

# Synthesis and Structure of a Novel Lithium Gallosiloxane Containing a Ga<sub>4</sub>Si<sub>4</sub>O<sub>8</sub> Macrocyclic Analogous to the S8R Building Unit of Zeolites<sup>†</sup>

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**Summary:** The reaction of LiGaMe<sub>4</sub> with diphenylsilanediol in THF at 50 °C leads to the formation of the title gallosiloxane Li<sub>2</sub>(Li(THF)<sub>2</sub>)<sub>2</sub>[Ph<sub>2</sub>SiO<sub>2</sub>GaMe<sub>2</sub>]<sub>2</sub>[Ph<sub>2</sub>SiO<sub>2</sub>GaMe(OH)]<sub>2</sub>·2THF (**1**), which is made up of a central tetraanionic Ga<sub>4</sub>Si<sub>4</sub>O<sub>8</sub> 16-membered macrocyclic core. The cavity that is created by this tetraanionic gallosiloxane ring and also the presence of two Ga–OH groups pointing toward the center of the macrocyclic ring facilitate the entrapment of two lithium cations in the core through two Li–O(siloxide) and two Li–OH(Ga) linkages. The other two lithium ions are located at the periphery and are bound to the gallosiloxane ring through the Li–O(Si) linkages. Compound **1** represents the first organic-soluble molecular model compound for the S8R secondary building unit of several gallo- and aluminosilicates.

## Introduction

Aluminosilicates are ubiquitous in nature, being constituents of several minerals. They have also been a well-investigated class of compounds over the last several decades, owing to their interesting physical and chemical properties. In contrast, only recently has there been a sudden upsurge in the synthesis and study of gallosilicates in view of their usefulness in catalytic conversions.<sup>1–3</sup> Studies on gallium- and indium-containing silicates also warrant further attention in light of their recently reported utility in the catalytic reduction of toxic NO<sub>x</sub> gases,<sup>4</sup> a process used in cleaning up exhaust gases of combustion engines.<sup>5</sup>

The utility of soluble metallasiloxanes as model compounds for open-framework silicates and also as precursors for the preparation of mixed-metal oxide

materials, e.g. SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>, has been well documented in recent times.<sup>6,7</sup> In this context, while a number of model compounds containing Al–O–Si<sup>8</sup> or Al–O–P<sup>9</sup> linkages have been synthesized in recent times, there have only been a few examples of well-characterized molecular siloxanes with Ga–O–Si linkages in the literature.<sup>6,7</sup> In fact, there are only two reports in the literature describing single-crystal X-ray structures of gallosiloxanes.<sup>10,11</sup> Gallosiloxanes were reported in the literature as early in 1962 by Schmidbaur et al.<sup>7,12</sup> The dimeric gallosiloxane [Ga(OSiMe<sub>3</sub>)<sub>3</sub>]<sub>2</sub> (**A**) was synthesized from a direct reaction between Me<sub>3</sub>SiONa and GaCl<sub>3</sub>.<sup>12</sup> The gallosiloxane **A** was further used as the starting material along with MOSiMe<sub>3</sub> (M = Li, Na, K) for the synthesis of the first anionic molecular gallosilicates M[Ga(OSiMe<sub>3</sub>)<sub>4</sub>] (**B**) (Chart 1) through a nucleophilic addition reaction.<sup>13</sup> On the basis of IR studies it has been established that the gallosiloxane units exist as discrete anions in the case of Na and K derivatives. Similarly, Schmidbaur et al. have also prepared the anionic gallosiloxane [Me<sub>4</sub>Sb][Ga(OSiMe<sub>3</sub>)<sub>4</sub>] (**C**; Chart 1) from **A** and Me<sub>4</sub>Sb–OSiMe<sub>3</sub>.<sup>14</sup> Although the properties of **C** suggested that the bonding in this molecule could be more covalent,<sup>14</sup> a subsequent crystal structure

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<sup>†</sup> Dedicated to Dr. J. P. Mittal on the occasion of his 60th birthday.

