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^{29}Si NMR Shifts and Relative Stabilities Calculated for Hypercoordinated Silicon–Polyalcohol Complexes: Role in Sol–Gel and Biogenic Silica Synthesis

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Penta- and hexa-coordinated silicon is rare, occurring as a transient species in some glasses, nonaqueous organosilicon solutions and organosilicon gels such as silicone, and is stable at high pressures within the earth in dense phases such as stishovite. The stable form expected in aqueous solution is quadra-coordinated silicon. A recent study proposed the existence of hypercoordinated silicon–polyalcohol complexes in aqueous solution, based on ^{29}Si NMR shifts at –102 to –103 ppm and –145 to –147 ppm. Here, we report ab initio molecular orbital calculations of ^{29}Si NMR chemical shifts and relative stabilities of silicon–polyalcohol monocyclic and spirocyclic complexes, from ethylene glycol ($C_2H_6O_2$) to arabitol ($C_5H_{12}O_5$) with Si in quadra-, penta- and hexa-coordination (^{Q}Si, ^{P}Si, ^{H}Si), calculated at the HF/6-311+G(2d,p)//HF/6-31G* level. Calculated shifts are accurate with a 1–8% error for ^{Q}Si and 2–9% for ^{P}Si. Shifts calculated for the hypercoordinated silicon complexes having structures proposed in the literature are much more negative (–128 and –180 ppm for ^{P}Si and ^{H}Si) than observed. We propose that cyclic trimers complexed by polyalcohols can explain the –102 ppm shift, where the Si atoms are all ^{Q}Si, or where two silicons are ^{Q}Si and one is ^{P}Si with rapid exchange between the Si sites. The –145 ppm resonance results from structures similar to those proposed in the experimental NMR study for the –102 ppm peak. Our relative stability calculations indicate that structures proposed in the literature for hypercoordinated silicon complexes are thermodynamically unstable in aqueous solution at acidic to neutral conditions but may exist in degrading silicone-gel breast-implants. Thus, aqueous hypercoordinated silicon–polyalcohol complexes are unlikely to play an important role in biological silicon uptake and hold little promise for novel silica synthesis routes from aqueous solutions under nonextreme conditions.

Introduction

Inorganic silicon usually occurs in tetrahedral coordination at earth's surface conditions in the form of silica and silicate minerals that make up the continents. Chemical weathering of silicates releases dissolved silicon which is carried to the oceans by rivers, where the dominant removal process is biogenic precipitation by marine diatoms, estimated to cycle over 6.7 Gtons of silicon annually.[1] Diatoms are unicellular algae that construct their cell walls of amorphous silica which the organisms precipitate out from seawater under ambient conditions. One of the most astounding features of biogenic silica is the vast diversity of physical shapes, forms, and pore sizes displayed. There are tens of thousands of diatom species, and each species has a strictly controlled species-specific pattern. This strict degree of control has inspired materials scientists to attempt biomimetic sol−gel silica synthesis,[1−3] and attempts have been made to identify the chemical forms in which silicon is transported to the organism and utilized by the organism.[4−13] Recent studies

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(1) Tacke, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 3015−3018.

(2) Vrieling, E. G.; Beelen, Th. P. M.; van Santen, R. A.; Gieskes, W. W. C. *J. Biotechnol.* **1999**, *70*, 39−51.

(3) Morse, D. E. *Trends Biotechnol.* **1999**, *17*, 230−232.

(4) Bhattacharya, P.; Volcani, B. E. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6386−6390.

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have shown that proteins rich in the basic amino acids and in polyamines are probably involved in the polymerization of silica,[10−13] but the chemical form in which silicon is transported to the organism is still being studied. Similarly, the starting silicon compound also plays an important role in the sol−gel synthesis of silica.[14,15] Thus, the form in which dissolved silicon occurs in aqueous solutions is significant both for natural, biogeochemical environments and for technological applications.

Silicon complexes with phenols, catechols, and polysaccharides are often hypothesized,[16] or have apparently been identified in phytoliths of higher plants such as Thuja Plicata,[17] although this is controversial.[18] Organosilicon complexes are also widely used as the starting compound in the sol−gel synthesis of silica.[14,15] Hypercoordinated species, in particular, would provide novel pathways for efficient synthesis of silicon polymers, molecular sieves, semiconductors, and ceramics under nonextreme conditions.[19−21] Hypercoordinated organic−silicon complexes are usually only known to exist in nonaqueous solutions. It was, therefore, very exciting when a recent study reported ^{29}Si NMR resonances at −102 to −103 ppm and at −141 or −145 to −147 ppm in highly alkaline aqueous solutions containing NaOH, dissolved Si, and polyalcohols or aliphatic sugar acids. The peaks were assigned to silicon−polyalcohol or silicon−sugar acid complexes with Si in 5- and 6-fold coordination.[22,23] It was also suggested that such complexes could provide a means of biological silicon transport and uptake.[22,23] If they did exist, it is logical to expect that such complexes could also be promising starting materials for novel sol−gel silica synthesis routes under nonextreme conditions. The existence of such compounds at ambient conditions in water is, however, completely unexpected. We have examined, therefore, the likelihood for the existence of the putative complexes using a well-established computational approach.

We present, here, the results of ab initio molecular-orbital calculations of ^{29}Si NMR shifts and relative reaction energies for the formation of polyalcohol−silicate complexes with systematically varied chemical composition, stoichiometry, structure, and coordination number for silicon. By combining these two sets of computational results (NMR shifts and relative stabilities) and comparing with experimental NMR results, we were able to infer the likelihood for the existence of the complexes under the ambient conditions of interest for biological uptake and for biomimetic, sol−gel silica synthesis.

Computational Method

All calculations were performed using the software packages GAMESS, Gaussian 94, and Gaussian 98.[24−26] Optimized geometries were obtained at the Hartree−Fock (HF)/6-31G* level.[27] Solvation was represented by the Onsager self-consistent reaction field model (SCRF), where the solute is embedded in a spherical cavity and the dielectric continuum of the medium was set to 78.5 for water or to 2.379 for toluene.[25] The radius (a_0) of the cavity was determined for the optimized gas-phase geometry of the molecule by selecting the "volume" option in Gaussian. These radii were then used for the size of the cavity in the dielectric continuum. In addition, single-point energies were determined using the isodensity polarizable continuum model (IPCM) for solvation at gas-phase geometries[28] in order to compare with SCRF model energies and geometries. Relative stabilities of complexes were obtained by comparing complex formation energies. Basis set superposition error (BSSE) was determined for the H-bonded complex using the counterpoise method.[29] The effects of BSSE and thermal contributions were determined for a smaller model system consisting of $Si(OH)_4$ and CH_3OH described in detail elsewhere[30] and applied here to the threitol−silicic acid system. Hydration energy of H^+ was taken as −0.4259 hartree,[31] and the energy of liquid water was calculated as the gas-phase value for a single H_2O molecule plus the experimental heat of vaporization equal to −0.0158 hartree.[32]

^{29}Si NMR isotropic shifts (δ, ppm) and anisotropic shifts were calculated at the HF/6-311+G(2d,p)//HF/6-31G* level[27] with respect to a tetramethylsilane (TMS) standard, consistent with the gauge including atomic orbital (GIAO) method.[33] We define anisotropic shifts or spread as the difference between the maximum and minimum eigenvalues of the shielding tensor ($|\sigma_{33} - \sigma_{11}|$, ppm).

