

X-ray crystallographic study of some pentacoordinated organogermanium compounds

Yoshito Takeuchi^{a,*}, László Párkányi^b, Alajos Kálmán^b, Miki Nishikawa^a,
Katsumi Tanaka^a, Wasuke Mori^a, Masashi Kinoshita^a

^a Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka-shi 259-1293, Japan

^b Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary

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Abstract

The X-ray crystallographic structures of 2-(2-phenyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetic acid (**2**), its pyridinium salt (**3**), and the pyridinium salt of 2-(2-*t*-butyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetic acid (**1**), (**4**), together with 2-(2-phenyl-1,3,2-oxathiagermolan-2-ylthio)ethanol (**5**) were determined and compared with that of **1**. All of compounds investigated, **2–5**, have the TBP-like, pentacoordinated structure. This fact seems to indicate that the driving force of pentacoordination of this type of compounds is the existence of an oxygen atom δ to the germanium atom that readily forms a five membered ring by hypercoordination.

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Keywords: Hypercoordination; X-ray crystallography; Organogermanium compounds

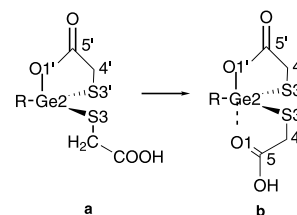
1. Introduction

Recently, hypercoordinated or hypervalent Group 14 element compounds have attracted considerable attention [1]. In particular, Corriu et al. [2] described a variety of penta-, hexa- or heptacoordinate silicon compounds where in most cases the donor is a nitrogen moiety (e.g. dimethylamino group), and the geometrical relation between the silicon and the donor is more or less sterically congested. Typical examples are 1-amino-8-silanaphthalene or -germanaphthalene [3] or tris(*o*-aminomethylphenyl)-silanes and -germanes [4,5]. Another example of this kind is silatranes or germanatranes where the lone pair of the donor moiety is necessarily directed to the acceptor [6].

In the previous communication [7], we found, by the X-ray crystallographic analysis, that 2-(2-*t*-butyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetic acid (**1a**) exists as a pentacoordinated species with a TBP (trigonal bipy-

amid) (**1b**) in the solid state with an equatorial *t*-butyl group and two equatorial Ge–S bonds and two apical Ge–O bonds, one is a covalent Ge–O bond of thiolactone moiety and the other is a Ge–O bond between the carbonyl oxygen of –SCH₂COOH moiety coordinated apically to the germanium atom.

We also found that by the variable temperature NMR study of **1–4**, these compounds remain in the pentacoordinated structure, and that there are concomitant Berry pseudorotation and prototropy which make the two protons of CH₂ moiety nonequivalent at lower temperatures [8].



1 R = *t*-Bu
2 R = Ph

The orientation of the substituents is in line with the Mutterties rule that predicts that the more electronega-

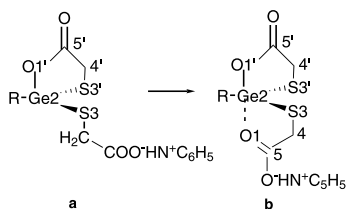
* Corresponding author. Tel.: +81-463-59-4111; fax: +81-463-58-9684.

E-mail address: yoshito@chem.kanagawa-u.ac.jp (Y. Takeuchi).

tive atoms tend to occupy the apical position [9]. Another interesting structural feature of **1** is the intermolecular hydrogen bonding in crystal where the hydrogen atom of the carboxy group is hydrogen-bonded to the thiolactone carbonyl oxygen of an adjacent molecule.

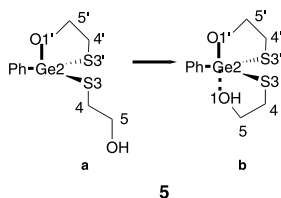
Though the phenomenon of pentacoordination has been well documented, **1** is particularly interesting in that it is a flexible molecule, and should be able to avoid pentacoordination because the S–C bond of the S–CH₂COOH moiety can rotate so that the COOH group will be apart from the Ge atom to cleave the hypercoordination. In this connection, it will be interesting to delineate the scope and limitation of pentacoordination of this type by modifying the structure of **1** as given below.