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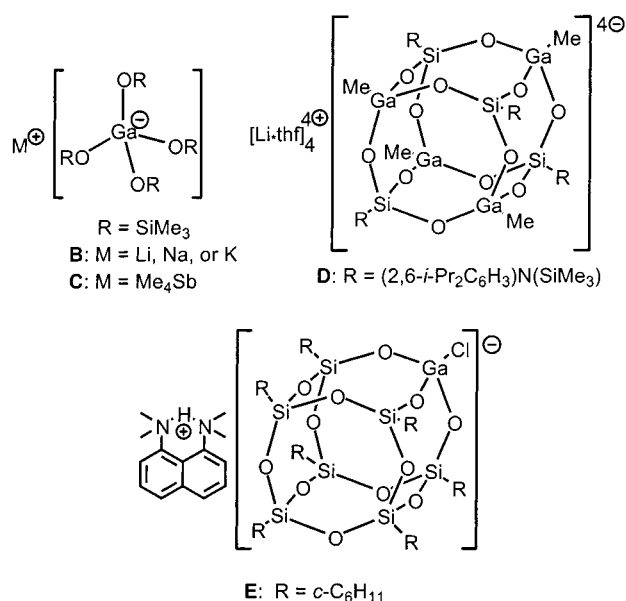
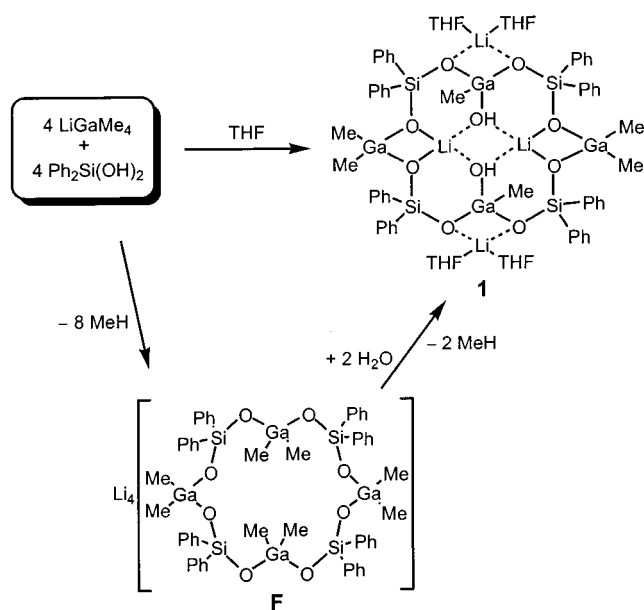
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Chart 1. Anionic Gallosiloxanes

Scheme 1. Synthesis of **1**

determination of the aluminum analogue [Me<sub>4</sub>Sb][Al(OSiMe<sub>3</sub>)<sub>4</sub>] has shown that even the tetramethylstibonium derivatives are ionic in nature.<sup>15</sup> More recently, Roesky et al. and Feher et al. have investigated the possibilities of using the silanetriols [RSi(OH)<sub>3</sub>] and trisilanols [R<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub>] (oligomeric silsesquioxanes) as precursors and synthesized a few interesting polyhedral gallosiloxanes, including anionic cubic gallosiloxanes **D** and **E** (Chart 1).<sup>10</sup> However, to date, only one anionic gallosiloxane molecule, viz. **E**, has been structurally characterized using X-ray crystallography.

Moreover, apart from the well-documented use of monosilanols [R<sub>3</sub>Si(OH)]<sub>7</sub>, silanetriols [RSi(OH)<sub>3</sub>]<sub>6a,b</sub> and oligomeric silsesquioxanes [R<sub>7</sub>Si<sub>7</sub>O<sub>9</sub>(OH)<sub>3</sub>]<sub>6c-e</sub> as starting materials for the synthesis of neutral and anionic gallosiloxanes, the ability of the silanediol [Ph<sub>2</sub>Si(OH)<sub>2</sub>]<sup>16</sup> to serve as a synthon for their preparation has not been investigated, despite its well-proven utility in the synthesis of cyclic and cage metallasiloxanes.<sup>6d,e,17</sup> In this contribution we report on the synthesis of a new gallosiloxane derived from diphenylsilanediol, which apart from representing the only polyanionic gallosiloxane to be characterized by single-crystal X-ray diffraction studies also serves as the first molecular

model for the single-8-ring (S8R) secondary building unit of zeolites.<sup>18</sup>

