>2</sub>Ge:, and elemental sulfur in solution. The structure and bonding nature of the germanethione have been compared to those of its oxygen congener, germanone, (Eind)<sub>2</sub>Ge=O. We also report the X-ray structure analysis of the hydroxy(mercaptop)germane, (Eind)<sub>2</sub>Ge(OH)(SH).

**Keywords:** Germanium, Germanethione, Germanone

Since the discrete molecules comprising the Ge=E double bond were independently synthesized by Lappert's and Masamune's groups,<sup>1,2</sup> various unsaturated compounds of germanium have been successfully isolated by employing appropriate bulky substituents.<sup>3</sup> Among them, stable heavy ketones (R<sub>2</sub>Ge=E) with a terminal heavier group 16 element (E = S, Se, or Te) have attracted much attention due to their highly reactive Ge=E double bonds.<sup>4</sup> Tokitoh and Okazaki reported the isolation of the first series of monomeric heavy ketones, (Tbt)(Tip)Ge=E [E = S (A), Se, and Te] using a combination of bulky 2,4,6-tris[tris(trimethylsilyl)methyl]phenyl (Tbt) and 2,4,6-triisopropylphenyl (Tip) groups (Figure 1).<sup>5,6</sup> Although there has been a number of studies on the Ge=S doubly bonded species by virtue of the coordination of ligands (Lewis bases) to the Ge atom,<sup>7</sup> the chemistry of the germanethione with a tricoordinate Ge center (R<sub>2</sub>Ge=S) has rarely been explored excepting A.



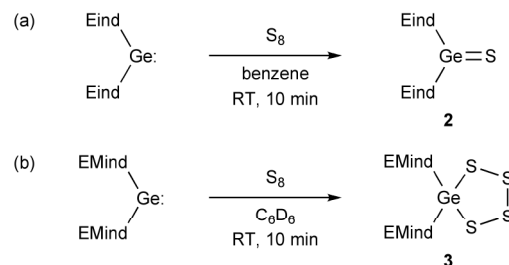
**Figure 1.** Stable heavy ketones.

In 2012, we reported the first isolation of a monomeric germanone, (Eind)<sub>2</sub>Ge=O (**1**), with a planar three-coordinate Ge atom and a terminal O atom, supported by the fused-ring bulky 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl (Eind) groups.<sup>8–10</sup> The germanone **1** can be prepared by the reaction of the diarylgermylene, (Eind)<sub>2</sub>Ge:, with trimethylamine *N*-oxide (Me<sub>3</sub>N<sup>+</sup>-O<sup>-</sup>). DFT calculations and chemical reactions

indicate that the Ge=O double bond is highly polarized with a contribution of the charge-separated canonical form, germylene oxide, (Eind)<sub>2</sub>Ge<sup>+</sup>-O<sup>-</sup>.

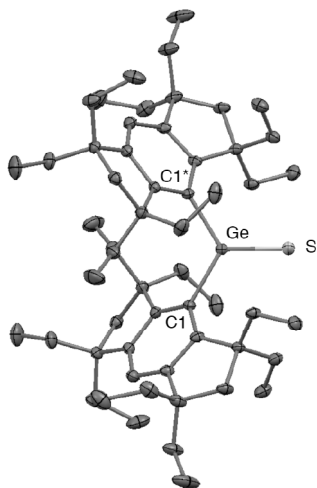
We now report the synthesis and characterization of a monomeric germanethione, (Eind)<sub>2</sub>Ge=S (**2**), bearing the fused-ring bulky Eind groups and discuss the structural features and bonding nature of **2** in comparison to those of the oxygen congener **1**.<sup>8</sup>

As shown in Scheme 1(a), the Eind-based germanethione **2** was straightforwardly synthesized by the oxidation reaction of the divalent diarylgermylene, (Eind)<sub>2</sub>Ge:, and elemental sulfur (S<sub>8</sub>) in benzene. The reaction was immediately completed at room temperature, and a yellow-orange suspension was obtained. Recrystallization from THF afforded yellow-orange crystals of **2** in 57% isolated yield.<sup>11</sup> Based on the NMR tube scale experiments, the germanethione **2** was formed as the sole product even using an excess amount of S<sub>8</sub>. This is in sharp contrast to the previously reported dehydrosulfurization of the tetravalent diaryldihydrogermane, (Tbt)(Tip)GeH<sub>2</sub>, and S<sub>8</sub>, which led to the formation of a five-membered ring compound, 1,2,3,4,5-tetrathiagermolane, (Tbt)(Tip)GeS<sub>4</sub>,<sup>12</sup> and could be cleanly converted to the germanethione, (Tbt)(Tip)Ge=S (A), by the desulfurization using triphenylphosphine (Ph<sub>3</sub>P).<sup>5</sup> We also found that another diarylgermylene, (EMind)<sub>2</sub>Ge:,<sup>13</sup> bearing the less bulky 1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-*s*-hydrindacen-4-yl (EMind) groups, reacted with S<sub>8</sub> to produce the 1,2,3,4,5-tetrathiagermolane, (EMind)<sub>2</sub>GeS<sub>4</sub> (**3**) [Scheme 1(b)], whose molecular structure was confirmed by a preliminary X-ray analysis.<sup>11</sup> These results indicated that the course of the sulfurization reaction of the germylenes significantly depends on the steric bulk of the substituents attached to the Ge atom.<sup>14,15</sup>



