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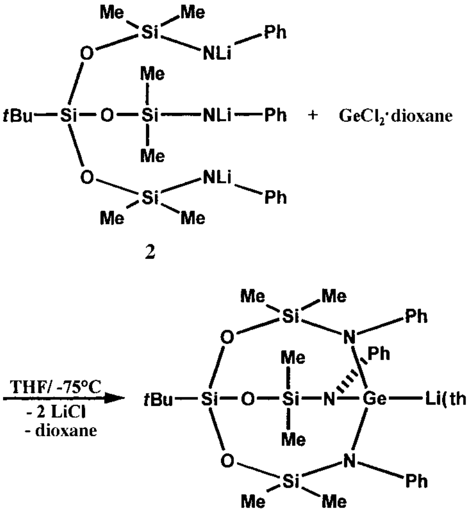
The First Crystal Structure of a Germanium(II) Amide with a Germanium–Lithium Bond and Its Behavior Towards Oxygen and Water[**]

Michael Veith,[*] Oliver Schütt, and Volker Huch

Dedicated to Professor Gerhard Fritz
on the occasion of his 80th birthday

Amides of Group 4 metals that contain metal–lithium bonds are relatively rare. A few years ago, Gade et al. reported the crystal structure of a tripodal silyl amide with a tin(II)–lithium bond.[1] A mixed germanium–lithium amide was also synthesized;[2] however, the structure of this compound could not be determined by X-ray structure analysis. In recent years only a few compounds containing germanium–lithium bonds have been synthesized and characterized by X-ray crystallography.[3–5] Very little is known about the chemistry of these compounds. We report here on the synthesis and crystal structure of a tripodal germanium(II) siloxamide with a germanium–lithium bond as well as on the reaction behavior of this bond towards water and oxygen. Interestingly, these reactions led to a simple Li/H exchange and an insertion of an oxygen atom into the germanium–lithium bond, respectively. We were able to isolate the reaction products from the hydrolysis and the oxidation and determine the structure of these compounds by X-ray crystallography.

The ligand system used was the tripodal amine tBuSi(OSiMe$_2$NHPh)$_3$ (**1**);[6] its lithium salt **2**[6] was taken as the starting material for the synthesis of the germanium(II) siloxamide **3**. Compound **2** reacted with an adduct of germanium (II) chloride and dioxane[7] (equimolar amounts with respect to **2**) in THF at $-75\,^{\circ}$C to give the heterometallic amide **3** in good yields [Eq. (1)]. The ^{1}H, ^{13}C, ^{29}Si, and ^{7}Li NMR spectra of **3** in solution showed only one singlet each for the dimethylsilyl groups, for the methyl groups of the *tert*-butyl group, and for the lithium atom. This indicates that in solution **3** should have, at least on a time-average, C_{3v} symmetry. The ^{1}H and ^{13}C NMR spectra also contain signals for coordinated THF molecules.



2 **3** (1)

Controlled hydrolysis of **3** in THF gave the solvent-free germanium hydride **4** in 63% yield [Eq. (2)] along with the soluble side product **1** (20–30%). The remarkably simple Li/H exchange, for which there are only a few analogies,[8] can be explained by an attack of the oxygen atom of the water molecule on the Lewis acidic lithium atom of the Ge–Li bond. The proton transfers to the partially negatively charged germanium atom to yield **4** and lithium hydroxide. This corresponds to a change in the partial charge on the germanium atom since the proton is now regarded as a hydride. In the IR spectrum of the product the characteristic