## Results and Discussion

Our initial attempts to synthesize molecular gallosiloxanes from diphenylsilanediol and commercially available GaR<sub>3</sub> precursors did not yield any characterizable products. However, the use of the non-Lewis-acidic ate complex [LiGaMe<sub>4</sub>]<sup>19</sup> in place of simple trialkyls leads to the clean formation of the analytically pure title lithium gallosiloxane Li<sub>2</sub>[Li(THF)<sub>2</sub>]<sub>2</sub>[Ph<sub>2</sub>SiO<sub>2</sub>GaMe<sub>2</sub>]<sub>2</sub>[Ph<sub>2</sub>SiO<sub>2</sub>GaMe(OH)]<sub>2</sub>·2THF (**1**) in 80% yield (Scheme 1). The formation of **1** could have proceeded via the all-alkyl intermediate Li<sub>4</sub>[Ph<sub>2</sub>SiO<sub>2</sub>GaMe<sub>2</sub>]<sub>4</sub> (**F**), which on reaction with the small traces of water<sup>20</sup> present in the reaction medium yields the final product as shown in Scheme 1. Siloxane **1** has been characterized by elemental analysis and IR, <sup>1</sup>H, <sup>7</sup>Li, and <sup>29</sup>Si NMR spectroscopic studies.

Because of the difficulties in deducing the molecular structure of **1** from the spectroscopic data (vide infra), the molecular structure of the reaction product has been unambiguously established by an X-ray diffraction study (Figure 1). There are several interesting features in the structure of **1**. Although at first sight the basic structural unit in molecule **1** may look like a dianionic gallosiloxane in which a molecular (LiOH)<sub>2</sub> dimeric unit is trapped inside,<sup>21-23</sup> a closer examination of the structure in terms of the metric parameters (Table 1) reveal that the molecule is based on a tetraanionic gallosiloxane core which is built around a Ga<sub>4</sub>Si<sub>4</sub>O<sub>8</sub> 16-membered ring system. The cavity, which is created by this tetraanionic gallosiloxane core, is sufficient enough to trap two lithium ions (Li<sup>2+</sup> and Li<sup>2+</sup>) inside the core, through two Li-O(siloxide) and two Li-OH(Ga) link-

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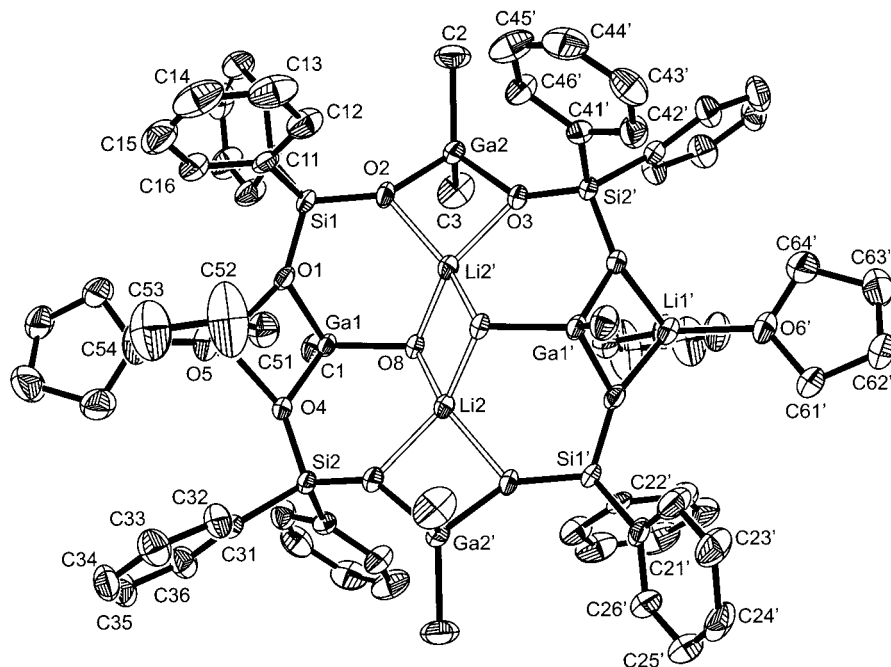
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(21) The incorporation of inorganic molecules such as Li<sub>2</sub>O inside a main-group or a transition-metal cluster unit<sup>22</sup> (or even inside an organic cluster unit)<sup>23</sup> has been very widely observed. However, molecule **1** does not belong to any of these types.

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**Figure 1.** Thermal ellipsoid plot of the molecular structure of **1** at the 50% probability level.

