

Synthesis and structural characterization of a remarkably stable, anionic, incompletely condensed silsesquioxane framework

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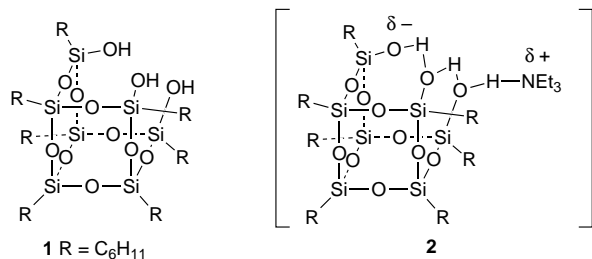
The reaction of [(C₆H₁₁)₇Si₇O₉(OH)₃] **1 (2 equiv.) with [(C₆H₁₁)₇Si₇O₉(OTf)₃] **3** affords a nonproportionation product that reacts with [PPh₄]Cl, [PBU_n]₄Cl and [NBu_n]₄Br to produce the corresponding salts of [(C₆H₁₁)₇Si₇O₉(OH)₂(OTf)]⁻ **5** (i.e. the monoanion derived from deprotonation of **1**); a single-crystal X-ray diffraction study of the [(NBu_n)]⁺ salt of **5** indicates that the molecules exist as isolated ion pairs with strong intramolecular hydrogen bonding; implications of this result for the chemistry of silica are discussed.**

Silicates hold a unique place among major industrial raw materials because their constituent elements, mainly silicon and oxygen, together comprise nearly 80% of the atoms available on the earth's surface.¹ The inexhaustible supply of silicates, coupled with their impressive versatility, has led to thousands of applications and stimulated an intense interest in both the chemistry and physical properties of silicates.²

Numerous approaches have been explored for gaining molecular-level insights into the complex surface chemistry of siliceous materials, but detailed structural characterization and mechanistic studies on surface complexes are still inherently difficult. In order to assist and guide the study of silica and silica-supported catalysts, we³ and others⁴ have been exploring the chemistry of soluble siloxanes and silsesquioxanes,⁵ as well as their metal-containing derivatives.⁶ A large fraction of our work has focused on silsesquioxanes and metallasilsesquioxanes derived from trisilanol **1**, which can be conveniently prepared from (C₆H₁₁)SiCl₃.^{3a,7}

The chemistry of **1** is similar in many respects to the chemistry of other silanols,^{6b} but there are a number of notable differences. For example, **1** is monosilylated with remarkable selectivity upon reaction with Me₃SiCl in NEt₃-thf.^{3b} Similarly, the reaction of **1** with an excess of SbMe₅ quickly produces a monofunctionalized product which only slowly reacts further with additional SbMe₅.^{3e} Mechanistic studies relating to these and other observations strongly suggested that the unique reactivity of **1** was a consequence of increased acidity caused by hydrogen bonding between the three siloxy groups. In the case of silylation reactions, the intermediacy of ion pairs (e.g. **2**) was strongly implicated.^{3b}

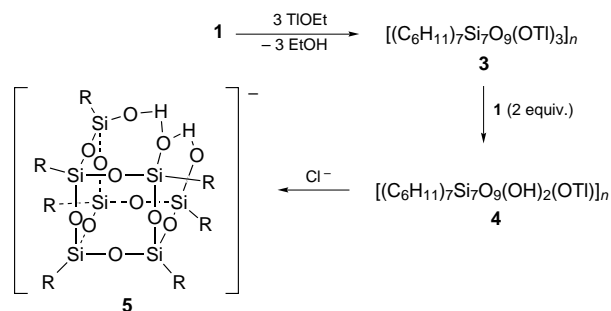
Here, we report the synthesis, spectroscopic characterization, and X-ray crystal structure of a remarkably stable anion that is formally derived from the deprotonation of **1**. In stark contrast to anions derived from simple alcohols and silanols, the monoanion of **1** does not react with phosphonium ions;^{3d} it is also stable with respect to cyclocondensation. The implications of this result for the chemistry of silica surfaces will be discussed.



