

Research paper

# Synthesis and structure of hypercoordinated germanate complexes with naphthalene-2,3-dialkoxide ligands

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## ABSTRACT

The synthesis of six-coordinated germanate complexes with naphthalene-2,3-dialkoxide ligands with alkali metals (Li, Na, and K) as counter ions are described. The molecular structures of lithium and potassium germanate complexes were clarified by X-ray diffraction analysis. Each germanium center atom is coordinated by six oxygen atoms to form slightly distorted octahedral configuration. All the compounds were thermally stable up to 300 °C determined by thermogravimetric analysis under air-flow conditions.

## 1. Introduction

Hypercoordinate species in organic chemistry play an important role as the key intermediates in nucleophilic substitution reactions. However, hypercoordinate carbon species are not stable enough to be isolated in order to study the reaction mechanisms. On the other hand, a number of hypercoordinate compounds with silicon center has been synthesized and reported [1]. For example, in Tamao-oxidation, Hosomi-Sakurai reaction, Hiyama-coupling reaction, it is well known that hypercoordinate silicon species play a role of the key intermediates in the course of these reactions [2–4]. Clarification of the structure of these hypercoordinate species is important for understanding their reaction mechanisms.

Recently, Syroeshkin, Jouikov, and co-workers reported synthesis of di-*tert*-butylcatecholate germanium complexes and the structure was determined by X-ray diffraction [5]. Baines, Frišćić, Lumb, and co-workers reported new synthetic approach for organogermanes to employ hypercoordinate germanium species as a unique intermediate without use of the chlorogermanes [6]. In their report, molecular structures of some intermediate hexa-coordinated germanium complexes were determined by X-ray diffraction analysis. These structures contain two catecholate ligands and one or two solvated amine molecules. Tris(oxalato)germanate complexes were synthesized by Paz, Rocha, and co-workers, and their crystal structures were also determined by X-ray crystallography [7]. Corriu and co-workers synthesized six-coordinated silicates having catecholate ligands by the reaction of tetramethyl orthosilicate and catechol in the presence of sodium or potassium alkoxides in methanol [8]. They also succeeded in synthesis

and characterization of six-coordinated germanate with catecholate ligands [9]. However, the molecular structures of these hypercoordinate heavier group 14-element ate-complexes were not determined by X-ray crystallography. We report here the synthesis and molecular structures of a series of six-coordinated germanates with naphthalene-2,3-dialkoxide ligands.

## 2. Results and discussion

The reaction of germanium oxide and three molar amounts of 2,3-naphthalenediol in the presence of two molar amounts of lithium methoxide in methanol led to the formation of lithium tris(naphthalene-2,3-dialkoxido)germanate **1** in 78% yield (Scheme 1). Although lithium silicate and germanate with catecholate ligands [8–9] are unstable in the air, lithium germanate **1** could be isolated as colorless crystals which were stable in the air. Germanate **1** was fully characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>7</sup>Li NMR spectroscopy in methanol-*d*<sub>4</sub>. The crystals were found to contain two equivalents of water molecules (Fig. S1). However, according to the elemental analysis, the composition was represented by 1-(H<sub>2</sub>O)<sub>5</sub>. We assumed that the reason for the inconsistency would be derived from the hygroscopic property of lithium germanate **1**. The <sup>13</sup>C NMR signal assigned to the oxygen substituted carbon was observed at 152.3 ppm, which is shifted to down field about 5 ppm compared to that found in 2,3-naphthalenediol. In a similar manner sodium and potassium germanates **2** and **3** were synthesized as colorless crystals in 93% and 81% isolated yields, respectively. In order to clarify the structure of **2**, we tried to prepare single crystals by recrystallization using a variety of solvents, a single crystal suitable for X-ray diffraction could not be

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obtained. Relatively good microcrystals of **2** were obtained by recrystallization from dimethyl sulfoxide (DMSO). The crystals included four equivalents of DMSO and more than ten equivalents of water based on **2** determined by  $^1\text{H}$  NMR spectroscopy (Fig. S6). Although part of the water might come from the NMR solvent, it suggests that sodium germanate **2** might also exhibit hygroscopicity. The elemental analysis of **2** was performed by using microcrystals recrystallized from methanol / DMSO (1:1) mixed solvent. The results indicated that the composition should be  $2\cdot(\text{CH}_3\text{OH})_3\cdot(\text{dmsO})_4$ . However, the amount of the sample was too small to measure the NMR spectra using the same sample as the elemental analysis. As similar to **1**, the crystals of **3** also contained water, which is determined by the elemental analysis ( $3\cdot(\text{H}_2\text{O})_4$ ). The water signal is also observed in the  $^1\text{H}$  NMR spectrum of the sample recrystallized from isopropyl alcohol (IPA) (Fig. S8). All the germanate complexes are hygroscopic and soluble in water. Especially, sodium germanate **2** in water could be kept without decomposition for a month.