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(5) Pickett-Heaps J.; Schmidt, A. M.; Edgar, L. A. *Prog. Phycol. Res.* **1990**, *7*, 1−186.
(6) Swift, D.; Wheeler, A. P. *J. Phycol*. **1992**, *8*, 202−209.
(7) Hildebrand, M.; Volcani, B. E.; Gassman, W.; Schroeder, J. I. *Nature* **1997**, *385*, 688−689.
(8) Kroger, N.; Bergsdorf, C.; Sumper, M. *EMBO J.* **1994**, *13*, 4676−4683.
(9) Kroger, N.; Bergsdorf, C.; Sumper, M. *Eur. J. Biochem*. **1996**, *239*, 259−264.
(10) Kroger N.; Deutzmann, R.; Sumper M. *Science* **1999**, *286*, 1129−1132. Kroger, N.; Deutzmann, R.; Bergsdorf, C.; Sumper, M. *Proc. Natl. Acad. Sci. U. S.A.* **2000**, *97*, 14133−14138.
(11) Shimizu, K.; Cha, J.; Stucky, G. D.; Morse, D. E. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95*, 6234−6238.
(12) Zhou, Y.; Shimizu, K.; Cha, J. N.; Stucky, G. D.; Morse, D. E. *Angew. Chem., Int. Ed*. **1999**, *38*, 780−781.
(13) Cha, J. N.; Shimizu, K.; Zhou, Y.; Christiansen, S. C.; Chmelka, B. F.; Stucky, G. D.; Morse, D. E. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 361−365.
(14) Iler, R. K. *The Chemistry of Silica*; Wiley: New York, 1979; pp 740−746.
(15) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33−72.
(16) Frausto da Silva, J. J. R.; Williams, R. J. P. *The Biological Chemistry of the Elements*; Clarendon Press: Oxford, U.K., 1991; p 450.
(17) Weiss, A.; Herzog, A. In *Biochemistry of Silicon and Related Problems*; Bend, G., Lindqvist, I., Eds.; Plenum Press: New York, 1978; pp 109−127.
(18) Peggs, A.; Bowen, H. *Phytochemistry* **1984**, *23*, 1788−1789.
(19) Bibby, D. M.; Dale, M. P. *Nature* **1985**, *317*, 157−158.
(20) Laine, R. M.; Blohowiak, K. Y.; Robinson, T. R.; Hoppe, M. L.; Nardi, P.; Kampf, J.; Uhm, J. *Nature* **1991**, *353*, 642−644.
(21) Herreros, B.; Carr, S. W.; Klinowski, J. *Science* **1994**, *263*, 1585−1587.
(22) Kinrade, S. D.; Del Nin, J. W.; Schach, A. S.; Sloan, T. A.; Wilson, K. L.; Knight, C. T. G. *Science* **1999**, *285*, 1542−1545.
(23) Kinrade, S.; Hamilton, R. J.; Schach, A. S.; Knight, C. T. G. *J. Chem. Soc., Dalton Trans*. **2001**, 961−963.
(24) Schmidt, M. W.; et al., *J. Comput. Chem.* **1993**, 1347−1363.
(25) Frisch, M. J.; et al. *Gaussian 94, Rev. B.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.
(26) Frisch, M. J.; et al., *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.
(27) Hehre, W. J.; et al. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1996.
(28) Foresman, J. B.; Keith, T. A.; Wiberg, K. B.; Snoonian, J.; Frisch, M. L. *J. Phys. Chem*. **1996**, *100*, 16098−16104.
(29) Boys, S. F.; Bernardi, F. *Mol. Phys*. **1970**, *19*, 553−566.
(30) Sahai, N.; Tossell, J. A. *Geochim. Cosmochim. Acta* **2001**, *65*, 2043−2053.
(31) Tawa, G. J.; et al. *J. Chem. Phys.* **1998**, *109*, 4852−4863.
(32) Ben-Naim, A.; Marcus, Y. *J. Chem. Phys.* **1984**, *81*, 2016−2027.
(33) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc*. **1992**, *112*, 8251−8260.

Table 1. Comparison of NMR Shifts Calculated for Geometries Optimized in the Gas-Phase and in Continuum Media Representing Water and Toluene[a]

	δ_{calc} (ppm)		
model complex	gas phase	SCRF water ($\epsilon = 78.5$)	SCRF toluene ($\epsilon = 2.379$)
$(C_2H_4O_2)_2{}^QSi$	44.0	44.0	44.0
$(C_3H_6O_3)_2{}^QSi$	83.4	82.5	83.0
$(C_4H_8O_4)_2{}^QSi$	75.0	74.0	74.0
$[C_2H_4O_2{}^PSi(OH)_3]^-$	116.2	116.9	117.7
$[C_4H_8O_4{}^PSi(OH)_3]^-$	129.2	128.3	128.8

[a] SCRF represents the Onsager self-consistent reaction field continuum solvation model.

The effect of including electron correlation at the B3LYP/6-311+G(2d,p)//HF/6-31G* level on calculated chemical shifts was investigated for selected molecules. Effect of solvation on calculated shifts was also examined. Comparison of isotropic shifts calculated for geometries optimized in the gas-phase versus solvated in the SCRF showed little difference even for molecules with quite a large difference in dipole moments, e.g. $\mu = 0$ for $(C_2H_4O_2)_2{}^QSi$ and $\mu = 3.66$ for $[C_4H_8O_4{}^PSi(OH)_3]^-$, and in two solvents with very different dielectric constants (Table 1). The lack of a significant effect from the physical environment has also been observed experimentally for pentacoordinated silicon, where shifts were measured for many silicon−organic compounds in crystalline form and in solution.[34]

We examined ligands that have one alcohol group on each carbon atom of the backbone up to a length of five carbon atoms. That is, we have examined silicon complexes with ethylene glycol ($C_2H_6O_2$), glycerol ($C_3H_8O_3$), threitol ($C_4H_{10}O_4$), and arabitol ($C_5H_{12}O_5$). In these complexes, the ligand is usually bidentate, where Si is bonded to two bridging oxygen groups. We considered monocyclic complexes (ligand:Si ratios = 1:1) and spirocyclic complexes (ligand:Si ratios > 1), where silicon is quadra- (${}^QSi$), penta- (${}^PSi$), and hexa- (${}^HSi$) coordinated. Among the monocyclic ${}^QSi$ complexes, we also compared H-bonded with covalently bonded complexes containing direct C−O−Si bonds.