- i) to replace the *t*-butyl group with a phenyl group to see the effect of the hydrocarbon residue on germanium; e.g. to study the structure of 2-(2-phenyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetic acid (**2**);
- ii) to convert the carboxy group into a carboxylate to see the role of carboxy hydrogen, e.g. to study the structure of the pyridinium salts of **1** and **2**, that is, pyridinium 2-(2-*t*-butyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetate (**3**) and pyridinium 2-(2-phenyl-5-oxo-1,3,2-oxathiagermolan-2-ylthio)acetate (**4**):



3 R = *t*-Bu
4 R = Ph

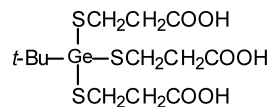
- iii) to reduce the –CH₂COOH moiety of **1** to –CH₂CH₂OH to see the role of the carbonyl group, e.g. to study the structure of 2-(2-phenyl-1,3,2-oxathiagermolan-2-ylthio)ethanol (**5**).



5

It must be pointed out that the formation of a five-membered ring is essential for this type of hypercoordination. Thus, we already reported that the reaction between *t*-butyltrichlorogermane and 3-mercaptopropionic acid afforded exclusively *t*-butyl[tris(2-carboxy-

ethylthio)]germane (**6**) [10]. In other words, it is essential for pentacoordination that the germanium atom should have an oxygen atom at δ position.

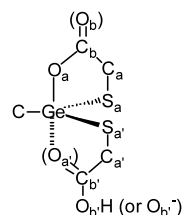


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2. Results and discussion

2.1. Structural parameters of 1–5

Since the X-ray analyses gave slightly different numbering for each compound, we will hereafter use the numbering given below in discussion and comparison of the solid state structure of **1–5** to avoid any possible confusion.



Thus, atoms associated with the heterocyclic ring (upper part of **1b–5b**) are designated as a and b, while those associated with the side-chain (lower part of **1a–5a**) are designated as a' and b'.

In Table 1, representative bond lengths and bond angles of **2–5** are summarized. For the sake of comparison, the data for **1** [7] were also included.

2.2. Solid state structure of 2

The ORTEP drawing of **2** is shown in Fig. 2.

It is clear from Fig. 1 and the data in Table 1 that **2** is also pentacoordinated with a TBP structure. Two sulfur atoms and the *ipso* carbon atom forms a triangle to which the O–Ge–O axis is nearly perpendicular. Two Ge–O bonds are both close to 2.0–2.1 Å as is the case with **1**. The O–Ge–O angle is a little deviated from 180°, the angle for an ideal TBP. A deviation to this extent is not rare in pentacoordinated organosilicon and -germanium compounds [11].

A better measure of structural feature is to calculate the extent to which the Ge–O donor distance has changed from the van der Waals sum of 3.62 Å compared to the Ge–O bond length of 1.624 Å. This method has successfully been used for cyclic silanes by Holmes et al. [12]. Values of the percent trigonal bipyramidal character (% TBP) obtained in this manner

Table 1
Representative structural parameters of 1–5

	1 ^a	2	3	4	5
<i>Bond lengths</i>					
Ge–C	1.989(2)	1.920(2)	1.985(5)	1.9345(16)	1.9395(15)
Ge–Oa	2.045(1)	2.095(1)	1.969(3)	1.9463(11)	1.8337(11)
Ge–Oa'	2.043(1)	2.037(1)	2.009(3)	2.0330(11)	2.4575(13)
Ge–Sa	2.2191(5)	2.2036(6)	2.222(1)	2.2202(5)	2.2060(5)
Ge–Sa'	2.2143(5)	2.1982(6)	2.222(1)	2.2165(5)	2.2013(4)
Ca–Sa	1.808(2)	1.800(2)	1.793(5)	1.8048(19)	1.830(2)
Ca'–Sa'	1.810(2)	1.790(2)	1.798(5)	1.8022(17)	1.8160(17)
Cb–Oa	1.258(2)	1.273(2)	1.286(5)	1.292(2)	1.4215(19)
Cb–Ob	1.265(2)	1.241(2)	1.217(5)	1.216(2)	–
Cb'–Oa'	1.259(2)	1.271(2)	1.287(5)	1.2804(18)	1.412(2)
Cb'–Ob'	1.262(2)	1.242(2)	1.228(5)	1.2330(18)	–
<i>Bond angles</i>					
Oa–Ge–Oa'	166.71(5)	168.82(6)	165.0(1)	169.85(5)	171.11(6)
C–Ge–Sa	120.05(5)	117.07(6)	118.7(2)	118.86(5)	116.03(5)
C–Ge–Sa'	119.73(5)	119.72(6)	118.1(2)	116.79(5)	116.94(4)
Sa–Ge–Sa'	120.19(2)	123.05(3)	123.14(6)	124.29(2)	122.01(2)
C–Ge–Oa	94.39(6)	93.41(7)	98.2(2)	94.75(6)	103.74(6)
C–Ge–Oa'	98.89(6)	97.77(7)	96.8(2)	95.31(5)	85.06(6)
Oa–Ge–Sa	86.88(4)	86.78(4)	87.44(9)	88.46(4)	92.83(4)
Oa–Ge–Sa'	86.91(4)	86.05(4)	87.33(9)	89.65(4)	96.17(4)
Oa'–Ge–Sa	86.25(4)	88.13(4)	84.51(9)	85.59(3)	84.30(4)
Oa'–Ge–Sa'	86.73(4)	88.40(4)	86.53(8)	86.94(3)	78.38(3)
Ge–Sa–Ca	97.97(6)	98.75(7)	96.8(2)	97.83(6)	93.41(6)
Ge–Sa'–Ca'	96.46(6)	96.87(7)	97.8(1)	97.58(5)	99.20(6)
% TBP	79.0	79.3	80.7	79.5	58.2