A single crystal of lithium germanate **1** could be obtained by the recrystallization from a mixed solvent, IPA / 1,2-dimethoxyethane (DME). The molecular structure of lithium germanate **1** was established by single crystal X-ray diffraction analysis. As the results of the X-ray diffraction, the obtained crystals contained 2.5 molecules of DME and 1.5 molecules of IPA for a lithium germanate. Therefore, the lithium germanate complex in the crystals obtained by recrystallization is denoted as  $1\cdot(\text{dme})_{2.5}\cdot(\text{ipa})_{1.5}$ . The selected bond distances and angles are summarized in Table 1. The crystal system is triclinic and the space group is  $P-1$  (#2). There are two independent molecules in the unit cell, which structures closely resemble each other (Fig. 1). The molecules including Ge1 or Ge2 are abbreviated as mol. A and mol. B, respectively. The germanium atom is coordinated by six oxygen atoms in a slightly distorted octahedral configuration. The Ge-O bond lengths are within the range from 1.870 Å (Ge1-O4) to 1.901 Å (Ge1-O3) in mol. A, and from 1.855 Å (Ge2-O14) to 1.913 pm (Ge2-O13) in mol. B. Considering that the typical  $\text{Ge}(\text{sp}^3)\text{-O}$  bond length is 1.73–1.75 Å [10], the Ge-O bond lengths in  $1\cdot(\text{dme})_{2.5}\cdot(\text{ipa})_{1.5}$  are clearly elongated for the hypercoordinate compound. These values are slightly longer than those found in tris(oxalato)germanium complexes (1.8641–1.8898 Å) [7] or octahedral bis(3,5-di-*tert*-butylcatecholato)germanium tetramethylethylenediamine adduct (1.8457–1.856 Å) [6] probably due to the weaker donor nature of naphthalene-2,3-dialkoxide ligands. The Ge-O bond lengths in  $1\cdot 2.5\text{DME}\cdot 1.5\text{IPA}$  are apparently longer than those found in bis(3,5-di-*tert*-butylcatecholato)germanium complexes (1.839–1.841 Å [5] or 1.847–1.849 Å [6]) or bis(3,6-di-*tert*-butylcatecholato)germanium complexes (1.819–1.8256 Å) [11], where it should be noted that two catecholate ligands in these complexes are bonded to germanium center in coplanar fashion. When O2 and O3 are in the apical position against the germanium center, the averaged vertical angle O-Ge-O is  $90.14^\circ$ , suggesting that four oxygen atoms O1, O4, O5, and O6 are located on a same square plane. However, the angle O2-Ge1-O3 is

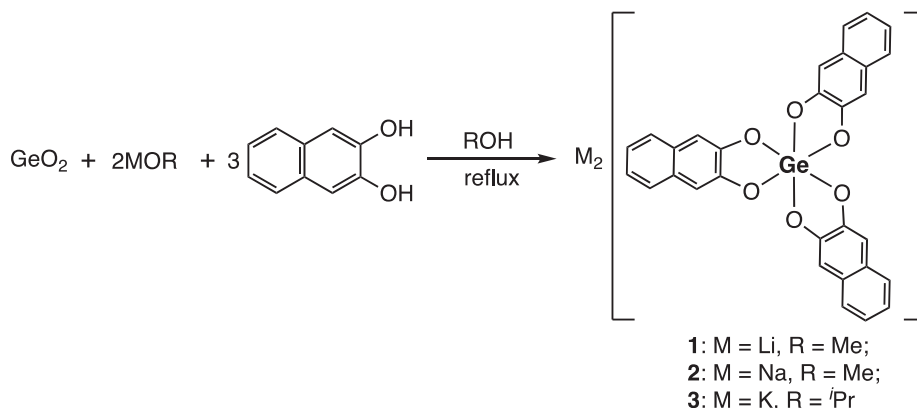
**Table 1**Selected bond distances (Å) and bond angles (degree) of germanate complex  $1\cdot(\text{dme})_{2.5}\cdot(\text{ipa})_{1.5}$ .