Results

^{29}Si NMR Shifts of Spirocyclic Complexes. We begin with the spirocyclic complexes, where sufficient experimental data exist for comparison with calculated shifts (Table 2). The calculations are for ^{29}Si NMR shifts of polyalcohol complexes and the experimental values available refer to the corresponding dialato compounds measured in toluene and ethylene glycol solvents.[21,34] The results indicate a very high level of accuracy in the predicted shifts, within 1−8% for ${}^QSi$ and within 2−9% for ${}^PSi$. A similar level of accuracy has been obtained previously for calculated ^{29}Si shifts of other silicon−organic complexes.[30] With one exception, the calculated isotropic shifts are all slightly more negative than the experimental values at the HF/6-311+G(2d,p) level. When electron correlation is included at the B3LYP/6-311+G(2d,p) level, the magnitude of error is comparable to the HF level, but there is no longer any consistent downfield shift of the calculated shifts relative to the experimental values.

The effects of ring size, hypercoordination, stoichiometry, and protonation are also shown in Table 2. The six- and seven-membered ring compounds, $(C_3H_6O_3)_2{}^QSi$ and $(C_4H_8O_4)_2{}^QSi$ (Figure 1a), have predicted isotropic shifts that are essentially identical to the values obtained for the acyclic organic analogues (e.g., $Si(OPr)_4$ with $\delta = -84.7$ ppm[37]), and to the −80 ppm value for Q^1 inorganic silicon. The Q^n notation represents a tetrahedral SiO_4 cluster, and the superscript denotes the number of oxygens in that tetrahedron that are bonded to other tetrahedra. However, Si is significantly deshielded at $\delta = -44.0$ ppm for the smaller five-membered ring compound, $(C_2H_4O_2)_2{}^QSi$, compared to the acyclic analogue, $Si(OEt)_4$ with $\delta = -82.4$ ppm,[37] and compared to inorganic Q^1 silicon. It has been observed previously that ring size affects the Si shift. This effect was interpreted as the effect of ring strain on Si deshielding, such that the smaller five-membered ring compound has the least negative shift compared to the larger and more flexible ring compounds.[35] We note, however, that the connection between an energetic effect such as strain and the nuclear shielding is not immediately apparent, and the shielding may be related more to the relative atomic arrangements around the Si associated with the smaller ring compared to the larger rings.

In general, the pentacoordinated silicon complexes have much larger negative shifts than the corresponding quadracoordinated silicon complexes. As with the ${}^QSi$ complexes, shifts for the pentacoordinated spirocyclic complexes show a dependence on ring size. The ${}^PSi$ five-membered ring, $[(C_2H_4O_2)_2{}^PSiOH]^-$ (Figure 1b), is significantly deshielded at $\delta = -108.9$ ppm compared to its "acyclic analogue" $Si(OEt)_5{}^-$ at −131.1 ppm[37] (we are using the terminology of the original authors[37]). The larger ring compounds, $[(C_3H_6O_3)_2{}^PSiOH]^-$ and $[(C_4H_8O_4)_2{}^PSiOH]^-$ (Figure 1c) have shifts essentially identical to the acyclic analogue such as $Si(OPr)_5{}^-$ at $\delta = -133.0$ ppm.[37] Increasing the ligand:Si ratio to 3:1 and 5:2 results in complexes $[(C_2H_4O_2)_3{}^PSiH]^-$ and $[(C_2H_4O_2)_5{}^PSi_2]_2{}^-$ (Figure 1d,e). The structure in Figure 1e is particularly interesting because it represents a dimer of silicon. Structures represented in Figure 1d,e have been proposed to exist as intermediate species in alkaline, nonaqueous solutions of ethylene glycol heated to temperatures ∼200 °C, based on X-ray diffraction patterns and ^{29}Si NMR peaks at −103 to −105 ppm in both the mother liquor and in the polymerized, solid product.[21] Our calculated values and trends for both ${}^QSi$ and ${}^PSi$ compounds are in strong agreement with experimental observation.[21,34] The experimental results confirm our calculations that the environment has little effect on the isotropic shift compared to the error of our calculation.

It is important to emphasize that the spirocyclic complex with threitol, $[(C_4H_8O_4)_2{}^PSiOH]^-$, has a large negative shift of −133 ppm. This is far different from the −102 to −103

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(34) Tacke, R.; Pulm, M.; Wagner, B. In *Advances in Organometallic Chemistry*, *44*; West, R., Hill, A. F., Eds.; Academic Press: San Diego, 1999; pp 221−273.

(35) Kemmitt, T.; Milestone, N. B. *Aust. J. Chem.* **1995**, *48*, 93−102.

(36) Bode, B. M.; Gordon, M. S. *J. Mol. Graphics Modell.* **1998**, *16*, 133−138.

(37) Kumara Swamy, K. C.; Chandrasekhar, V.; Harland, J. J.; Holmes, J. M.; O'Day, Roberta; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2341−2348.

Table 2. ^{29}Si NMR Isotropic Shifts and Anisotropic Shifts ($|\sigma_{33} - \sigma_{11}|$) Reported in Parts per Million with Respect to TMS Standard, for Silicon−Polyalcohol Spirocyclic Complexes[a]

model complex	ligand: Si ratio	δ_{expt}	δ_{calc}, HF/6-311+G(2d,p)	δ_{calc}, B3LYP/6-311+G(2d,p)	$\|\sigma_{33} - \sigma_{11}\|$,[b] HF/6-311+G(2d,p)
Effect of Ring Size, ^{Q}Si					
$(C_2H_4O_2)_2{}^{Q}Si$	2:1	43.6[c]	44.0	42.2	46.9
$(C_3H_6O_3)_2{}^{Q}Si$	2:1	81.7[c−e]	83.4	83.4	31.7
$(C_4H_8O_4)_2{}^{Q}Si$	2:1	81.6[c,e]	75.0	75.0	8.8
Effect of Ring Size and Hypercoordination, ^{P}Si					
$[(C_2H_4O_2)_2{}^{P}SiOH]^-$	2:1	102.7[e]	108.9	100.3	102.7
$[(C_3H_6O_3)_2{}^{P}SiOH]^-$	2:1	130.4[e]	140.3	144.1	133.9
$[(C_4H_8O_4)_2{}^{P}SiOH]^-$	2:1	130.8, 131.1[e]	133.3	133.6	127.9
Effect of Decreasing Ligand:^{P}Si Ratio at Fixed Ring Size					
$[(C_2H_4O_2)_3{}^{P}SiH]^-$	3:1	103, 104, 105[f]	110.2		81.7
$[(C_2H_4O_2)_5{}^{P}Si_2]_2$	5:2	103, 104, 105[f]	114.4, 114.4		76.8, 90.9
Effect of Protonating an O_{br}[g]					
$[(C_2H_4O_2)_3{}^{P}SiH_2]_{\mathrm{bidentate}} \rightarrow$	3:1				
$[(C_2H_4O_2)_3{}^{Q}SiH_2]_{\mathrm{monodentate}}$			64.7		33.2
Standard					
$^{Q}Si(CH_3)_4$ (TMS)			0.0 ($\sigma = 386.0$)	0.0 ($\sigma = 327.9$)	0.0