The reaction of **1** with thallium(i) ethoxide (Tl/SiOH = 1) affords an excellent yield of [(C₆H₁₁)₇Si₇O₉(OTf)₃]_n **3**,⁸ which upon addition to a solution of **1** (2 equiv.) in C₆D₆ immediately produces a new complex which exhibits three methine (SiCH) resonances (3:3:1) in the room-temperature ¹³C NMR spectrum; the most downfield resonance is exchange-broadened. On the basis of our previous work with Tl-substituted silsesquioxanes,⁸ this data is most consistent with a C_s-symmetric nonproportionation product (e.g. **4**) which undergoes facile exchange of one Tl^I and two protons H between three siloxy groups on a C₃-symmetric [R₇Si₇O₁₂]³⁻ framework.[†]

The addition of [PPh₄]Cl, [PBU_n]₄Cl or [NBu_n]₄Br to a solution of **4** in toluene immediately precipitates thallium halide to afford a quantitative NMR yield of a single silsesquioxane framework, which is spectroscopically indistinguishable from the product formed upon reaction of **1** with Ph₃PCH₂.^{3d} ¹H, ¹³C, ²⁹Si and ³¹P NMR spectra of the products obtained from the reaction of **4** with [PPh₄]Cl and [PBU_n]₄Cl indicate the formation of a common silsesquioxane framework with free [PPh₄]⁺ and [PBU_n]₄⁺ as the only P-containing species in solution.[‡] The NMR data provide no basis for distinguishing between a monomeric anionic silsesquioxane framework (e.g. **5**) and more complex oligomeric structures that are often adopted by silanols and incompletely condensed silsesquioxanes,⁹ so a single-crystal X-ray diffraction study was performed to examine the nuclearity and extent of hydrogen bonding.[§]

Well formed crystals of the [NBu_n]₄⁺ salt of **5** were obtained from toluene-hexane (2:1) at -35 °C. As illustrated in Fig. 1, the molecule crystallizes as isolated ion-pairs with strong intramolecular hydrogen bonding. The Si/O framework is remarkably symmetric and is nearly superimposable with a fully condensed R₈Si₈O₁₂ framework.^{5,10} The O(1)⋯O(3) and O(2)⋯O(3) distances (2.576 and 2.569 Å) are shorter than O⋯O separations observed for most neutral, hydrogen-bonded silanols,⁹ but they are well within the range observed for other hydrogen-bonded oxygen atoms.¹¹ Hydrogen atoms from the two siloxy groups, H(1) and H(2), were located and refined. In both cases, the atoms are involved in grossly unsymmetrical, nearly linear, hydrogen-bonding interactions with one short (0.88–0.89 Å) O–H bond and one long (1.68–1.70 Å) O⋯H bond. Similarly unsymmetrical hydrogen bonds are not uncommon when short O–H–O bonds do not straddle a symmetry element.¹¹ The structure represented by **5** nicely describes the overall hydrogen-bonding arrangement.



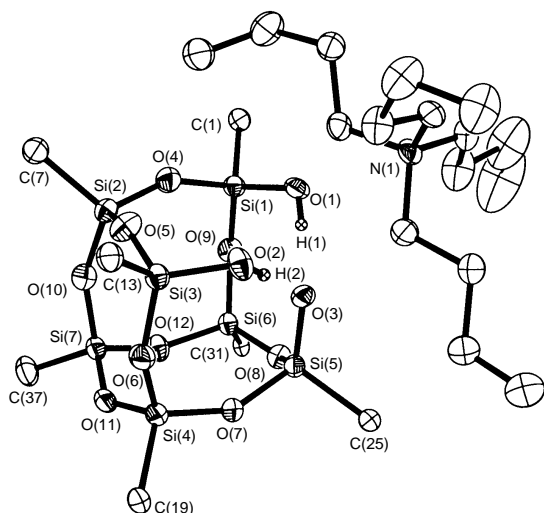


Fig. 1 ORTEP plot of $[\text{NBu}_4]^+ \mathbf{5}$. For clarity, thermal ellipsoids have been plotted at 50% probability and only C attached to Si are shown for cyclohexyl groups. Selected distances (Å) and angles ($^\circ$): Si(1)–O(1) 1.618(3), Si(1)–O(4) 1.630(3), Si(3)–O(2) 1.606(4), Si(3)–O(5) 1.627(3), Si(5)–O(3) 1.588(3), Si(5)–O(7) 1.645(3), Si(1)–O(9) 1.637(3), Si(2)–O(4) 1.616(3), Si(3)–O(6) 1.624(3), Si(4)–O(7) 1.614(3), Si(5)–O(8) 1.651(3), Si(6)–O(9) 1.608(3), Si–C (av.) 1.862(5), N–C (av.) 1.521(6), Si(1)–O(1)–H(1) 113.8, Si(3)–O(2)–H(2) 114.2, O(1)–Si(1)–O(4) 110.9(2), O(1)–Si(1)–O(9) 110.7(2), O(2)–Si(3)–O(5) 111.0(2), O(2)–Si(3)–O(6) 110.4(2), O(3)–Si(5)–O(7) 112.3(2), O(3)–Si(5)–O(8) 111.7(2), Si(2)–O(4)–Si(1) 152.5(2), Si(2)–O(5)–Si(3) 153.6(2), Si(4)–O(6)–Si(3) 146.7(2), Si(4)–O(7)–Si(5) 149.8(2), Si(6)–O(8)–Si(5) 138.7(2), Si(6)–O(9)–Si(1) 147.5(2), Si(7)–O(10)–Si(2) 153.4(2), Si(7)–O(11)–Si(4) 138.6(2), Si(7)–O(12)–Si(6) 149.7(2), O–Si–C (av.) 109.1(2), C–N–C (av.) 109.5(4), C–C–N (av.) 115.2(5).