Bond distances			
Ge1 – O1	1.8939(19)	Ge1 – O2	1.8866(18)
Ge1 – O3	1.9008(18)	Ge1 – O4	1.8701(18)
Ge1 – O5	1.890(2)	Ge1 – O6	1.8760(19)
Ge2 – O13	1.9125(19)	Ge2 – O14	1.8554(19)
Ge2 – O15	1.9030(19)	Ge2 – O16	1.896(2)
Ge2 – O17	1.8606(19)	Ge2 – O18	1.911(2)
Ge1 – Li1	3.045(5)	Ge1 – Li2	3.265(6)
Ge2 – Li3	3.024(5)	Ge2 – Li4	3.577(6)
Bond angles			
O1 – Ge1 – O2	86.06(8)	O1 – Ge1 – O3	88.64(8)
O1 – Ge1 – O4	98.20(8)	O1 – Ge1 – O5	169.36(8)
O1 – Ge1 – O6	84.15(8)	O2 – Ge1 – O3	171.94(8)
O2 – Ge1 – O4	89.36(8)	O2 – Ge1 – O5	90.13(8)
O2 – Ge1 – O6	96.02(8)	O3 – Ge1 – O4	85.39(8)
O3 – Ge1 – O5	96.12(8)	O3 – Ge1 – O6	89.46(8)
O4 – Ge1 – O5	91.69(8)	O4 – Ge1 – O6	174.27(8)
O5 – Ge1 – O6	86.37(8)	O13 – Ge2 – O14	85.69(8)
O13 – Ge2 – O15	87.43(8)	O13 – Ge2 – O16	94.90(8)
O13 – Ge2 – O17	172.38(9)	O13 – Ge2 – O18	88.04(8)
O14 – Ge2 – O15	172.76(8)	O14 – Ge2 – O16	93.01(9)
O14 – Ge2 – O17	90.03(9)	O14 – Ge2 – O18	99.58(9)
O15 – Ge2 – O16	85.34(8)	O15 – Ge2 – O17	97.06(9)
O15 – Ge2 – O18	82.41(8)	O16 – Ge2 – O17	91.60(9)
O16 – Ge2 – O18	167.26(8)	O17 – Ge2 – O18	86.46(9)

$171.96^\circ$ , which deviates from linear form due to the influence of the bulky naphthalene rings.

There are two kind of lithium atoms in the crystal unit cell. Li1, Li2, and Li3 are coordinated by one IPA, one DME, and two oxygen atoms of a germanate complex, respectively. Only Li4 is solvated by two DME and is coordinated by one oxygen atom (O16) of a germanate complex. Li1, Li3, and Li4 atoms are coordinated by five oxygen atoms to form distorted trigonal bipyramid, and Li2 atom is coordinated by four oxygen atoms to form tetrahedral configuration. The interatomic distances between germanium and lithium are  $>3.024$  Å, suggesting that there is no covalent or electrostatic interaction between them.

Growing a single crystal of potassium germanate **3** was also successful by the recrystallization from 1,4-dioxane with small amount of water. The crystal structure of **3** was determined by X-ray diffraction analysis, and selected bond lengths and angles are summarized in Table 2. As the results of the X-ray diffraction, the obtained crystals contained four molecules of 1,4-dioxane and two molecules of water for a potassium germanate. Therefore, the potassium germanate complex in the single crystal is denoted as  $3\cdot(\text{C}_4\text{H}_8\text{O}_2)_4\cdot(\text{H}_2\text{O})_2$ . The crystal structure contained four clathrate dioxane molecules in the unit cell. The germanium center is coordinated by six oxygen atoms of 2,3-naphthalenedialkoxide ligands to form an octahedral arrangement, as shown in Fig. 2. The average length of Ge-O bonds is 1.874 Å, which is slightly