[a] Geometries were obtained at the HF/6-31G* level. Experimental values for isotropic shifts are included for error estimation on our calculated values. [b] Anisotropic shifts reported are the absolute value of the difference between the maximum and the minimum eigenvalues of the shielding tensor. [c] Reference 35. [d] Assigned to polymeric Si spirocyclic complex in ref 35. [e] Values for the analogous dialato complexes. [f] Reference 21. [g] O_{br} represents a bridging oxygen.

ppm shifts observed in aqueous solutions of $Si(OH)_4$ with threitol, arabitol ($C_5H_{10}O_5$) and larger polyalcohols.[22] The value for $[(C_4H_8O_4)_2{}^{P}SiOH]^-$ is actually closer to the −145 to −147 ppm resonances observed in the experiment.[22]

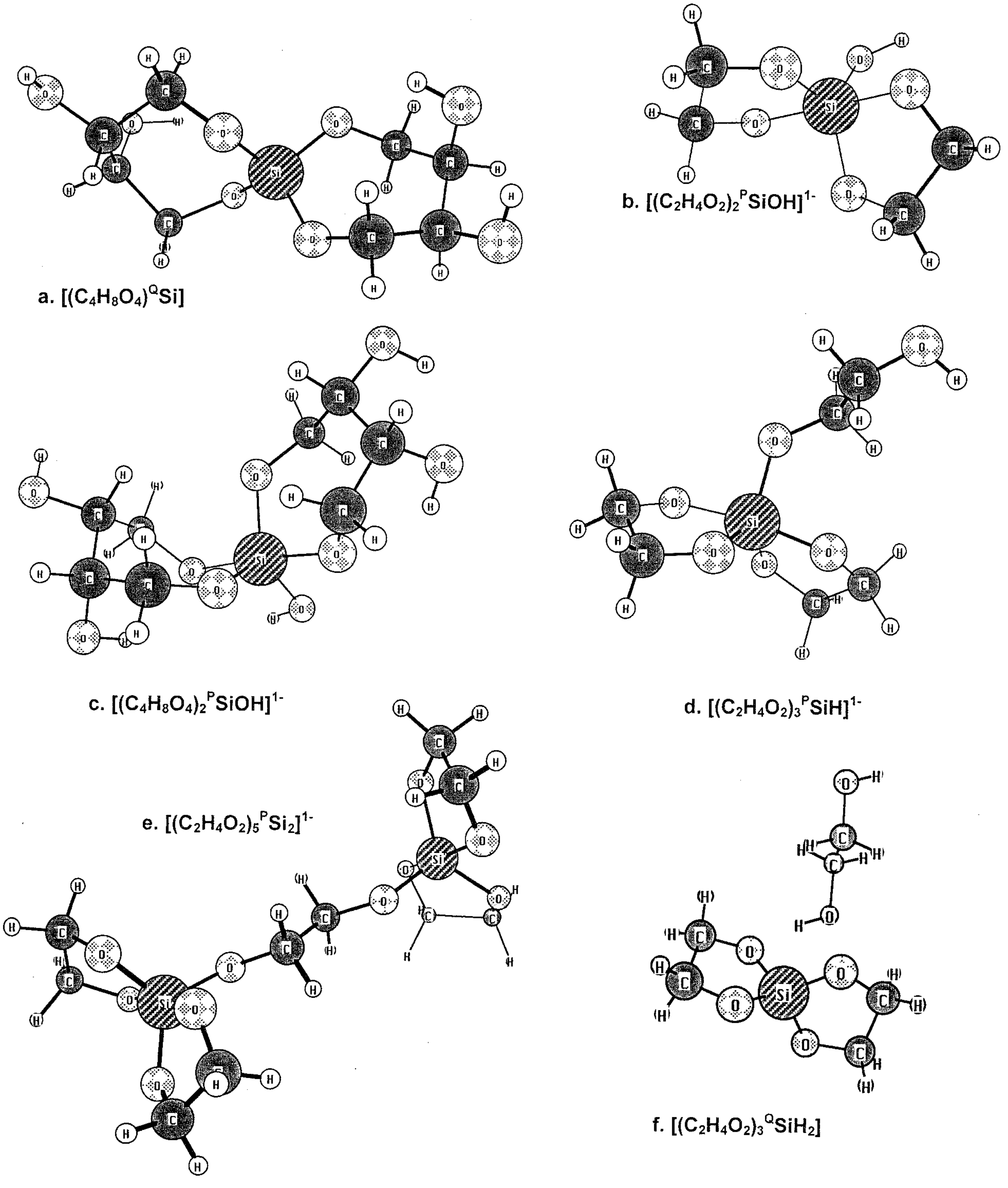
Attempts to modify the $[(C_4H_8O_4)_2{}^{P}SiOH]^-$ structure by protonation of the bridging oxygen (O^{br}) and reoptimization of the structure did not bring the calculated value any closer to the experimentally obtained resonance at −102 to −103 ppm. Instead, protonation resulted in the O_{br} detaching from ^{P}Si such that the ligand became monodentate and the silicon became ^{Q}Si. When a similar process was attempted for a related ethylene glycol complex, $[(C_2H_4O_2)_3{}^{P}SiH]$ (Figure 1d), one ligand detached completely, leaving behind $(C_2H_4O_2)_2{}^{Q}Si$ (Figure 1f), with a shift of only −64.7 ppm.

^{29}Si NMR Shifts of Monocyclic Complexes. The calculated ^{29}Si NMR isotropic shifts of monocyclic complexes are reported in Table 3. For the five-membered rings formed with ethylene glycol, $C_2H_4O_2{}^{Q}Si(OH)_2$, the shift is only −57.2 ppm. The larger six-membered ring compound, $C_3H_6O_3{}^{Q}Si(OH)_2$, has a shift of −77 ppm very close to −75.2 ppm obtained for the seven-membered ring compound, $C_4H_8O_4{}^{Q}Si(OH)_2$ (Figure 2a). Thus, the ring-size effect is analogous to that obtained for spirocyclic complexes. Values for covalently bonded and hydrogen-bonded (Figure 2b) threitol−^{Q}Si complexes can also be compared in Table 3. The shifts are similar to each other and to unpolymerized inorganic H_4SiO_4 at −71 ppm. These results indicate that if such organic complexes were present in the experimental system, they would be very difficult to detect by ^{29}Si NMR because of peak overlap with inorganic Q^1 Si species.