^a Data taken from Ref. [7].

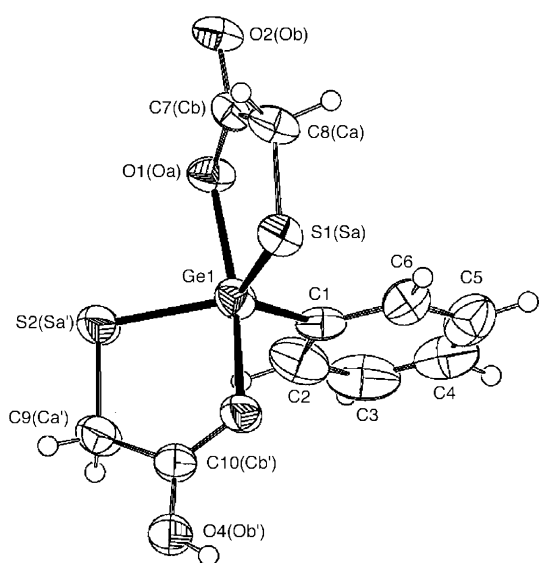


Fig. 1. ORTEP drawing of 2.

are listed in Table 1 for 1–5. For 1 and 2% TBP is high, which is consistent with the other structural data.

2.3. Solid state structure of the pyridinium salts 3 and 4

Now that the carbonyl oxygen, rather than hydroxy oxygen, of the carboxy group coordinates with the

germanium atom in 1 and 2, it is expected that the same pentacoordinated structure can be expected for the salts 3 and 4. In Figs. 2 and 3 ORTEP drawing of 4 and 5 are given. Large % TBP values for 3 and 4 suggest slightly distorted TBP structures for these. The O–Ge–O angle is close to those of 1 and 2, and two sulfur atoms and the *ipso* carbon atom forms a triangle with the O–Ge–O axis nearly perpendicular to the triangle. Two Ge–O bonds are both close to 1.9–2.0 Å as is the case with 1 and 2.

For 3 the difference between the two Ge–O distances is small (0.04 Å) while for 4 the difference is larger (0.09 Å). This is likely to be due to the difference in the extent

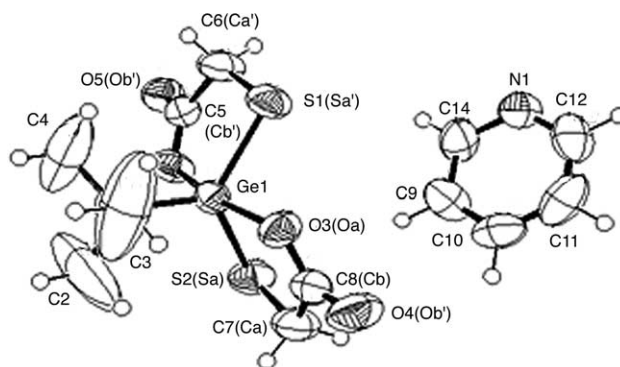
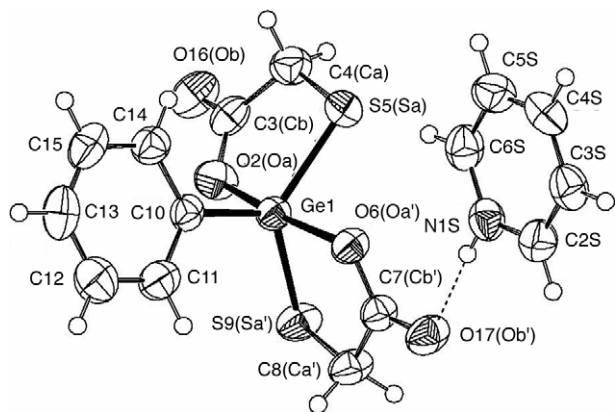


Fig. 2. ORTEP drawing of 3.