**Scheme 1.** Synthesis of germanethione **2** (a) and 1,2,3,4,5-tetrathiagermolane **3** (b)

The molecular structure of **2** was clearly determined by X-ray crystallography, as shown in Figure 2. The molecule of **2** assumes the  $C_2$  symmetry in the crystal with the two-fold axis passing through the Ge=S double bond. Table 1 summarizes the structural parameters of **2** together with those of **1** for comparison.<sup>8</sup> The Ge=S double bond length found in **2** [2.0569(9) Å] is comparable to that in **A** [2.049(3) Å],<sup>5</sup> which are shorter than the common Ge-S single bond lengths (2.26 Å),<sup>16</sup> but rather longer than the Ge=O double bond length in **1** [1.6468(5) Å], mainly attributable to the larger covalent atomic radius of S [1.05(3) Å] relative to O [0.66(2) Å] (Entry 1).<sup>17</sup> The Ge-C bond lengths in **2** [2.003(2) Å] are slightly longer than those in **1** [1.9768(5) and 1.9724(6) Å] and **A** [1.953(9) and 1.91(1) Å],<sup>5</sup> probably due to the severe steric congestion between the two bulky Eind groups and S atom (Entry 2). The central Ge atom adopts a trigonal planar geometry with the sum of the surrounding bond angles ( $\Sigma\text{Ge}$ ) equal to 360.0° [S-Ge-C = 120.85(6) and C-Ge-C = 118.31(9)°] (Entries 3–5). Thus, the chemical bonding at the Ge atom can be described as an  $sp^2$ -hybridization.



**Figure 2.** Molecular structure of **2**. The thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ge-S = 2.0569(9), Ge-C1 = 2.003(2), S-Ge-C1 = 120.85(6), C1-Ge-C1\* = 118.31(9).

Notably, while the germanone **1** exhibits a very high solubility in hydrocarbon solvents (even in pentane), the germanethione **2** is barely soluble in common organic solvents at room temperature, unfortunately, which hampers the investigations of its reactivity. The space-filling models display that the shorter Ge=O group is much more efficiently encapsulated by the two bulky Eind groups relative to the longer Ge=S group.<sup>11</sup> Both compounds **1** and **2** are air- and moisture-sensitive (vide infra) but thermally well-stable, which can be stored in the solid state at ambient temperature in a glove box filled with argon gas.

The structure of **2** in solution ( $C_6D_6$ ) was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy at elevated temperature

(70 °C). Only one set of resonances due to the peripheral and proximate ethyl groups of the Eind groups was observed on the NMR time scale, indicating the free-rotation around the C-Ge bonds.<sup>18</sup> In the UV-vis spectra of **2** in cyclohexane, a weak absorption peak appeared at 474 nm ( $\epsilon = 80$ ), similar to that observed in **A** (450 nm,  $\epsilon = 100$  in hexane),<sup>5</sup> which are assignable to the forbidden  $n-\pi^*$  transition (Entry 6). The Ge=S stretching frequency was observed at 519  $\text{cm}^{-1}$  in the Raman spectrum of **2** in the solid state,<sup>11</sup> which is much lower than that of **1** (917  $\text{cm}^{-1}$ ) (Entry 7) and comparable to that of **A** (521  $\text{cm}^{-1}$ )<sup>5</sup> and  $\text{Me}_2\text{Ge}=\text{S}$  (518  $\text{cm}^{-1}$ ).<sup>19</sup>