Like their spirocylic analogues, the ^{P}Si monocyclic complexes all have large negative shifts from −117 to −130 ppm that are distinct from the shifts for inorganic monomer and inorganic polymerized silica with $\delta \sim -80$ to −110 ppm. The threitol−silicon complex, $[C_4H_8O_4{}^{P}Si(OH)_3]^-$ (**I**; Figure 2c), where Si is bonded to the oxygens of the C_1 and C_4 carbons, was the structure originally proposed in the literature.[22] But the predicted shift is a particularly large negative value at −128.3 ppm compared to the −102 to −103 ppm obtained experimentally in aqueous solutions.[22] Computational error or computational representation of solvation cannot account for this discrepancy of ∼25 ppm. We also calculated the geometry for an alternative complex, $[C_4H_8O_4{}^{P}Si(OH)_3]^-$ (**II**; Figure 2d), which is similar to the originally proposed structure **I** but differs in that Si is bonded to the oxygens of the C_1 and C_2 carbons. The alternative structure results in a somewhat smaller shift of −117.3 ppm consistent with the smaller ring-size ethylene glycol compounds. This result is closer to the observed resonance at −102 to −103 ppm, but, even so, the value is beyond computational error.

Protonation of a bridging oxygen of the type **I** structure and geometry reoptimization results in the O(H) group detaching from Si in a manner analogous to the spirocyclic case. As seen in Table 3, the shift for the resulting structure, $[C_4H_8O_3(OH){}^{Q}Si(OH)_3]^-$, is −75.2 ppm (Figure 2e). A similar effect was also observed for both the type **II** complex, for which the resulting reoptimized structure yielded a shift of −78.8 ppm (Figure 2f), and for the smaller ethylene glycol complex, resulting in $C_2H_4O(OH){}^{Q}Si(OH)_3$. Increasing the size of the polyalcohol from threitol to arabitol also had no affect on the shift in the complex $[C_5H_{10}O_5{}^{P}Si(OH)_3]^-$ compared to the **I** structure. Another complex we tried was $[C_4H_7O_4{}^{P}Si(OH)_2]^-$, where the ligand is tridentate, but this structure also resulted in a large negative shift of −122.4 ppm (Figure 2g).

Finally, we calculated the geometries and shifts for two polymeric silicon−threitol complexes in the cyclic trimer form. In both these complexes, each silicon atom is bonded through O_{br} to two other silicon atoms and to two tetrahedral carbon atoms. In the first case, $(C_3H_6O_2)_3{}^{Q}Si_3O_3$, all three silicon atoms are quadracoordinated and the shift is −96.9



a. $[(C_4H_8O_4)^{Q}Si]$

b. $[(C_2H_4O_2)_2{}^{P}SiOH]^{1-}$

c. $[(C_4H_8O_4)_2{}^{P}SiOH]^{1-}$

d. $[(C_2H_4O_2)_3{}^{P}SiH]^{1-}$

e. $[(C_2H_4O_2)_5{}^{P}Si_2]^{1-}$

f. $[(C_2H_4O_2)_3{}^{Q}SiH_2]$

Figure 1. Optimized geometry for spirocyclic threitol−silicon and ethylene glycol−silicon complexes (a) $(C_4H_8O_4)_2{}^{Q}Si(OH)_2$, (b) $[(C_4H_8O_4)_2{}^{P}SiOH]^-$, (c) $[(C_2H_4O_2)_2{}^{P}SiOH]^-$, (d) $[(C_2H_4O_2)_3{}^{P}SiH]^-$, (e) $[(C_2H_4O_2)_5{}^{P}Si_2]^{2-}$, and (f) $[(C_2H_4O_2)_3{}^{Q}Si_2]$, representing the effect of protonation of the O_{br}. Molecules were drawn using MacMolplt.[36] The geometry optimizations for ^{Q}Si complexes yield tetrahedral Si with $^{Q}Si-O$ bond lengths of 1.64 Å, similar to inorganic species. For ^{P}Si complexes, the geometry is usually closer to square pyramidal rather than trigonal bipyramidal. The $^{P}Si-O$ bond lengths are much longer and more variable from 1.77 to 1.90 Å. So, if $^{P}Si-O-C$ complexes exist, they should be identifiable on the basis of the characteristically long Si−O bond, in addition to large anisotropic shifts.

ppm (Figure 2h). For the next complex, $[(C_3H_6O_2)_3{}^{Q}Si_2O_2{}^{P}SiO(OH)]^-$, one Si is pentacoordinated and the remaining two are ^{Q}Si (Figure 2i). The calculated resonances are −143.1, −87.5, and −90.3 ppm. If rapid exchange occurs between these silicon sites, then the measured value would reflect the arithmetic mean equal to −107 ppm. If computational error is considered, this value is very close to the observed −102 to −103 ppm peak. Note that the calculation was performed on the gylcerol complex because of limitations on our computer memory. On the basis of our calculations in Table 2 and experimental results obtained for the dialato complexes,[35] we expect that shifts calculated

Table 3. ^{29}Si HF/6-311+G(2d,p) NMR Isotropic Shifts and Anisotropic Shifts ($|\sigma_{33} - \sigma_{11}|$) Reported with Respect to TMS Standard, for Silicon−Polyalcohol Monocyclic Complexes[a]

model complex	δ (ppm)	$|\sigma_{33} - \sigma_{11}|^{b}$ (ppm)
Effect of Ring Size, ^{Q}Si		
$C_2H_4O_2{}^{Q}Si(OH)_2$	57.2	24.5
$C_3H_6O_3{}^{Q}Si(OH)_2$	77.0	42.5
$C_4H_8O_4{}^{Q}Si(OH)_2$	75.2	35.6
$C_4H_{10}O_4\cdots{}^{Q}Si(OH)_4$	71.2	22.0
Effect of Ring Size and Hypercoordination		
$[C_2H_4O_2{}^{P}Si(OH)_3]^-$	116.9	130.6
$[C_3H_6O_3{}^{P}Si(OH)_3]^-$	130.4	139.0
$[C_4H_8O_4{}^{P}Si(OH)_3]^-$ (**I**) Si bonded to O on C_1, C_4	128.3 [c]	140.8
$[C_4H_8O_4{}^{P}Si(OH)_3]^-$ (**II**) Si bonded to O on C_1, C_2	117.3	124.4
$[C_5H_{10}O_5{}^{P}Si(OH)_3]^-$	128.0	137.5
$[C_4H_8O_4{}^{H}Si(OH)_4]_2$ hexacoordinated Si	179.9 [d]	8.4
Effect of Protonating an O_{br}		
$C_2H_4O(OH){}^{P}Si(OH)_3$ (bidentate) → $C_2H_4O(OH){}^{Q}Si(OH)_3$ (monodentate)	75.0	14.3
$[C_4H_8O_3(OH){}^{P}Si(OH)_3]^-$ (**I**, bidentate) → $[C_4H_8O_3(OH){}^{Q}Si(OH)_3]^-$ (**I**, monodentate)	75.2	21.7
$[C_4H_8O_3(OH){}^{P}Si(OH)_3]^-$ (**II**, bidentate) → $[C_4H_8O_3(OH){}^{Q}Si(OH)_3]^-$ (**II**, monodentate)	73.8	17.3
Effect of Chelate Denticity		
$[C_4H_7O_4{}^{P}Si(OH)_2]^-$ Si bonded to O on C_1, C_2, C_4 (tridentate ligand)	122.4	101.7
Effect of Polymerization, ^{Q}Si and ^{P}Si		
$(C_3H_6O_2)_3{}^{Q}Si_3O_3$	96.9	32.8
$[(C_3H_6O_2)_3{}^{Q}Si_2O_2{}^{P}SiO(OH)]^-$	87.5, 90.3, 143.1 (mean = 107.0)	61.1, 97.2, 42.6
Standard		
$^{Q}Si(CH_3)_4$ (TMS)	0.0 (σ = 386.0)	0.0