**Scheme 1.** Syntheses of germanate complexes (**1** – **3**).

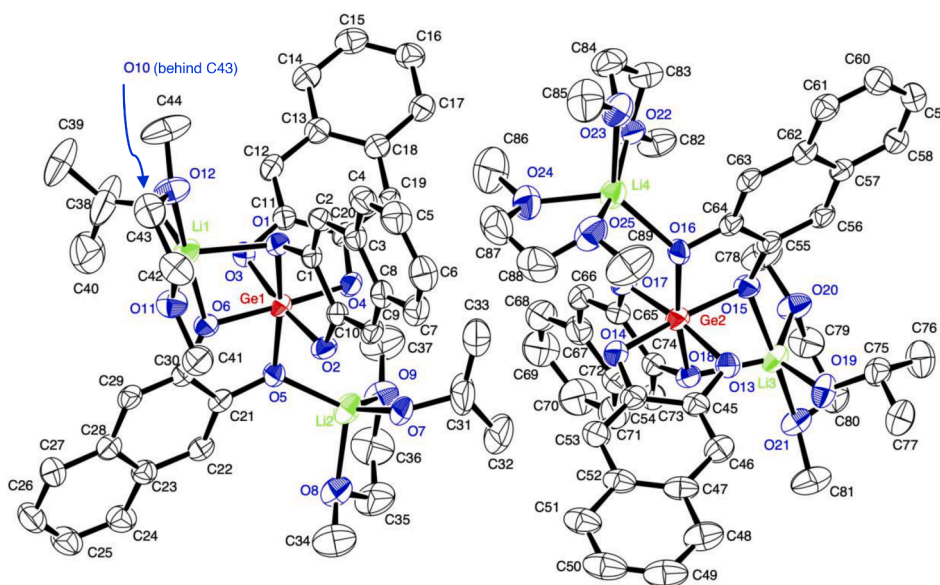


Fig. 1. Molecular structure of germanate complex 1-(dme)<sub>2.5</sub>-(ipa)<sub>1.5</sub> (50% probability level). Hydrogen atoms are omitted for clarity.

Table 2

Selected bond distances (Å) and bond angles (degree) of germanate complex 3-(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)<sub>4</sub>·(H<sub>2</sub>O)<sub>2</sub>.

Bond distances			
Ge1 – O1	1.887(8)	Ge1 – O2	1.854(5)
Ge1 – O3	1.872(6)	Ge1 – O4	1.871(5)
Ge1 – O5	1.875(7)	Ge1 – O6	1.886(5)
K1 – O1	2.808(10)	K1 – O6	2.749(13)
K1 – O7	2.706(10)	K1 – O7 <sup>a</sup>	2.740(7)
K1 – O8	2.696(7)	K1 – O10	2.660(7)
K2 – O3	2.830(14)	K2 – O5 <sup>b</sup>	2.951(14)
K2 – O12	2.620(8)	K2 – O12 <sup>b</sup>	2.645(7)
K2 – O13	2.720(7)	K2 – O15	2.643(8)
Bond angles			
O1 – Ge1 – O2	86.5(3)	O1 – Ge1 – O3	95.3(3)
O1 – Ge1 – O4	87.3(3)	O1 – Ge1 – O5	175.15(12)
O1 – Ge1 – O6	89.4(3)	O2 – Ge1 – O3	89.6(3)
O2 – Ge1 – O4	172.88(12)	O2 – Ge1 – O5	91.2(3)
O2 – Ge1 – O6	96.3(2)	O3 – Ge1 – O4	87.3(3)
O3 – Ge1 – O5	89.0(3)	O3 – Ge1 – O6	172.69(11)
O4 – Ge1 – O5	95.2(3)	O4 – Ge1 – O6	87.3(3)
O5 – Ge1 – O6	86.6(3)		

<sup>a</sup> Generated by symmetry operation of  $(-x + 1, -y, -z)$ .

<sup>b</sup> Generated by symmetry operation of  $(-x + 2, -y + 1, -z + 1)$ .