Fig. 3. ORTEP drawing of **4**.

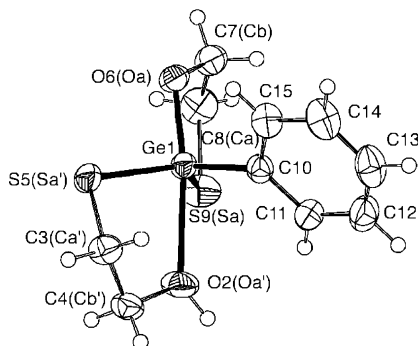
of interaction between carbonyl oxygen and the pyridinium moiety. In **3**, the distances between carbonyl oxygen and pyridine nitrogen are 2.75 (O2–N) and 3.19 (O4–N) Å while in **4** these are 2.91 (O17–N) and 5.26 (O16–N) Å. In other words, in **4** one of the carbonyl group has no interaction with pyridine moiety which will make the relevant Ge–O bond longer.

2.4. Solid state structure of **5**

The alcohol **5** was chosen to clarify whether the existence of the carbonyl group is essential or not for pentacoordination of this type. In Fig. 4 ORTEP drawing of **5** is given.

The crucial point is whether **5** is also pentacoordinated with a TBP structure or not. The O–Ge–O angle is 171°, which is even closer to 180° than those of **1–4**. However, % TBP for **5** (calculated based on the Ge–O(H)CH₂CH₂R distance, 2.46 Å), is only 58%, indicating a weaker coordination. This will imply that a hydroxy group is less nucleophilic than a carboxy group.

There are some other differences between **1–4** and **5**. In **1–4**, some values of the pair of structural parameters such as C–Ge–Sa and C–Ge–Sa' are very close, while for **5** the difference is much larger, reflecting a large distortion from a perfect TBP structure. Another difference is the difference between two C–Ge–O angles

Fig. 4. ORTEP drawing of **5**.

which show how far perpendicular is the O–Ge–O axis to the S–C–S triangle. For **5**, there is a difference of 18°, while for the other four compounds the difference is less than 5°.

2.5. Conclusion

It is clear that all compounds investigated are a little skewed trigonal bipyramidal (TBP) in that the angles O–Ge–O are in the range of 165–171°. In all compounds, three equatorial bonds (Ge–C, Ge–S and Ge–S) form a triangle, and the angle formed by an apical and an equatorial bond is always close to 90°.

Since the salts **3** and **4**, and alcohol **5** also form pentacoordination, the presence of Ge–S–CH₂COOH moiety is not a prerequisite for pentacoordination. It seems that the presence of Ge–S–C–C–O moiety, i.e. an oxygen atom δ to germanium, is sufficient for pentacoordination.

3. Experimental

3.1. General

The preparation and dynamic NMR study of **1–4** was already published [8].

¹H-NMR spectra were determined on a JEOL ECP 500 spectrometer operating at 500 MHz, and the chemical shifts were reported in δ (ppm) with respect to Me₄Si. ¹³C-NMR spectra were determined on the same instrument operating at 125 MHz and the chemical shifts were reported in δ (ppm) with respect to Me₄Si. Elemental analysis was carried out by the Microanalytical Laboratory, Department of Chemistry, The School of Science, The University of Tokyo.