**Table 1.** Comparison between **1** and **2**

Entry		<b>1</b>	<b>2</b>
experimental			
1	Ge-E (Å)	1.6468(5)	2.0569(9)
2	Ge-C (Å)	1.9768(5)	2.003(2)
		1.9724(6)	
3	E-Ge-C (°)	118.95(3)	120.85(6)
		116.59(3)	
4	C-Ge-C (°)	124.27(2)	118.31(9)
5	$\Sigma\text{Ge}$ (°)	359.8	360.0
6	$\lambda_{\text{max}}(\text{abs})$ (nm)	297	450
	$\epsilon$ ( $\text{cm}^{-1} \text{M}^{-1}$ )	6010	100
7	$\nu(\text{Ge}=\text{E})$	917	519
calculations			
8	Ge-E (Å)	1.6736	2.0777
9	Ge-C (Å) (av)	1.9433	1.9838
10	E-Ge-C (°) (av)	118.00	119.92
11	C-Ge-C (°)	123.99	120.17
12	$\Sigma\text{Ge}$ (°)	360.0	360.0
13	WBI (Ge-E)	1.263	1.635
14	NPA (Ge-E)	Ge (+1.821) O (-1.039)	Ge (+1.336) S (-0.613)
15	HOMO (eV)	-5.95	-5.46
16	LUMO (eV)	-1.55	-1.96
17	$\Delta E$ (eV)	4.39	3.50
18	$\lambda_{\text{max}}(\text{abs})$ (nm)	382	504
	$f$	0.0004	0.0002
19	$\nu(\text{Ge}=\text{E})$	928	511

To elucidate the electronic structure and bonding properties of the germanethione, we performed DFT calculations for **2** at the B3LYP-D3/6-31G(d,p) level by using the Gaussian 09 suite of programs.<sup>20</sup> DFT calculations were also carried out for **1** at the same level with dispersion corrections.<sup>11</sup> Several pertinent data of **2** are listed in Table 1, along with those of **1** for comparison. The optimized structure of **2** with a  $C_1$  symmetry approximately reproduces the X-ray structure found in the crystal (Entries 8–12). The Ge-S bond order based on the Wiberg bond index (WBI)<sup>21</sup> in **2** (1.635) is higher than that in **1** (1.263) (Entry 13). The natural population analysis (NPA)<sup>22</sup> charge distribution of **2** shows a large charge difference on the Ge-S bond with a positive Ge (+1.336) and negative S (-0.613), however, the Ge-O bond in **1** is much more highly charge-separated with the positive Ge (+1.821) and negative O (-1.039) (Entry 14).

These results indicated that while the Ge–O bond in **1** is totally polarized with the lower double-bonding character, the Ge–S bond in **2** is rationally polarized, containing some  $\pi$ -bonding character.

The selected molecular orbitals (MOs) of **2** are shown in Figure 3. While the HOMO involves the non-bonding pairs of electrons on the S atom, the LUMO mainly corresponds to the Ge–S  $\pi^*$ -bond. The HOMO-3 represents the Ge–S  $\pi$ -bond. Such a pattern of MOs in **2** appears to be similar to that in **1**; the non-bonding pairs of electrons on the O atom in the HOMO, the Ge–O  $\pi^*$ -bond in the LUMO, and the Ge–O  $\pi$ -bond in the HOMO-5.<sup>11</sup> The energy levels of the HOMO and LUMO of **2** are –5.46 and –1.96 eV, each of which is higher and lower than those of **1** (–5.95 and –1.55 eV), respectively (Entries 15 and 16). Thus, the HOMO–LUMO energy gap ( $\Delta E$ ) of **2** (3.50 eV) is smaller than that of **1** (4.39 eV) (Entry 17), being in good agreement with the UV-vis results. The TD-DFT computations of **2** reproduce the experimental absorption spectrum. The HOMO  $\rightarrow$  LUMO transition was calculated to be a weak absorption peak at 504 nm due to the forbidden  $n\text{--}\pi^*$  transition, which may be responsible for the yellow-orange color of **2** (Entry 18). The calculated Ge=S stretching frequency (511  $\text{cm}^{-1}$ ) is comparable to the experimental value (509  $\text{cm}^{-1}$ ) (Entry 19).

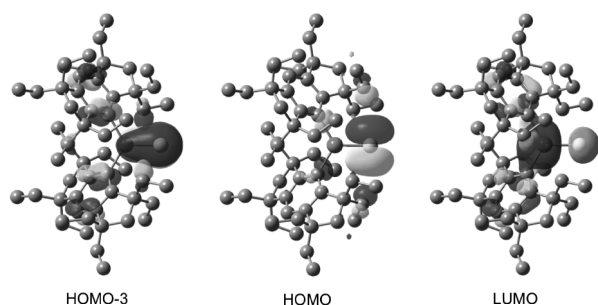
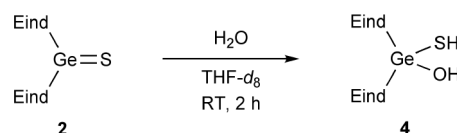


Figure 3. Selected MOs of **2**.