**Table 1. Selected Structural Parameters for 1**

Distances (Å)			
Ga1–O4	1.864(3)	Li2–O8	2.005(8)
Ga1–O1	1.874(3)	Li2–O3'	2.027(8)
Ga1–O8	1.880(3)	Li2–O8'	2.061(8)
Ga2–O3	1.896(3)	Si1–O1	1.625(3)
Ga2–O2	1.903(3)	Si1–O2	1.606(3)
Li1–O4	1.952(8)	Si2–O3'	1.608(3)
Li1–O1	1.957(9)	Si2–O4	1.623(3)
Li2–O2'	1.997(8)		
Angles (deg)			
Si1–O1–Li1	138.8(3)	Si2–O4–Ga1	129.1(2)
Ga1–O1–Li1	90.5(3)	Si2–O4–Li1	134.8(3)
Si1–O2–Ga2	139.3(2)	Ga1–O4–Li1	91.0(3)
Si1–O2–Li2'	124.5(3)	Ga1–O8–Li2	118.7(3)
Ga2–O2–Li2'	91.3(3)	Ga1–O8–Li2'	115.7(2)
Si2'–O3–Ga2	143.8(2)	Li2–O8–Li2'	87.9(3)
Si2'–O3–Li2'	122.0(3)	O8–Li2–O8'	92.1(3)
Ga2–O3–Li2'	90.6(2)		

ages. The other two lithium ions that are required for the charge balance in the molecule (*viz.* Li1 and Li1') are located at the periphery and are bound to the gallosiloxane ring through the Li–O(Si) linkages. Two solvent THF molecules additionally coordinate each of the latter lithium ions. Further, there is also a THF solvent molecule of crystallization in each asymmetric part of the unit cell.

The molecule has a 2-fold axis of symmetry. All four silicon atoms in **1** are in a similar chemical environment. However, there are two distinctly different types of gallium atoms. While each of the gallium atoms of the first type (Ga2 and Ga2') are surrounded by two siloxy oxygen atoms and two methyl groups, the gallium atoms of the second type (Ga1 and Ga1') are bound to two siloxy oxygen atoms, one methyl group, and one hydroxyl group. The Ga–O distances involving the former type of gallium atoms (Ga2) are somewhat longer (average 1.900(3) Å) than the Ga–O distances involving Ga1 (average 1.873(3) Å). In general, the observed Ga–O(Si) distances in **1** are, however, significantly longer than the corresponding distances in the only other structurally characterized monoanionic gallosiloxane **E** (average 1.806(5) Å). There are also two types of Si–O

distances at each silicon in **1**. For example, the Si–O(GaMe<sub>2</sub>) bonds (average 1.607(3) Å) are shorter than the Si–O(GaMe(OH)) bonds (average 1.624(3) Å).

The Li–O distances associated with Li2 (average 2.023(8) Å) are somewhat longer than the corresponding distances of Li1–O(Si) bonds (average 1.955(9) Å). Further, the longer Li2–O8 (or Li2–O8') distances in **1** compared to the shorter Li–O distances found in the crystal structure of LiOH·H<sub>2</sub>O (1.95 Å)<sup>24</sup> rule out a (LiOH)<sub>2</sub> dimeric unit formulation for the two lithium ions within the cavity.

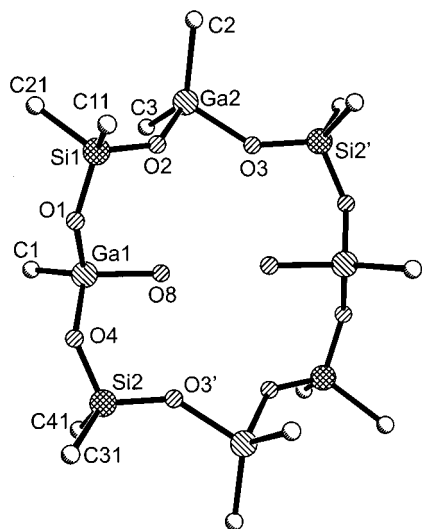
Another striking structural feature of this molecule is its resemblance to the S8R building units of zeolites.<sup>18</sup> Although the recent work of Roesky et al. on molecular siloxanes and phosphonates has produced a number of model compounds for the secondary building blocks (SBU)<sup>18</sup> of open-framework silicates and phosphates (notably compounds with S4R, D4R, D6R, and C6R building blocks),<sup>6a,9</sup> there are no known examples of siloxane or phosphonate molecules that display a zeolite S8R or D8R (in general, a 8-ring) structure in the literature. The gallosiloxane molecule **1**, with a 16-membered Si<sub>4</sub>Ga<sub>4</sub>O<sub>8</sub> macrocyclic core (Figures 2 and 3), thus represents the first molecular model compound to be synthesized with a silicate S8R secondary building unit as the basic structural motif. In this context, it should be noted that while several aluminosilicates and -phosphates primarily containing 8-ring channels have been known for a fairly long time,<sup>25</sup> gallosilicates such as gallosilicate-ABW and gallosilicate-ANA with 8-ring channels were only recently reported.<sup>26,27</sup> It is also worth