shorter than that found in lithium germanate 1-(dme)<sub>2.5</sub>-(ipa)<sub>1.5</sub> (1.886 Å in mol. A and 1.890 Å in mol. B). When O1 and O5 are in the apical positions of germanate complex 3-(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)<sub>4</sub>·(H<sub>2</sub>O)<sub>2</sub>, sum of the vertical angles of O2-Ge-O3, O2-Ge-O6, O3-Ge-O4, and O4-Ge-O6 is 360.5°, suggesting that Ge1, O2, O3, O4, and O6 are on the same square plane. However, the angle O1-Ge-O5 (175.2°) is slightly bent due to the steric hindrance of naphthalenedialkoxide ligands. Each of the potassium atoms is solvated by two 1,4-dioxane molecules and one water molecule, and is coordinated by two oxygen atoms of the naphthalenedialkoxide ligand. Interestingly, to generate all found atoms by symmetry operations, the germanate complexes are lined with each other through a square planar four-membered ring consisting of two potassium cations and two oxygen atoms of solvated water molecules, as shown in Fig. 3. The bond distances of K1-O7, K1-O7', K2-O12, and K2-O12'' are 2.706 Å, 2.740 Å, 2.620 Å, and 2.645 Å, respectively. The distance is shorter than that found in coordination bonding between potassium and oxygen atoms in the germanate complex (K1-O1 = 2.808 Å, K1-O6 = 2.749 Å, K2-O3 = 2.830 Å, K2-O5' = 2.951 Å). The bond angles of O7-K1-O7', K1-O7-K1', O12-K2-O12'', and K2-O12-K2'' are 89.7°, 90.3°, 88.2°, and

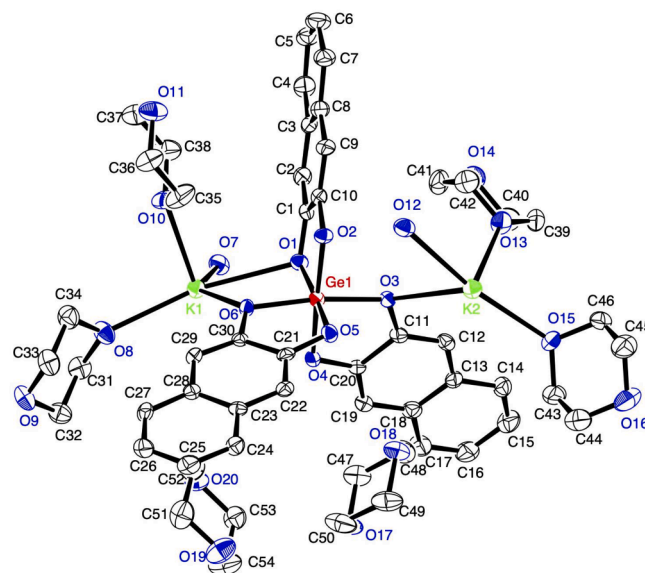
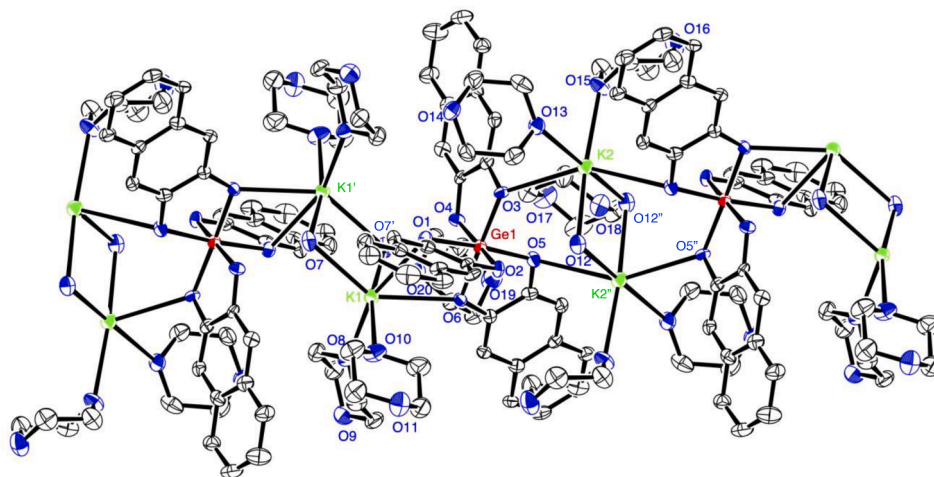


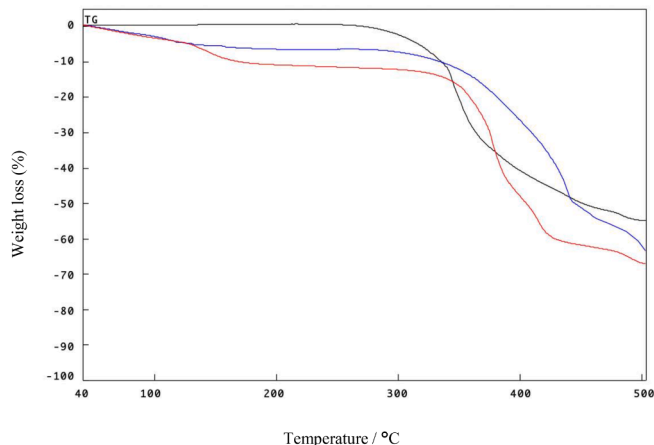
Fig. 2. Crystal structure of germanate complex 3-(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)<sub>4</sub>·(H<sub>2</sub>O)<sub>2</sub> with two clathrate dioxane molecules (50% probability level). Hydrogen atoms are omitted for clarity.