Additionally, we sometimes observed that during the synthesis of the germanethione **2**, the presence of adventitious water results in the formation of trace amounts of hydroxy(mercapto)germane,<sup>5,23</sup> (Eind)<sub>2</sub>Ge(OH)(SH) (**4**). Indeed, we found that a suspension of **2** in THF-*d*<sub>8</sub> reacted with a sufficient amount of H<sub>2</sub>O to produce **4** (Scheme 2),<sup>5d</sup> which was examined by single-crystal X-ray diffraction analysis and high-resolution electrospray ionization mass spectrometry (HRESI-MS). Figure 4 shows the molecular structure of **4**. The crystal has two disordered diethylether (Et<sub>2</sub>O) molecules as a crystal solvent in the asymmetric unit, which are omitted for clarity in Figure 4. The Ge-bound O and S atoms are over the two positions with the occupancy factors of 0.771 and 0.229; only the major parts of the disordered OH and SH groups are shown in Figure 4. The H atoms bound to the O and S atoms have been located from the difference Fourier maps and isotropically refined. The Ge–O1 bond length of **4** [1.725(2) Å] is similar to the typical Ge–O single bond length (1.76 Å) with a tetracoordinate Ge(IV) center,<sup>24</sup> and longer than the Ge=O

double bond length of **1** [1.6468(5) Å].<sup>8</sup> Also, the Ge–S bond length of **4** [2.2984(7) Å] is comparable to the common Ge–S single bond lengths (2.26 Å),<sup>16</sup> and longer than the Ge=S double bond length of **2** [2.0569(9) Å]. The Ge–C bond lengths of **4** [2.0350(19) and 2.0288(18) Å] are longer than those of **1** [1.9768(5) and 1.9724(6) Å] and **2** [2.003(2) Å], in accordance with the increased *p*-character of the Ge–C bonds. The O1 $\cdots$ O(Et<sub>2</sub>O) intermolecular atomic distance is observed to be about 2.8–3.1 Å, suggestive of the presence of a moderate hydrogen bonding in the crystal structure.



Scheme 2. Reaction of germanethione **2** with H<sub>2</sub>O.

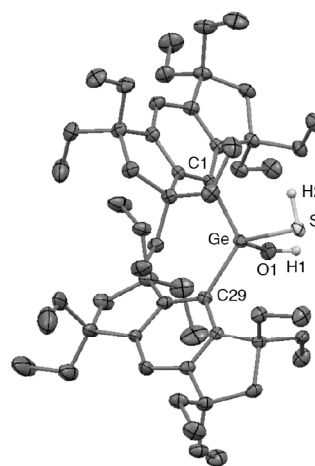


Figure 4. Molecular structure of **4**. The thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms are not shown except for the OH and SH groups. The disordered O, S, and C atoms, and Et<sub>2</sub>O molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ge–O1 = 1.725(2), Ge–S = 2.2984(7), Ge–C1 = 2.0350(19), Ge–C29 = 2.0288(18), O1–Ge–S = 101.08(8), O1–Ge–C1 = 116.37(11), O1–Ge–C29 = 98.77(10), S–Ge–C1 = 98.83(6), S–Ge–C29 = 120.65(6), C1–Ge–C29 = 120.47(8).

In conclusion, the introduction of the fused-ring bulky Eind groups allowed us to isolate a stable germanethione with a planar tricoordinate Ge atom and a terminal S atom as a new member of discrete monomeric heavy ketones. The steric effects of the bulky protecting groups are crucial for the product selectivity in the sulfurization of the gemylenes. While the germanone has a low Ge=O  $\pi$ -bonding character with an extraordinarily large charge separation with Ge<sup>+</sup> and O<sup>–</sup>, the sulfur congener, germanethione demonstrates a moderate Ge=S double-bonding character, even ensuring a polarization with Ge( $\delta^+$ ) and S( $\delta^-$ ). These chemical bonding features may be reflected by the electronegativities of the

elements [O (3.50), S (2.44), and Ge (2.02)]<sup>25</sup> and the efficiency of the p-orbital overlaps involving a planar Ge atom. Further investigations into the chemistry of heavier-element ketones are now in progress.

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