The unexpected stability of **5** has a number of important implications for the chemistry of silica surfaces. Our results demonstrate that extensive hydrogen bonding can stabilize anions derived from multiply hydrogen-bonded silanols. In the case of **5**, the anion is so stable that it does not coordinate to a phosphonium ion, even in a hydrocarbon solvent. Because conjugate acids of stable anions are generally more acidic than conjugate acids of less stable anions, the acidity of silica surface sites possessing multiply hydrogen-bonded siloxy groups must be greater than the acidity of isolated SiOH groups. Although somewhat controversial, this conclusion is completely consistent with recent work by Drago¹² and Morrow,¹³ which implicates the existence of a significant subset of hydrogen-bonded siloxy groups which is both more acidic and more reactive toward SbMe_5 than isolated siloxyl groups.

It is interesting to consider whether surface sites analogous to **5** could be detected on silica because similar arrangements should be both accessible and stable. Detailed examination of IR spectra might provide an answer, but the OH stretching frequency for the $[\text{NBu}_4]^+$ salt of **5** (3563 cm^{-1} in thf) appears within the range assigned to vicinally hydrogen-bonded disilanols. It might, however, be possible to detect the hydrogen-bonded protons (δ ca. 11–12) by using solid-state NMR techniques.¹⁴ We are currently exploring this possibility, as well as the rich reaction chemistry of **5**.

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Footnotes

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† $[(\text{C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OH})_2(\text{OTI})] \mathbf{4}$: $(\text{C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OH})_3$ **1**^{3a} (30 mg, 0.031 mmol) and $(\text{C}_6\text{H}_{11})_7\text{Si}_7\text{O}_9(\text{OTI})_3$ **3**⁸ (24 mg, 0.015 mmol) were dissolved in C_6D_6 (ca. 0.5 ml). Examination of the NMR spectra (^1H and ^{13}C) revealed the formation of a single silsesquioxane product. Although this product cannot be isolated in pure form, it reacts with a variety of halide salts to afford stable salts of **5**.

‡ $[\text{NBu}_4]^+$, $[\text{PBu}_4]^+$, and $[\text{PPh}_4]^+$ salts of $[(\text{C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{10}(\text{OH})_2]^- \mathbf{5}$: in a typical reaction, 1 mol. equiv. of $[\text{NBu}_4]\text{Br}$, $[\text{PBu}_4]\text{Cl}$ or $[\text{PPh}_4]\text{Cl}$ was

added to a solution of **4** prepared from **1** (339 mg, 0.348 mmol) and **3** (276 mg, 0.174 mmol) in toluene (10 ml); in all cases, a white precipitate formed immediately. The solution was stirred for 8 h and then filtered to remove TI halide. The $[\text{NBu}_4]^+$ salt of **5** was obtained in 83% yield as large rectangular crystals from hexane–toluene ($-35 \text{ }^\circ\text{C}$). The $[\text{PBu}_4]^+$ and $[\text{PPh}_4]^+$ salts were obtained as white microcrystalline precipitates in 71 and 59% yields by crystallization ($-35 \text{ }^\circ\text{C}$) from toluene–hexane and toluene–acetonitrile, respectively.

§ *Crystallographic data*: for $[\text{NBu}_4]^+ \mathbf{5}$: $\text{C}_{58}\text{H}_{115}\text{NO}_{12}\text{Si}_7$, $M = 1215.14$, monoclinic, space group $P2_1/c$, $a = 15.329(4)$, $b = 18.943(6)$, $c = 24.109(7)$ Å, $U = 6838.6(35)$ Å³, $Z = 4$. Intensities were measured at 158 K with Mo-K α radiation ($\lambda = 0.71073$ Å) and corrected for Lorentz and polarization effects. The mean intensity of three standard reflections decreased by <1% during the experiment. The structure was solved by direct methods; final refinements were carried out with anisotropic thermal parameters for all non-H atoms: 9506 unique reflections collected; 711 parameters refined; $R_1 = 0.0548$, $wR_2 = 0.1165$ for 9502 reflections with $I > 2\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/412.

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