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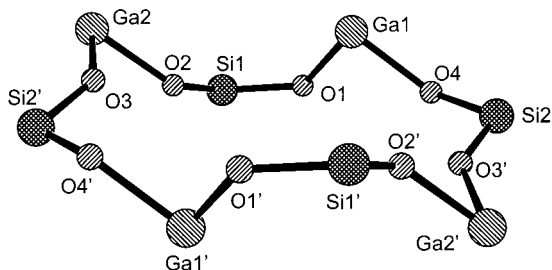
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**Figure 2.** Core structure of **1** showing the resemblance of the  $\text{Ga}_4\text{Si}_4\text{O}_8$  ring to S8R in zeolites.



**Figure 3.** Diagram depicting the nonplanar  $\text{Ga}_4\text{Si}_4\text{O}_8$  ring in **1**.

noting that the 16-membered siloxane ring in **1** adopts an interesting nonplanar conformation, as shown in Figure 3.

The IR spectrum of **1** shows a strong broad absorption at  $3406\text{ cm}^{-1}$  corresponding to the OH absorption of the Ga–OH moiety, which also bridges two  $\text{Li}^+$  cations present in the cavity. The  $^1\text{H}$ ,  $^7\text{Li}$ , and  $^{29}\text{Si}$  NMR spectra of analytically pure single crystals of **1**, initially recorded in  $\text{CDCl}_3$ , showed the presence of more than one species. For example, there were 7 resonances in the region  $-0.2$  to  $-0.8$  ppm for the Ga– $\text{CH}_3$  protons. Similarly, despite the high symmetry of **1**, 10  $^{29}\text{Si}$  NMR signals were observed. The change of solvent to  $\text{THF}-d_8$  also did not alter the observed spectral pattern (see Experimental Section). However, cooling this  $\text{THF}-d_8$  solution deposits the crystals of **1** almost quantitatively in the NMR tube. Hence, it appears that there is some dynamic process involving the movement of the Li cations in solution (probably the loosely bound lithium cations which are inside the cavity), causing some skeletal rearrangement. The nature of this process is unclear, and hence the NMR spectroscopic studies are not very useful in deducing a solution structure of the siloxane **1**.

In summary, it has been shown that the change of metal source from neutral  $\text{GaMe}_3$  to the ate complex  $[\text{LiGaMe}_4]$  allows the isolation of the unusual gallosiloxane **1**. Our further studies in this area are aimed

at not only expanding this methodology for the preparation of other bimetallic heterosiloxanes which incorporate other alkali-metal and alkaline-earth-metal ions, but also synthesizing molecular silicates with larger ring sizes which can model zeolites with larger pores (e.g., cloverite).<sup>28</sup> Furthermore, it would also be interesting to study the ability of **1** and related molecules as homogeneous catalysts for the organic transformations catalyzed by gallosilicates.<sup>1–3</sup>

## Experimental Section

**General Considerations.** All the experimental manipulations were carried out in a dry prepurified nitrogen atmosphere using Schlenk techniques excluding moisture and air. Solvents were purified by conventional procedures and were freshly distilled prior to use. Unless otherwise stated, reagents were obtained from commercial sources and used as received.  $\text{LiGaMe}_4$  was prepared by starting from  $\text{GaMe}_3$  and  $\text{MeLi}$  using the procedure as described earlier.<sup>19</sup> The IR spectrum was recorded in Nujol mulls between CsI pellets over the range  $4000\text{--}400\text{ cm}^{-1}$  on a Nicolet Impact-400 FT-IR spectrophotometer. The  $^1\text{H}$ ,  $^7\text{Li}$ , and  $^{29}\text{Si}$  NMR spectra were recorded on either a Bruker AM 200 or a Bruker AS 400 instrument. C, H, and N analyses were carried out on a Carlo Erba 1106 microanalyzer.