91.8°, respectively. The two water molecules interact with the clathrate dioxane molecules via hydrogen bond (Fig. S10). The interatomic distances of O7(water)-O4(germanate), O7-O20(dioxane), and O12(water)-O18(dioxane) are 2.714 Å, 2.881 Å, and 2.704 Å, respectively, which value is less than the sum of the corresponding van der Waals radii (3.04 Å).

Thermal stabilities of lithium germanate 1, sodium germanate 2, and potassium germanate 3 were also investigated by thermogravimetry (TG) under air flow. The crystals used for the TG measurements were dried overnight at room temperature under reduced pressure (20 Pa). These TG charts are summarized in Fig. 4. A weight of degradation (~7%) were observed up to ~130 °C in germanate 1, suggesting that a part of solvated IPA was lost, which is comparable to one molecule of IPA per germanate 1 unit. According to the X-ray diffraction analysis, 2.5 molecules of DME and 1.5 molecules of IPA were included in germanate 1 unit. The 7% weight of the crystals of germanate 1 corresponds



**Fig. 3.** Polymeric association in the crystal of  $3-(C_4H_8O_2)_4 \cdot (H_2O)_2$  (50% probability level). Hydrogen atoms are omitted for clarity. K1' and O7' are generated by a symmetry operation of  $(-x + 1, -y, -z)$ , respectively. K2'', O5'', and O12'' are generated by a symmetry operation of  $(-x + 2, -y + 1, -z + 1)$ , respectively.



**Fig. 4.** TG chart of germanate complexes **1** (blue line), **2** (red line), and **3** (black line) under air flow condition. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to an IPA molecule. From the viewpoint of solvation ability, DME is stronger than IPA due to the chelating effect. It is reasonable that heating causes an IPA molecule to be eliminated from the crystals of **1**. A decomposition point, which is determined by 5% degradation point from the plateau of the first weight loss, was observed at 338 °C, and residual yield was 36.2% after 500 °C heating. It is very surprising that lithium germanate **1** is stable in the air over 300 °C in spite of its hypercoordination.

Two-stage weight loss was observed in germanate **2**. The first stage ( $\sim 100$  °C) is suggested that one IPA molecule is lost, and then one more IPA molecule is extruded from the crystals at  $\sim 130$  °C. The decomposition point of **2** was observed at 330 °C, and residual yield was 33.2% after 500 °C heating. On the other hand, gradual weight degradation was not observed in potassium germanate **3** below 250 °C. The decomposition point (313 °C) of **3** is similar to that found in **1** and **2**. Based on the plateau after the solvent is removed, the residual yields of **1**–**3** at 500 °C were 43.5%, 44.1%, and 45.1%, respectively. These values are very close to each other. However, analysis of the components of the residues was not successful. It is considered that the weight loss might be still in progress at 500 °C.

### 3. Conclusion

We synthesized six-coordinated germanate complexes with alkali-metal counter-ions, and the molecular structures of these complexes were unequivocally determined by X-ray crystallography. In the crystal, lithium germanate **1** forms a contact ion pair, and two lithium cations are coordinated by oxygen atoms in the germanate complex and are solvated by DME and IPA. Potassium germanate **3** is the polymeric association in the solid state through a four-membered ring made of two potassium cations and two oxygen atoms of solvated water. These germanate centers are coordinated by six oxygen atoms of naphthalene-2,3-dialkoxide ligands, forming a slightly distorted octahedral configuration. The Ge–O bond lengths in octahedral germanates **1** and **3** tend to be longer than those in neutral planar bis(catecholato)germanium complexes. These germanate complexes were stable in the air and decomposed at the temperatures above 300 °C.