[a] Geometries were obtained at the HF/6-31G* level. [b] Anisotropic shifts reported refer to the absolute value of the difference between the maximum and the minimum eigenvalues of the shielding tensor. [c] This structure was proposed to explain a ^{29}Si resonance seen at −102 to −103 ppm in an experimental study of aqueous silicon−polyalcohol solutions.[22] [d] This structure was proposed to explain a ^{29}Si resonance seen at −145 to −147 ppm.[22]

would be similar for the threitol mixed-coordination analogue, $[(C_4H_8O_4)_3{}^{Q}Si_2O_2{}^{P}SiO(OH)]^-$.

Finally, the hexacoordinated complex, $[C_4H_8O_4HSi(OH)_4]_2^-$ (Figure 2j), yields a very large negative shift of −179.9 ppm. Thus, the hexacoordinated complex cannot be responsible for the resonances observed at −145 to −147 ppm in the experimental system even when computational error (or whatever negligible environmental effects that might be present) are taken into account. We note that in a very recent abstract published by an independent group of researchers,[38] the same question of hypercoordinated silicon−polyalcohol complexes has been examined using ab initio calculations very similar to ours.[39] The results of this new study show that "the isolated $^{[V]}$Si-sorbitol and solvated $^{[V]}$Si-sorbitol$\cdot$18(H$_2$O) clusters resulted in model δ ^{29}Si values of −123 and −129 ppm, respectively".[38] Thus, even explicit solvation appears to have little effect (within computational error) on the calculated ^{29}Si shifts.

Relative Stability of Complexes. Reaction energies for formation of monocyclic silicon−threitol complexes are reported in Table 4, suggesting that the relative stability of the complexes decreases as C−O−^{Q}Si > COH$\cdots$HO^{Q}Si ≫ C−O−^{P}Si (reactions 1−3). Moreover, formation of the covalent penta coordinated complex, $[C_4H_8O_4{}^{P}Si(OH)_3]^-$, is highly endothermic when H_4SiO_4 is the reactant, and only becomes more favorable when the reactant is changed to $H_3SiO_4^-$ (reaction 3 vs reaction 4). We also compared the relative stability calculated using the SCRF solvation model with the IPCM model and obtained the same result. Specifically, the energy change for reaction 3 using the IPCM model was calculated to equal 55.84 kcal mol^{-1} and the corresponding change for reaction 4 was 7.656 kcal mol^{-1}. Thus, reaction 4 is more favorable than reaction 3 by about 48 kcal mol^{-1} for both IPCM and SCRF treatments of solvation. Even explicit solvation does not change the relative stability.[38] These results are consistent with previous conclusions that the Onsager-type solvation model is successful (if only due to cancellation of errors) and that results from different types of polarizable continuum models are similar to each other, although further work is needed for a more realistic representation of solvation.[28]

Discussion

There is precedence for the idea that a ^{P}Si complex with direct C−O−Si bonds is a precursor or stable intermediate to polymerized, quadracoordinated silica. Stable intermediates consisting of pentacoordinated silicon−ethylene glycol complexes have been noted in the "mother liquor" during sol−gel silica synthesis where the starting material was a silicon alkoxide such as $Si(OCH_2CH_3)_4$.[20,21] ^{P}Si intermediates have even been recorded in the solid phase for at least the first 24 h after reaction.[21] The pentacoordinated intermediates were postulated on the basis of their ^{29}Si NMR shifts of

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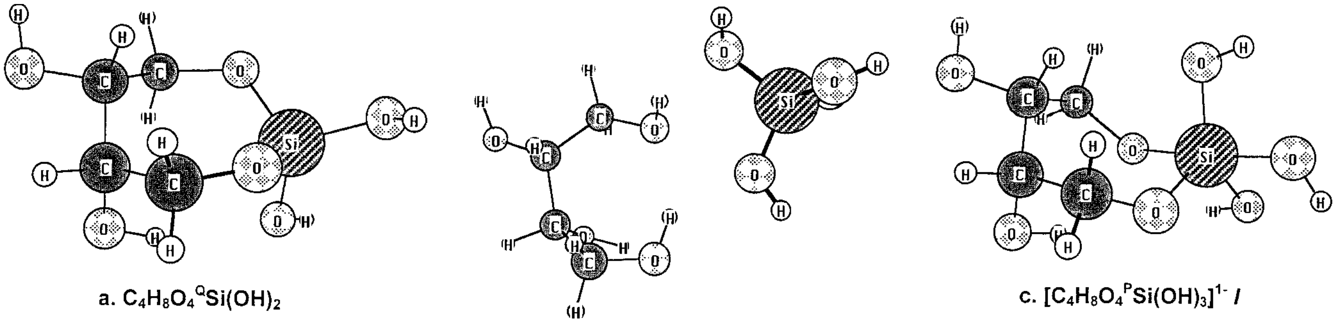
(38) Kubicki J. D.; Heaney P. J. *Eleventh Annnual V. M. Goldschmidt Conference*; LPI Contribution No. *1088*; Lunar and Planetary Institute: Houston, 2001 (CD-ROM)).