**Synthesis of 1.** To a solution of  $\text{LiGaMe}_4$  (1 mmol, 137 mg) in 30 mL of dry THF at  $0^\circ\text{C}$ , the diphenylsilanediol (1 mmol, 216 mg) in THF (15 mL) was added slowly. After the addition, the reaction mixture was warmed to room temperature and subsequently stirred at  $50^\circ\text{C}$  for 30 min. The reaction mixture was concentrated to half of its volume and left for crystallization at room temperature. Large colorless single crystals of **1** formed after 24 h (344 mg, 80%). Anal. Calcd for  $\text{C}_{78}\text{H}_{108}\text{Ga}_4\text{Li}_4\text{O}_{16}\text{Si}_4$  (1720.64): C, 54.45; H, 6.33. Found: C, 53.28; H, 6.05. IR ( $\text{cm}^{-1}$ ; Nujol): 3405 (br, Li–OH), 1429 s, 1303 w, 1262 w, 1195 s, 1116 s, 1048 s, 966 vs, 911 vs, 742 s, 702 s.  $^1\text{H}$  NMR ( $\text{THF}-d_8$ , 200 MHz):  $\delta$   $-0.78$ ,  $-0.56$ ,  $-0.49$ ,  $-0.45$ ,  $-0.35$  (s,  $\text{GaCH}_3$ ), 1.75 (m,  $\text{OCH}_2\text{CH}_2$ ), 3.63 (m,  $\text{OCH}_2$ ), 7.16–7.66 (m,  $\text{C}_6\text{H}_5$ ).  $^7\text{Li}$  NMR ( $\text{THF}-d_8$ , 97.2 MHz):  $\delta$  0.67 (s, br).  $^{29}\text{Si}$  NMR ( $\text{THF}-d_8$ , 99.4 MHz):  $\delta$   $-35.1$ ,  $-35.4$ ,  $-37.5$ ,  $-38.2$ ,  $-39.4$ ,  $-42.1$ .

**X-ray Structure Determination of 1.** Single crystals of **1** suitable for X-ray structural analysis were directly obtained from the reaction mixture at room temperature. A suitable crystal was mounted on a Siemens STOE AED2 four-circle diffractometer for cell parameter determinations and intensity data collection. The cell parameters were derived from 40 well-centered reflections chosen over a wide  $2\theta$  range. The intensity data obtained were corrected for absorption effects using  $\psi$ -scan data (maximum and minimum transmission factors are 0.316 and 0.205). The structure solution was achieved by direct methods as implemented in SHELXS-97.<sup>29</sup> The final refinement of the structure was carried using full least-squares methods on  $F^2$  using SHELXL-97.<sup>30</sup>

Crystal data:  $\text{C}_{78}\text{H}_{108}\text{Ga}_4\text{Li}_4\text{O}_{16}\text{Si}_4$ ,  $M_r = 1720.64$ , monoclinic,  $P2_1/n$ ,  $a = 15.517(3)\text{ \AA}$ ,  $b = 12.125(2)\text{ \AA}$ ,  $c = 22.543(4)\text{ \AA}$ ,  $\beta = 94.41(3)^\circ$ ,  $V = 4229(2)\text{ \AA}^3$ ,  $D_c = 1.351\text{ Mg/m}^3$ ,  $Z = 2$ ,  $F(000) = 1792$ , size  $0.6 \times 0.4 \times 0.2\text{ mm}$ ,  $\lambda = 0.71073\text{ \AA}$ ,  $\mu = 1.378\text{ mm}^{-1}$ , total/unique reflections 9883/7335 ( $R_{\text{int}} = 0.1112$ ),  $T = 200(2)\text{ K}$ ,  $\theta$  range  $3.5\text{--}25.0^\circ$ , final  $R(I > 2\sigma(I)) R_1 = 0.061$ ,  $wR_2 = 0.157$ ,  $R$  (all data)  $R_1 = 0.077$ ,  $wR_2 = 0.176$ .

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**Supporting Information Available:** X-ray data (including tables of experimental details, atomic coordinates, all bond lengths and angles, and anisotropic thermal parameters) for compound **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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