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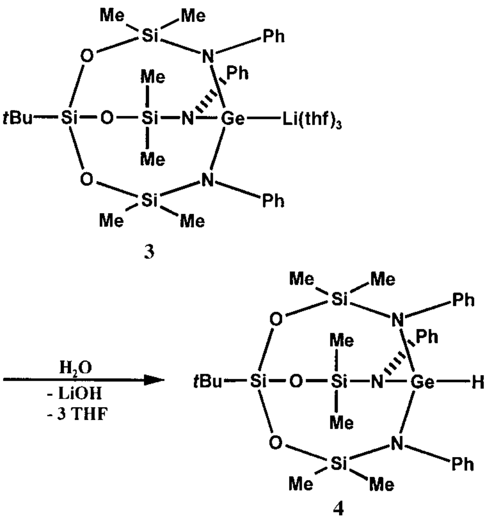
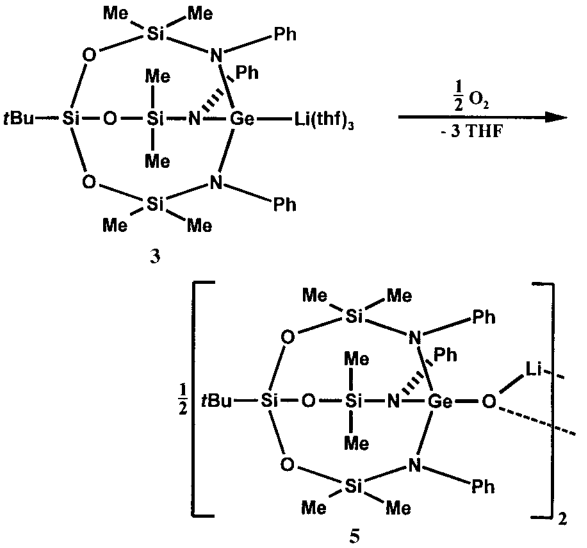
[**] This work was supported by the Fonds der Chemischen Industrie as part of the DFG project "Spezifische Phänomene in der Siliciumchemie".



(2)

Ge–H vibration at $\tilde{\nu} = 2105\,cm^{-1}$ is present, which indicates that **4** has indeed been formed. The IR spectra of other germanium hydrides show bands at similar wavenumbers.[9–13] The ^1H, ^{13}C, and ^{29}Si NMR spectra of **4** also contain only one singlet each for the dimethylsilyl groups and the methyl groups of the *tert*-butyl group. Therefore, it is assumed that there are C_{3v}-symmetric molecules in solution as well. The ^1H NMR spectrum also contains a singlet for the hydride hydrogen atom at $\delta = 5.66$.

When dry oxygen was bubbled through a solution of **3** in benzene for a short time the color lightened from orange to yellow. The reason for the color change is the insertion of an oxygen atom into the germanium–lithium bond. This oxidation of germanium(II) produces a germanium(IV) center in the dimeric, solvent-free lithium germanolate **5** [Eq. (3)]. A simultaneous hydrolysis, possibly caused by traces of water, to afford the hydroxide $tBuSi(OSiMe_2NPh)_3GeOH$ (**6**) and a subsequent in situ lithiation to the germanolate **5** can be excluded, since in the NMR spectrum of the reaction solution no compounds other than **5** were detected. The soluble germanol **6** was synthesized independently by hydrolysis of **5** and was completely characterized.[14] The NMR spectra of **5** in solution are similar to those of **3** and **4**.



(3)

An X-ray crystal structure analysis was undertaken for all three germanium compounds,[15] and the structures obtained are shown in Figures 1–3. The compounds all contain the bicyclic cage $[tBuSi(OSiMe_2NPh)_3Ge]$ and only differ in the functionalization of the tetrahedrally coordinated germanium atom. The SiO_3 and GeN_3 units of the bicycles are twisted relative to one another. The germanium amide **3** and the hydride **4** are almost C_3-symmetric; however, dimeric **5** has crystallographic C_i symmetry. In **3** the bond length between the germanium and the lithium atom (2.904(12) Å) is unusually large (Figure 1); in other compounds with germanium–lithium interactions,[3–5] the bond length is much closer to the sum of the covalent radii (2.56 Å). The relatively large Ge–N bond lengths (av 1.982(4) Å) along with the large Ge–Li bond length suggest a germanate which forms a contact ion pair with the lithium atom.