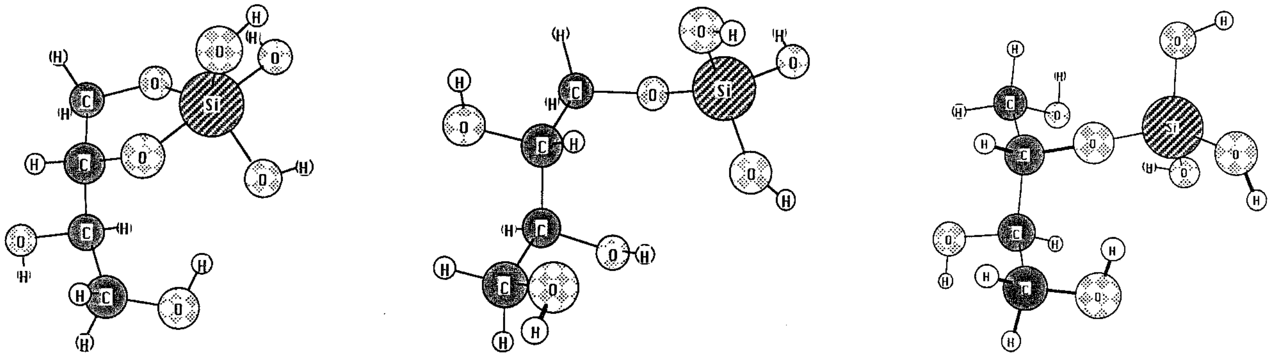
(39) Sahai, N.; Tossell, J. A. *Eleventh Annnual V. M. Goldschmidt Conference*; LPI Contribution No. *3294*; Lunar and Planetary Institute:, Houston, 2001 (CD-ROM)).



a. $C_4H_8O_4{}^QSi(OH)_2$

b. $C_4H_{10}O_4...{}^QSi(OH)_4$

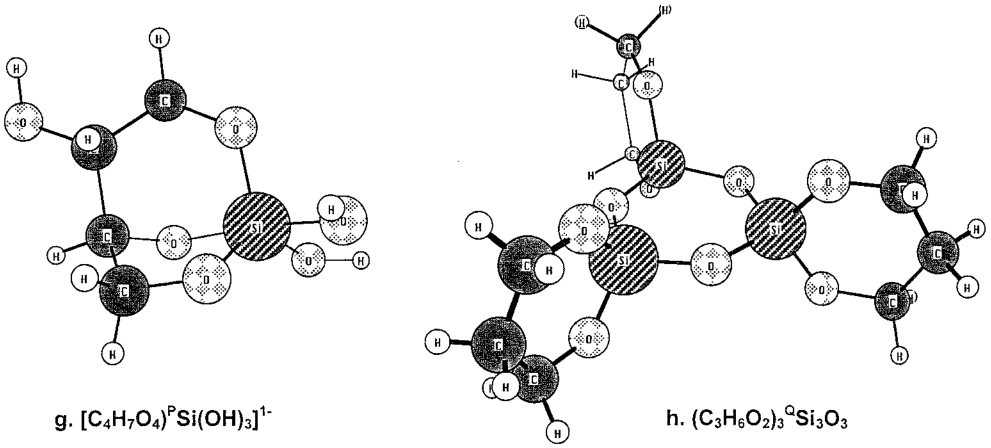
c. $[C_4H_8O_4{}^PSi(OH)_3]^{1-}$ *I*



d. $[C_4H_8O_4{}^PSi(OH)_3]^{1-}$ *II*

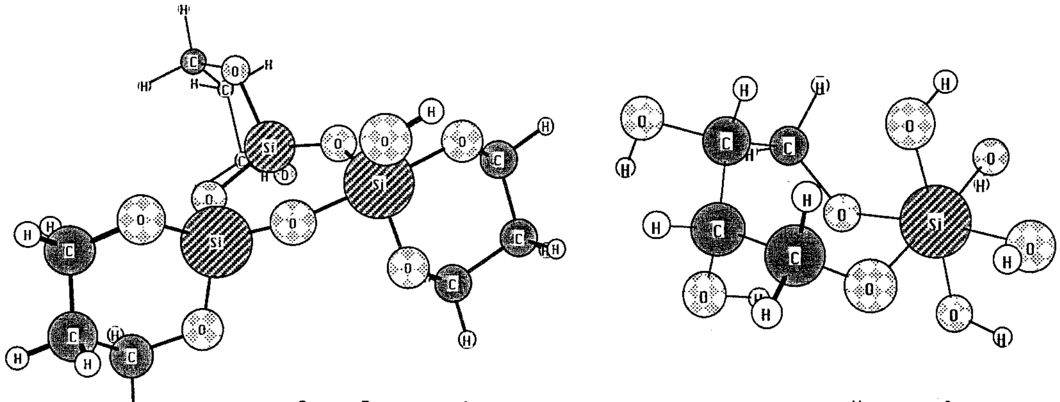
e. $C_4H_8O_3(OH){}^QSi(OH)_3$ *I*

f. $C_4H_8O_3(OH){}^QSi(OH)_3$ *II*



g. $[C_4H_7O_4)^PSi(OH)_3]^{1-}$

h. $(C_3H_6O_2)_3{}^QSi_3O_3$



i. $[(C_3H_6O_2)_3{}^QSi_2O_2{}^PSiO(OH)]^{1-}$

j. $[C_4H_8O_4{}^HSi(OH)_4]^{2-}$

Figure 2. Optimized geometry for monocyclic threitol−silicon complexes (a) $C_4H_8O_4{}^QSi(OH)_2$, (b) $C_4H_{10}O_4{\cdots}{}^QSi(OH)_4$, (c) $[C_4H_8O_4{}^PSi(OH)_3]^-$ (**I**), and (d) $[C_4H_8O_4{}^PSi(OH)_3]^-$ (**II**). Protonation of (c) and (d) at a bridging oxygen site and geometry reoptimization results in the O(H) group detaching from ${}^PSi$ and forming ${}^QSi$, as shown in (e) **I** and (f) **II**. Also shown are (g) the tridentate complex $[C_4H_7O_4{}^PSi(OH)_2]^-$, (h) the cyclic trimer complex with quadracoordinated silicon, $(C_3H_6O_2)_3{}^QSi_3O_3$, (i) the cyclic trimer complex with mixed-coordination number silicon, $[(C_3H_6O_2)_3{}^QSi_2O_2{}^PSiO(OH)]^-$, and (j) the hexacoordinated $[C_4H_8O_4{}^HSi(OH)_4]^-$ complex.

Table 4. Reaction Energies (kcal mol^{-1}) for Polyol−Silicate Complex Formation, at the HF/6-31G* Level in the Gas Phase and in a SCRF Representing Solvation[a]

no.	reaction	ΔE_r, gas	$\Delta H^0{}_{r,gas} = \Delta E_{r,gas} + \Delta H_{therm}$	$\Delta E_{r,SCRF}$	$\Delta H^0{}_{r,SCRF} = \Delta E_{r,SCRF} + \Delta H_{therm}$
1	$C_4H_{10}O_4 + Si(OH)_4 = C_4H_{10}O_4\cdots{}^{Q}Si(OH)_4$	−8.91 (−7.34)	−7.78 (−6.21)	−9.10 (−7.53)	−7.97 (−6.40)
2	$C_4H_{10}O_4 + Si(OH)_4 = C_4H_8O_4{}^{Q}Si(OH)_2 + 2H_2O$	+6.59	+5.96	11.99	12.61
3	$C_4H_{10}O_4 + Si(OH)_4 = [C_4H_8O_4{}^{P}Si(OH)_3]^- + H_2O + H^+$	+354.84	+351.14	+33.26	+29.56
4	$C_4H_{10}O_4 + Si(OH)_3O^- = [C_4H_8O_4{}^{P}Si(OH)_3]^- + H_2O$	−13.18	−11.36	−21.15	−19.33

[a] Values in parentheses are corrected for basis set superposition error (BSSE). BSSE and thermal contributions were estimated elsewhere.[30] (1 Hartree = 627.6 kcal mol^{-1}.)