### 4. Experimental

#### 4.1. General method

The NMR spectra were obtained using JEOL ECX-500 ( $^1H$ : 500 MHz,  $^{13}C$ : 125 MHz,  $^7Li$ : 194 MHz) NMR spectrometer. X-ray crystallographic data and diffraction intensities were collected on Rigaku Rapid-S diffractometer utilizing graphite-monochromated Mo- $K\alpha$  ( $\lambda = 0.71073$  Å) radiation at  $-123$  °C. The structures were solved by the program system of Rigaku CrystalStructure with direct methods using SIR-92 [12] and the refinement methods using SHELXL program [13]. Thermogravimetric analyses were performed on Rigaku Thermo plus EVO-II instrument. Methanol, isopropyl alcohol (IPA), 1,2-dimethoxyethane (DME), and other solvents were distilled prior to use.

#### 4.2. Synthesis

##### 4.2.1. Synthesis of lithium tris(naphthalene-2,3-dialkoxido)germanate (**1**)

Lithium metal (0.31 g, 44 mmol) was reacted with methanol (30 mL) under Ar atmosphere to prepare lithium methoxide. Germanium oxide (2.30 g, 22 mmol) was added to the solution, and then three molar equivalents of 2,3-naphthalenediol (10.47 g, 65 mmol) in methanol (20 mL) were added dropwise to the mixture, and the mixture was stirred for 3 days under reflux. After evaporation of the solvent, pale brown solid was obtained. The solid was washed by ethyl acetate to give lithium germanate **1** as colorless crystals in 78.0% yield. M.p.  $> 200$  °C (instrumental limit).  $^1H$  NMR ( $CD_3OD$ )  $\delta$  6.96 (s, 6H), 7.03–7.05 (m, 6H), 7.43–7.45 (m, 6H);  $^{13}C\{^1H\}$  NMR ( $CD_3OD$ )  $\delta$  106.4, 122.3, 126.4,

130.8, 152.3;  $^7\text{Li}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  0.02. Anal. Calcd. for  $\text{C}_{30}\text{H}_{28}\text{O}_{11}\text{GeLi}_2$  ( $1\text{-(H}_2\text{O)}_5$ ) (%): C, 55.34; H, 4.34. Found (%): C, 55.51; H, 4.64.

#### 4.2.2. Synthesis of sodium tris(naphthalene-2,3-dialkoxido)germanate (2)

Sodium metal (0.92 g, 40 mmol) was reacted with methanol (50 mL) under nitrogen atmosphere to prepare sodium methoxide. Germanium oxide (2.18 g, 21 mmol) was added to the solution, and then three molar equivalents of 2,3-naphthalenediol (9.70 g, 61 mmol) in methanol (50 mL) were added dropwise to the mixture, and the mixture was stirred for 3 days under reflux. After evaporation of the solvent, pale brown solid was obtained. The solid was washed by diethyl ether to give sodium germanate **2** as colorless crystals in 93.2% yield. The obtained crystals were further recrystallized by dimethylsulfoxide to give pure colorless crystals (however, a single crystal was not obtained). M.p. > 200 °C (instrumental limit).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  2.58 (s, 24H, DMSO), 6.95 (s, 6H), 7.02–7.06 (m, 6H), 7.42–7.46 (m, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  40.3 (DMSO), 106.4, 122.4, 126.5, 130.8, 152.4; Anal. Calcd. for  $\text{C}_{41}\text{H}_{54}\text{O}_{13}\text{GeNa}_2\text{S}_4$  ( $2\text{-(CH}_3\text{OH)}_3\text{-(dmsO)}_4$ ) (%): C, 49.16; H, 5.43; S, 12.81. Found (%): C, 48.80; H, 4.89; S, 12.79.

#### 4.2.3. Synthesis of potassium tris(naphthalene-2,3-dialkoxido)germanate (3)

Potassium metal (2.05 g, 52 mmol) was reacted with isopropyl alcohol (100 mL) under nitrogen atmosphere to prepare potassium alkoxide. Germanium oxide (2.74 g, 26 mmol) was added to the solution, and then three molar equivalents of 2,3-naphthalenediol (12.59 g, 79 mmol) in isopropyl alcohol (50 mL) were added dropwise to the mixture, and the mixture was stirred for 5 days under reflux. After evaporation of the solvent, pale brown solid was obtained. The solid was washed by diethyl ether to give potassium germanate **3** as colorless crystals in 86.9% yield. M.p. > 200 °C (instrumental limit).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  6.95 (s, 6H), 7.02–7.04 (m, 6H), 7.43–7.45 (m, 6H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  106.4, 122.4, 126.5, 130.9, 152.4. Anal. Calcd. for  $\text{C}_{30}\text{H}_{26}\text{O}_{10}\text{GeK}_2$  ( $3\text{-(H}_2\text{O)}_4$ ) (%): C, 51.67; H, 3.76. Found (%): C, 51.59; H, 3.53.