3.2. 2-(2-Phenyl-1,3,2-oxathiagermolan-2-ylthio)ethanol (**5**)

To a mixture of 2-mercaptoethanol (2.34 g, 30 mmol) and pyridine (1.6 g) in benzene (10 ml), there was added phenyltrichlorogermane (2.57 g, 10 mmol) in THF (20 ml) at room temperature under nitrogen, and the mixture was stirred for 15 h. The mixture was neutralized with aq. HCl (1 mol dm⁻³), the organic layer was separated and washed with water, and dried over Na₂SO₄. The solvent was removed to obtain the crude residual solid that was recrystallized from a mixture of THF/Et₂O to give colorless crystals of **5** (1.00 g, 33%). M.p. 122–124 °C. ¹H-NMR (acetone-*d*₆, 500 MHz); δ 11.0 (b, OH, 1H), 3.73 (s, CH₂, 4H), 1.23 (s, *t*-Bu, 9H), ¹³C NMR (acetone-*d*₆, 125 MHz); δ 176.1 (s, C=O), 39.3 (s, C(CH₃)₃), 31.9 (t, SCH₂), 27.9 (q, CH₃). Anal. Calc. for C₁₀H₁₄GeO₂S₂: C, 39.64; H, 4.60; S, 21.16. Found: C, 39.58; H, 4.60; S, 21.39%.

Table 2
Crystallographic data for compounds 2–5

	2	3	4	5
	Colorless prism	Colorless prism	Colorless prism	Colorless prism
Molecular weight	330.89	389.00	409.99	302.92
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 21/ <i>c</i>	<i>P</i> 1 ₂ /1 ₁	<i>P</i> 21/ <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	7.347(1)	10.9954(6)	7.401(1)	6.294(1)
<i>b</i> (Å)	10.148(2)	7.7073(6)	14.948(1)	8.794(1)
<i>c</i> (Å)	16.817(2)	21.618(2)	15.464(2)	11.819(1)
α (°)	90.00	90.00	90.00	86.206(7)
β (°)	96.11(1)	103.525(4)	94.43(1)	85.691(6)
γ (°)	90.00	90.00	90.00	69.90(1)
<i>V</i> (Å ³)	1246.7(3)	1781.2(2)	1705.7(3)	612.03(13)
<i>Z</i>	4	4	4	2
Temperature (K)	293(2)	296.2	293(2)	293(2)
<i>D</i> _{calc} (g cm ⁻³)	1.763	1.450	1.597	1.644
2 θ _{max} (°)	63.94	54.96	69.92	69.92
Number of reflections collected	4519	12 406	8076	11 720
Number of unique reflections	2437	2227	3967	3956
<i>R</i> _{int}	0.0084	0.043	0.0121	0.0140
Goodness-of-fit	0.935	1.367	0.871	0.638
<i>R</i> ₁	0.0297	0.0384	0.0324	0.0249
<i>wR</i> ₂	0.0646	0.0497	0.0695	0.0770
μ (mm ⁻¹)	2.790	1.965	2.058	2.821
Number of reflections with <i>I</i> > 2 σ (<i>I</i>)	4263	3635	7417	5317
Minimum transmission factor	0.665	0.470	0.9653	1.000

3.3. *t*-Butyl[tris(2-carboxyethylthio)]germane (6)

To a mixture of 3-mercaptopropanoic acid (1.59 g, 15 mmol) and pyridine (0.8 g) in benzene (5 ml), there was added *t*-butyltrichlorogermane (1.18 g, 5 mmol) in THF (10 ml) at room temperature under nitrogen, and the mixture was stirred for 12 h. The mixture was neutralized with aq. HCl (1 mol dm⁻³), the organic layer was separated and washed with water, and dried over Na₂SO₄. The solvent was removed to obtain the crude residual solid that was recrystallized from a mixture of THF/Et₂O to give colorless crystals of **6** (1.12 g, 25%). m.p. 152–155 °C. The solubility of **6** in water is modest; 0.4966 g/100 g as determined by inductive combination plasma (ICP) method and its p*K*_a value is 4.2. Anal. Calc. for C₁₃H₂₄GeO₆S₃: C, 35.07; H, 5.43. Found: C, 35.25; H, 5.30%.

3.4. X-ray crystallographic analysis

For **2**, **4** and **5**, the structure was solved using SHELXS-97 [13] and refined using SHELXL-97.

Crystal data from **3** were collected at room temperature on a Rigaku R AXIS-RAPID Imaging Plate four-circle diffractometer. Intensity data were collected by the scan techniques. Structures were solved by direct methods using the programs SIR 92. Structures were refined by full-matrix least-squares interactions. Perspective views of the molecules (Figs. 1–3) were made by

the use of ORTEP for teXsan [14]. The crystallographic data are summarized in Table 2.

4. Supplementary material

Final atomic parameters of **2–5** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 211701 (**2**), 211702 (**3**), 211703 (**4**) and 211704 (**5**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

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