∼103−106 ppm. Those experiments, however, were conducted in ethylene glycol solutions that were heated to ∼200 °C, whereas the polyalcohol and sugar acid experiments were performed in aqueous solutions at room temperatures.[22,23]

Our calculations show that the pentacoordinated silicate complexes with glycerol and threitol have large negative ^{29}Si NMR shifts, in the range −117 to −140 ppm. The original structure proposed in the literature could not explain the peaks observed at −102 to −103 ppm. Three alternative structures suggested here that might be responsible are **II**, where Si is bonded to oxygens on C_1 and C_2, the cyclic trimer complex, $(C_4H_8O_4)_3{}^{Q}Si_3O_3$, and the cyclic trimer complex with the mixed-coordination number silicon, $[(C_4H_8O_4)_3{}^{Q}Si_2O_2{}^{P}SiO(OH)]^-$. The first structure yields a shift slightly larger than required if computational error is ignored, but it cannot be ruled out entirely. We favor the cyclic trimers because, in the sense of being oligomers, they are similar to the structure proposed for silicon−ethylene glycol complexes[21] (e.g. Figure 1e). Further, the cyclic form may be expected under the highly alkaline conditions of the original experiment.[22,23] We note that in the case of the ethylene glycol solutions, where hypercoordinated silicon was observed, the experimental solutions were also extremely alkaline.[21]

The complex with the mixed-coordination number of silicon atoms is particularly interesting. It is not unreasonable to expect that the silicon atoms in that structure can exchange rapidly between the three Si sites, so that the measured value would be an average of the three individual shifts. The average shift calculated for the mixed valence polymer is very close to the observed value, with or without computational error.

The resonances observed at −141 ppm in silicon−sugar acid solutions or at −145 to −147 ppm in silicon−polyalcohol solutions cannot be explained by the hexacoordinated complex for which the calculated shift is −179.9 ppm. The resonances at −141 or −145 to −147 ppm may be due to spirocyclic and monocyclic pentacoordinated silicon−threitol complexes (Figure 1c or 2c), although admittedly the calculated values are just out of the range of computational error. It is interesting to note here that ^{29}Si magic angle spinning (MAS) NMR resonances at −129, −141, and −190 ppm have been reported for ex vivo and in vivo studies of the biodegradation of silicone in breast implants.[40,41] Silicone is a partially cross-linked polymer containing O−Si−O−Si− and Si−CH_3 bonds, and can be represented schematically as $[-(O_{0.5})_2Si(CH_3)_2]_n$. The resonances at −129 and −140 ppm were assigned to pentacoordinated silicon, and the −190 ppm peak was assigned to hexacoordinated silicon. These peaks were not seen in the silicon spectra before implantation, suggesting that they are intermediate species formed during the biodegradation of silicone. The assignments are consistent with our calculations for the ^{P}Si and ^{H}Si polyalcohol complexes.

Seawater has a mildly basic pH of 8.5, and the pK_a of silicic acid is 9.5.[42] H_4SiO_4 is, therefore, the dominant form of silicon expected in seawater, and $H_3SiO_4^-$ would only become dominant at high pHs. The calculated relative reaction energies show that the pentacoordinated complex is favored only when $H_3SiO_4^-$ is the reactant. These observations suggest that the concentration of hypercoordinated complexes formed in reaction with seawater would be very low. Diatoms deposit silica within a vesicle called the silica deposition vesicle (SDV). It was recently determined that, within the SDV, solution pH is ∼ 5−6,[43] so significant concentrations of hypercoordinated silicon−polyalcohol complexes are even less likely in this acidic environment. Thus, it is improbable that such complexes are involved in the transport and utilization of dissolved silicon by marine organisms. Further, the weak complexation of silicon with polyalcohols at near-neutral pHs is consistent with experimental and theoretical results for other organics, such as carboxylic acids, phenol, catecholamines, glycine, and serine,[30,44−46] and indicates that the organism does not have a *thermodynamic* advantage in utilizing SiO−organic complexes instead of $Si(OH)_4$, which is the dominant form of dissolved silicon in most natural waters.

The chemical shifts measured in the silicon degradation studies are consistent with our results. That system, however, differs from ours in that the silicone studies were performed on a gel in the process of breaking down, whereas our study refers to the reverse process of gel formation from dissolved species in aqueous solution. Our relative stability calculations show that the hypercoordinated complexes are favored at high pHs. Even so, given a large enough thermodynamic

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(40) Garrido, L.; Plfeiderer, B.; Papisov, M.; Ackerman, J. L. *Magn. Reson. Med.* **1993**, *29*, 839−843.

(41) Pfleiderer, B.; Ackerman, J. L.; Garrido, L. *Magn. Reson. Med.* **1993**, *30*, 534−543.

(42) Sjoberg, S.; Nordin, A.; Ingri, N. *Marine Chem.* **1981**, *10*, 521−532.

(43) Vrieling, E. G.; Gieskes, W. W. C.; Beelen, T. P. M. *J. Phycol.* **1999**, *35*, 548−559.

(44) Ohman, L.-O.; Nordin, A.; Sedeh, I. F.; Sjoberg, S. *Acta Chem. Scand.* **1991**, *45*, 335−341.

(45) Sedeh, I. F.; Sjoberg, S.; Ohman, L.-O. *J. Inorg. Biochem.* **1993**, *50*, 119−132.

(46) Pokrovski, G. S.; Schott, J. *Geochim. Cosmochim. Acta* **1998**, *62*, 3413−3428.

driving force (as provided by the large concentration of silicone gel in a breast implant), it is possible that hypercoordinated species are obtained in sufficient concentration to be measured at circumneutral pHs. If this is the case, recall that the hypercoordinated species seen by MAS NMR in the silicone are in the solid (gel) phase,[40,41] which is consistent with the observation of pentacoordinated Si by MAS NMR in sol−gel synthesized silica from alcohol solutions.[21] In the case of seawater, however, total dissolved silicon concentrations are probably too low to permit hypercoordinated silicate species concentrations large enough to be an effective biological uptake mechanism, unless somehow enzymatically catalyzed.

Conclusions

^{29}Si NMR shifts were determined for complexes with systematically varying chemical composition, stoichiometry, and structures. By combining these two sets of results (NMR shifts and energies) and comparing to experimental results, we conclude that hypercoordinated silicon−polyalcohol complexes are thermodynamically unfavorable in aqueous solution under mild conditions and are unlikely to play a role in biological silicon uptake from aqueous solution or in sol−gel synthesis from aqueous solution under nonextreme conditions.

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