#### 4.3. Crystal structure determination of germanates 1 and 3

A single-crystal of germanate **1**- ( $\text{dme}$ ) $_{2.5}$ - ( $\text{ipa}$ ) $_{1.5}$  was obtained by recrystallization from IPA and DME mixed solvent (1:1). A single-crystal of germanate **3**- ( $\text{C}_4\text{H}_8\text{O}_2$ ) $_4$ - ( $\text{H}_2\text{O}$ ) $_2$  was obtained by recrystallization from 1,4-dioxane with small amount of water. Both single-crystal X-ray diffraction analyses were performed under cold nitrogen flow, and the crystallographic data for **1**- ( $\text{dme}$ ) $_{2.5}$ - ( $\text{ipa}$ ) $_{1.5}$  and **3**- ( $\text{C}_4\text{H}_8\text{O}_2$ ) $_4$ - ( $\text{H}_2\text{O}$ ) $_2$  are summarized in Table 3. The X-ray diffraction data for **3**- ( $\text{C}_4\text{H}_8\text{O}_2$ ) $_4$ - ( $\text{H}_2\text{O}$ ) $_2$  was not always enough due to the single crystal quality which was quite small. Although we have tried multiple measurements for several years, the best data which we could collect is submitted data. Supplementary crystallographic data are available as CCDC-2083392 (for **1**- ( $\text{dme}$ ) $_{2.5}$ - ( $\text{ipa}$ ) $_{1.5}$ ) and 2,083,391 (for **3**- ( $\text{C}_4\text{H}_8\text{O}_2$ ) $_4$ - ( $\text{H}_2\text{O}$ ) $_2$ ).

#### CCRediT authorship contribution statement

**Masato Nanjo:** Conceptualization, Formal analysis, Investigation, Methodology, Supervision, and Writing - original draft. **Mitsuki Goto:** Formal analysis and Investigation. **Yuta Nakashima:** Formal analysis and Investigation.

**Table 3**

Crystallographic data for germanate complexes **1**- ( $\text{dme}$ ) $_{2.5}$ - ( $\text{ipa}$ ) $_{1.5}$  and **3**- ( $\text{C}_4\text{H}_8\text{O}_2$ ) $_4$ - ( $\text{H}_2\text{O}$ ) $_2$ .

	<b>1</b> - ( $\text{dme}$ ) $_{2.5}$ - ( $\text{ipa}$ ) $_{1.5}$	<b>3</b> - ( $\text{C}_4\text{H}_8\text{O}_2$ ) $_4$ - ( $\text{H}_2\text{O}$ ) $_2$
Formula	$\text{C}_{89}\text{H}_{110}\text{Ge}_2\text{Li}_4\text{O}_{25}$	$\text{C}_{54}\text{H}_{70}\text{GeK}_2\text{O}_{20}$
Mol. weight	1752.78	1189.92
Crystal system	Triclinic	Triclinic
Space group	P-1 (No.2)	P-1 (No.2)
Unit cell dimensions		
<i>a</i> (Å)	13.807(3)	13.90(4)
<i>b</i> (Å)	14.450(3)	15.49(3)
<i>c</i> (Å)	25.167(4)	15.54(5)
$\alpha$ (°)	105.793(9)	109.88(19)
$\beta$ (°)	94.804(8)	102.5(2)
$\gamma$ (°)	108.320(9)	110.17(18)
<i>V</i> (Å <sup>3</sup> )	4506.9(16)	2735(15)
<i>Z</i>	2	2
<i>D</i> <sub>calc.</sub> (g cm <sup>-3</sup> )	1.291	1.445
Unique reflections	19,622	10,909
No. variables	1093	710
<i>R</i> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0530	0.0585
<i>wR</i> <sub>2</sub> (all data)	0.1320	0.1422
GO F	0.967	0.929

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ica.2021.120608>.

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