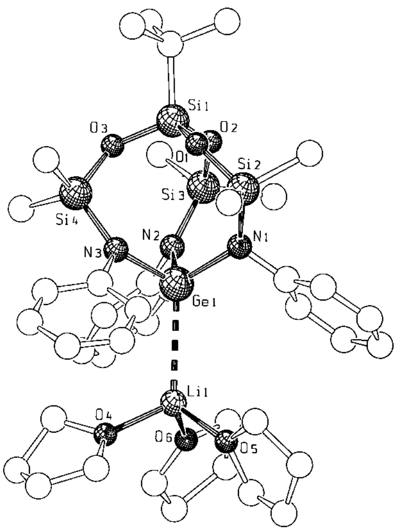


Figure 1. Crystal structure of **3**. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.983(4), Ge1–N2 1.983(4), Ge1–N3 1.979(4), Ge1–Li1 2.904(12), Si2–N1 1.734(5), Si3–N2 1.746(4), Si4–N3 1.740(4); N3-Ge1-N1 101.43(18), N3-Ge1-N2 102.25(18), N1-Ge1-N2 101.55(18), N3-Ge1-Li1 114.0(3), N1-Ge1-Li1 119.3(3), N2-Ge1-Li1 115.8(3). The hydrogen atoms are omitted for clarity. The unlabeled atoms are carbon atoms.

In the germanium hydride **4**,[15] the length of the Ge–H bond (1.40(3) Å, Figure 2) is similar to that found in other germanium hydrides.[9, 10, 16–20] The formal oxidation of Ge^{II} by the hydrolysis of **3** to give Ge^{IV} in **4** is reflected in the considerably shorter average N–Ge bond length of 1.848(3) Å (compared to 1.982(4) Å in **3**). In contrast, the average bond angle increases from 101.74(18)° in **3** to 111.84(13)° in **4**.

Lithium germanolate **5**, which is formed by the insertion of oxygen into the Ge–Li bond, is a dimer as a result of the Lewis acid–Lewis base interactions between the lithium and the oxygen atom to give an approximately rhombic, planar, four-membered Li_2O_2 ring; the inversion center of the dimer lies in the center of this ring (Figure 3). Because of the low coordination numbers, the Li–O bond lengths in **5** are smaller than those of other compounds that contain planar four-membered Li_2O_2 rings. [21–25] The lithium atoms are not only

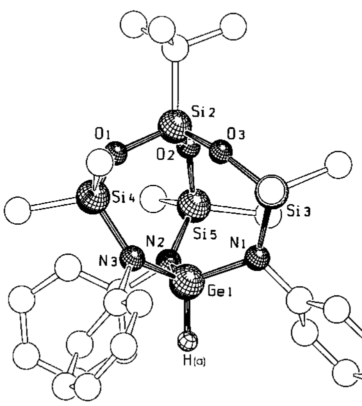


Figure 2. Crystal structure of **4**. Selected bond lengths [Å] and angles [°]: Ge1–N3 1.848(3), Ge1–N2 1.848(3), Ge1–N1 1.849(3), Ge–H(a) 1.40(3), Si3–N1 1.733(3), Si4–N3 1.738(3), Si5–N2 1.749(3); N3-Ge1-N2 110.29(13), N3-Ge1-N1 113.65(13), N2-Ge1-N1 111.59(13), N1-Ge1-H(a) 106.1(12), N2-Ge1-H(a) 109.9(13), N3-Ge1-H(a) 105.0(13). The hydrogen atoms are omitted for clarity. The unlabeled atoms are carbon atoms.

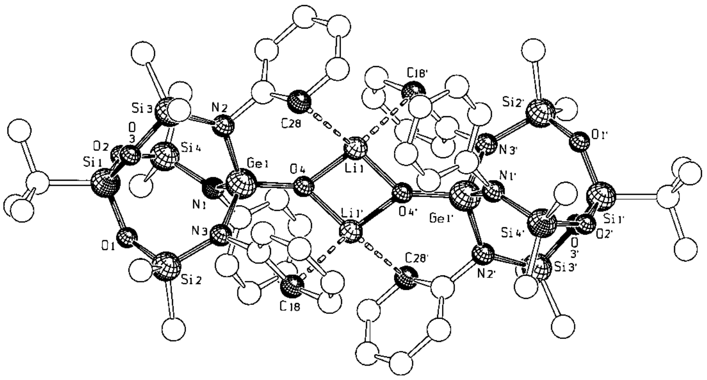


Figure 3. Crystal structure of **5**. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.847(6), Ge1–N3 1.866(5), Ge1–N2 1.866(6), Ge1–O4 1.702(4), Si2–N3 1.725(5), Si3–N2 1.738(6), Si4–N1 1.729(6), Li1–O4′ 1.806(15), O4–Li1 1.784(15), Li1–Li1′ 2.31(3), C18–Li1′ 2.61(2), C28–Li1 2.71(2); N1-Ge1-N3 109.6(2), N1-Ge1-N2 110.0(3), N3-Ge1-N2 109.6(3), Li1-O4-Li1′ 80.0(7), O4-Li1-O4′ 100.0(7). The hydrogen atoms are omitted for clarity. The unlabeled atoms are carbon atoms.

coordinated to two oxygen atoms, they also weakly interact with the π electrons of the phenyl groups (shortest Li–C bond lengths: 2.61(2), 2.71(2) Å), so that they have distorted tetrahedral coordination. The shortening of the Ge–O bond (1.702(4) Å) is remarkable: This bond is not only 0.25 Å shorter than the sum of the covalent radii of germanium and oxygen, but it is also shorter than typical Ge–O single bonds.[13, 26–29] This is apparently caused by the high electronegativity of the "charged" oxygen atom. As in **4**, the oxidation state of Ge^{IV} in **5** is responsible for the shorter Ge–N bonds (av 1.860(6) Å) and larger N-Ge-N angles (av 109.73(3)°) than in **3**. Our results are remarkable in that there is a simple change of charge on the germanium atom in **3** as a consequence of the lithium–hydrogen exchange (**4**) and a simple insertion of oxygen into a bond between two electropositive elements (**5**).

Experimental Section

3: To a solution of **2** (0.60 g, 1 mmol) in THF (20 mL) at −75 °C was added $GeCl_2 \cdot$ dioxane (0.23 g, 1 mmol) in THF (5 mL). The mixture was stirred for 2 h at ≈25 °C, concentrated under vacuum, taken up in diethyl ether, and filtered. Slow concentration of the filtrate under reduced pressure resulted in precipitation of colorless prisms of **3**. Yield: 0.70 g (80 %). ^1H NMR (200.13 MHz, C_6D_6): $\delta = 0.63$ (s, 18 H; $OSi(CH_3)_2N$), 1.30 (s, 9 H; $SiC(CH_3)_3$), 1.32 (m, 12 H; THF), 3.25 (m, 12 H; THF); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 3.95$ (s, 6 C; $OSi(CH_3)_2N$), 16.96 (s, 1 C; $Si\mathit{C}(CH_3)_3$), 26.65 (s, 3 C; $SiC(\mathit{C}H_3)_3$), 25.51 (s, 6 C; THF), 68.35 (s, 6 C; THF), 118.48, 126.31, 128.10, 154.65 (4s; arene C); ^{29}Si NMR (39.7 MHz, C_6D_6): $\delta = -8.96$ (s, 3 Si; $OSi(CH_3)_2N$), −56.05 (s, 1 Si; $SiC(CH_3)_3$); ^7Li NMR (77.7 MHz, C_6D_6): $\delta = -3.57$ (s, 1 Li; GeLi); correct elemental analysis; cryoscopy: calcd 876.85, found 890.

4: To **2** (0.65 g, 1.08 mmol) in THF (20 mL) at −75 °C was added dropwise $GeCl_2 \cdot$ dioxane (0.25 g, 1.08 mmol) in THF (5 mL). After stirring for 2 h at about 25 °C, the mixture was cooled with ice and a 1 M solution of water in dioxane (1 mL) was slowly added. The mixture was stirred for 2 h at about 25 °C. The solvent was evaporated to give a solid residue, which was taken up in hexane (20 mL). The LiCl precipitate was filtered off, and the filtrate was slowly concentrated under reduced pressure until colorless parallelipeds of **4** began to precipitate. Yield: 0.44 g (63 %). ^1H NMR (200.13 MHz, C_6D_6): $\delta = 0.40$ (s, 18 H; $OSi(CH_3)_2N$), 1.18 (s, 9 H; $SiC(CH_3)_3$), 5.66 (s, 1 H; GeH); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 2.37$ (s, 6 C; $OSi(CH_3)_2N$), 16.59 (s, 1 C; $Si\mathit{C}(CH_3)_3$), 25.92 (s, 3 C; $SiC(\mathit{C}H_3)_3$), 123.86, 128.20, 129.34, 147.34 (4s; arene C); ^{29}Si NMR (39.7 MHz, C_6D_6): $\delta = -4.64$ (s, 3 Si; $OSi(CH_3)_2N$), −56.91 (s, 1 Si; $SiC(CH_3)_3$); IR (NaCl, hexane): $\tilde{\nu} = 2105.3\ cm^{-1}$; correct elemental analysis; cryoscopy: calcd 654.60, found 660.

5: Compound **3** (0.9 g, 1.03 mmol) was dissolved in benzene (20 mL) and dry oxygen was bubbled through the solution for approximately 10 s at about 25 °C. The mixture was stirred for 30 min. The solvent was evaporated to give a yellow solid which was recrystallized from hexane to afford **5** as colorless, cuboid rods with a total yield of 0.51 g (73 %). ^1H NMR (200.13 MHz, C_6D_6): $\delta = 0.38$ (s, 36 H; $OSi(CH_3)_2N$), 1.20 (s, 18 H; $SiC(CH_3)_3$); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 2.57$ (s, 12 C; $OSi(CH_3)_2N$), 16.65 (s, 2 C; $Si\mathit{C}(CH_3)_3$), 26.04 (s, 6 C; $SiC(\mathit{C}H_3)_3$), 123.31, 128.77, 129.95, 148.26 (4s; arene C); ^{29}Si NMR (39.7 MHz, C_6D_6): $\delta = -6.37$ (s, 6 Si; $OSi(CH_3)_2N$), −55.85 (s, 2 Si; $SiC(CH_3)_3$); ^7Li NMR (77.71 MHz, C_6D_6): $\delta = -4.99$ (s, 2 Li; GeOLi); correct elemental analysis; cryoscopy: calcd 1353.07, found 1340.

Received: July 9, 1999 [Z13699]

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[15] Crystal structure analysis: diffractometer: Stoe IPDS (**3**), Stoe AED 2 (**4**, **5**). **3**: Monoclinic, $C2/c$, $a = 19.401(4)$, $b = 15.434(3)$, $c = 34.151(7)$ Å, $\beta = 98.31(3)°$, $V = 10119(4)$ Å^3, $Z = 8$, 5535 "observed"

reflections, 496 parameters, $R = 0.0633$. **4**: Triclinic, $P\bar{1}$, $a = 10.689(2)$, $b = 11.170(2)$, $c = 15.330(6)$ Å, $\alpha = 84.2(3)$, $\beta = 89.39(3)$, $\gamma = 73.24(3)^\circ$, $V = 1743.3(6)$ Å^3, $Z = 2$, 3849 "observed" reflections, 356 parameters, $R = 0.0373$. The hydride hydrogen atom H(a) was localized by differential Fourier synthesis and refined with a free isotropic B value. **5**: Monoclinic, $C2/c$, $a = 25.090(5)$, $b = 10.798(2)$, $c = 30.262(6)$ Å, $\beta = 106.99(3)^\circ$, $V = 7841(3)$ Å^3, $Z = 8$, 4103 "observed" reflections, 370 parameters, $R = 0.0598$. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata§fiz-karlsruhe.de) on quoting the depository numbers CSD-133780 (**3**), -133781 (**4**), and 133782 (**5**).

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Crystal Design of Barium Sulfate using Double-Hydrophilic Block Copolymers

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The controlled growth of crystals with respect to size, shape, and crystal structure, the so-called "crystal design", is a preindustrial manufacturing procedure known since the Middle Ages, but has returned as a key aspect of modern materials science. The reasons for this are obvious, since the use of powders as abrasives, fillers, or ceramic precursors relies on the homogeneity of the powders to certain particle sizes and shapes. Further, the patterns of bioceramic matter such as bone, teeth, or seashells, with their properties superior to current man-made ceramics, show that control of the growth of single nanocrystals as well as their simultaneous alignment in some ordered superstructure is a motive to generate water-borne, environmentally friendly materials.[1] In this Communication, biological principles to control crystal growth are mimicked with easily synthesized polymers where the growth of $BaSO_4$ is affected to effect a wide variety of well-defined morphologies.

The morphology of single nanocrystals or colloidal microparticles is classically controlled by application of low molecular mass additives or salts, hydrothermal hydrolysis of amorphous solids, or special crystallization conditions.[2] In recent years, biological molecules were isolated from living systems, for example from seashells, and the crystal growth control was repeated in in-vitro experiments.[3] Recently, a new class of crystal modifiers, the double-hydrophilic block copolymers, was developed[4a] and found to be very active in the control of the crystal morphologies of calcium carbonate[4a, 5] and hydroxyapatite.[6] Those polymers are designed as "molecular tools", where one block interacts strongly with the mineral surface whereas the other block just keeps the "construction site" in solution. In this work, we report on the control and generation of unconventional crystal superstructures of barite, $BaSO_4$, using such block copolymers.

We varied the functional polymer block over a broad range, building polymer-bound arrays of carboxylate groups, aspartic acids, sulfonates, and phosphonates. Poly(ethyleneglycol)-*block*-poly(ethyleneimine)-poly(acetic acid) (PEG-*b*-PEIPA, PEG = 5000 g mol^{-1}, PEIPA = 1800 g mol^{-1}) was obtained as described in ref. [4a]. Poly(ethyleneglycol)-*block*-poly(ethyleneimine)-poly(sulfonic acid) (PEG-*b*-PEIPSA, PEG = 5000 g mol^{-1}, PEIPSA = 2360 g mol^{-1}) was prepared similarly by quantitative reaction with 1,3-propanesultone[4b]. A commercial poly(ethyleneglycol)-*block*-poly(methacrylic acid) (PEG-*b*-PMAA, PEG = 3000 g mol^{-1}, PMAA = 700 g mol^{-1}; Goldschmidt AG) was used as received. PEG-*b*-PMAA-Asp, with amino acid side chains, was prepared by amidation of PEG-*b*-PMAA with aspartic acid (27 %),[4b] while PEG-*b*-PMAAP was prepared by partially monophosphonating (21 %) the COOH groups of PEG-*b*-PMAA[5]. All polymers were purified by exhaustive dialysis. Crystal modification data is presented for these five double-hydrophilic block copolymers together with poly(methacrylic acid) (PMAA, as sodium salt; Aldrich, PMMA = 6500 g mol^{-1}).

The "synthesis" of the $BaSO_4$ particles involves simultaneous addition of 0.5 M $Ba(OAc)_2$ (Aldrich), 0.5 M $(NH_4)_2SO_4$ (Aldrich), and a 1 g L^{-1} aqueous solution of the different polymers (at pH 5 unless otherwise specified) in a double-jet reactor[4a] maintained at 25 °C. The continuous reactant supply of 0.5 mL h^{-1}, leading to a $BaSO_4$ formation rate of 1.39×10^{-5} mol L^{-1} min^{-1}, was stopped when the solution became turbid or crystal formation could be observed. The precipitates were left to stand in their mother solutions for at least 24 h to ensure equilibration.

The resulting $BaSO_4$ precipitates were characterized by scanning electron microscopy (SEM), and by transmission

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0570-0833/00/3903-0604 $ 17.50+.50/0