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NMR evidence of pentaoxo organosilicon complexes in dilute neutral aqueous silicate solutions

Stephen D. Kinrade,*[a] Andrew S. Schach,[a] Robin J. Hamilton[a] and Christopher T. G. Knight[b]

[a] *Department of Chemistry, Lakehead University, Thunder Bay, ON P7B5E1, Canada.*
E-mail: Stephen.Kinrade@lakeheadu.ca
[b] *School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana IL 61801, USA*

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Silicon-29 NMR spectra of a neutral, dilute aqueous silicic acid solution, with a pH and Si concentration typical of soil solutions, reveal that a significant fraction of the silicon is incorporated in two five-coordinated organosilicon complexes when sodium gluconate is present.

The solubility of silica in aqueous solution is markedly pH dependent above pH 8.0, although it is nearly constant across the pH range typical of groundwater and soil solutions, varying from *ca.* 5 ppm for α-quartz to 130 ppm for amorphous silica at pH 7.[1] At these concentrations, silica exists primarily as tetravalent monosilicic acid, $Si(OH)_4$, although some also occurs as disilicic acid, $(OH)_3SiOSi(OH)_3$.[2] Indeed, small quantities of higher oligomers are also expected since the speciation of aqueous silicates is governed by the rules of polymer chemistry, and monomeric silicic acid is always in dynamic equilibrium with more condensed species.[3–5] No other silicon containing species have ever been identified in neutral aqueous solutions, and there has never been any evidence to suggest that silicic acid reacts with organic species at these pH values and concentrations. Although it has often been proposed that organosilicon compounds are key to molecular level processes underpinning the weathering of minerals and biosilicification in plants, such claims have always been speculative.

We have shown elsewhere,[6,7] however, that silicon–carbohydrate compounds readily form in aqueous solution, although at pH values and silica concentrations much greater than are generally found in nature. Surprisingly, the Si centres in such complexes are not tetravalent, but instead exist with either pentaoxo or hexaoxo coordination, or both.[6] Such hypervalent species only form when the carbohydrate ligand contains four or more adjacent hydroxy groups, with two in *threo* configuration, and are especially stable if the ligand also contains a carboxylic acid end group.[7] Accordingly, simple sugar acids like gluconic, saccharic and glucoheptonic acid show great affinity for aqueous silicate anions at high pH.

Here we present evidence for the existence of stable silicon–carbohydrate compounds in *neutral* solution. This represents the first observation of an organosilicon compound forming at biologically relevant Si concentrations and pH. Indeed, with the exception of the well attested monosilicic and disilicic acid species, no other Si-containing molecule has ever been observed in neutral aqueous solution.

Fig. 1 shows the $^{29}Si\text{-}\{^1H\}$ NMR spectrum of an aqueous sodium gluconate solution which has been tumbled with amorphous silica (enriched to 75 atom% in the NMR active ^{29}Si nuclide) for 4 weeks at 311 K. The solution has a measured pH of 7.0† and a silicon concentration of 1.4×10^{-3} mol kg^{-1}, a figure that is consistent with Si levels in soil solutions. As expected, most of the silicon is present as monosilicic and disilicic acid, and the corresponding signals at -71.0 and -80.2 ppm, respectively, are labeled in the figure. Two additional signals are seen at -101.3 and -102.0 ppm, in the region characteristic of five-coordinated Si,[8] and account for 31% of the silicon in solution. Analogous signals appear in the ^{29}Si spectra of high pH silicate solutions that contain gluconic acid or other aliphatic carbohydrate molecules having the requisite hydroxy group configuration.[6,7] Analysis of ^{29}Si–^1H scalar coupling and the corresponding ^{13}C NMR spectra for those solutions showed unequivocally that the ^{29}Si signals originate from Si centres coordinated to two or more carbohydrate –OC≡ linkages.[6,7] Since a –OC≡ group is significantly less shielding than –OSi≡, the peaks at -101.3 and -102.0 ppm almost

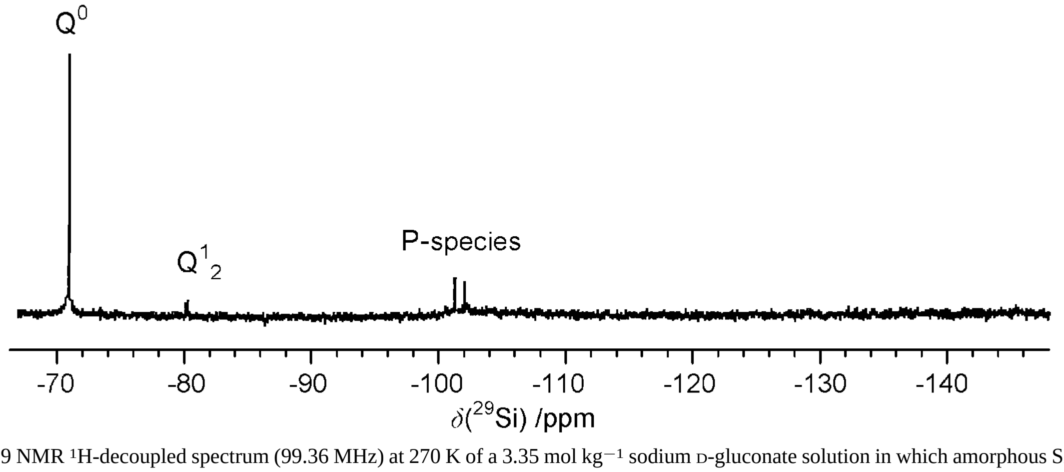

Fig. 1 Silicon-29 NMR ^1H-decoupled spectrum (99.36 MHz) at 270 K of a 3.35 mol kg^{-1} sodium D-gluconate solution in which amorphous SiO_2 (75% ^{29}Si-enriched) was tumbled for 4 weeks at 311 K, followed by 0.1 μm filtration. The final solution composition was 1.4×10^{-3} mol kg^{-1} Si (by ICAP), with a measured pH of 7.0 (298 K). The spectrum was recorded using 8414 $\pi/2$ pulses with an interpulse delay of 47 s, and processed using 2 Hz artificial line broadening. Spectral integration shows that 66 ± 2% of the dissolved silicon exists as the four-coordinated silicate monomer [$Si(OH)_4$, Q^0; -71.0 ppm, $\Delta\nu_{\frac{1}{2}} = 2.5$ Hz], 3 ± 1% as the dimer [$(OH)_3SiOSi(OH)_3$, Q^1_2; –80.2 ppm, $\Delta\nu_{\frac{1}{2}} = 2.5$ Hz], and 31 ± 2% as one of two five-coordinated silicon (denoted ‘P’ for pentafunctional[6]) complexes that correspond to the signals at -101.3 ($\Delta\nu_{\frac{1}{2}} = 8.2$ Hz) and -102.0 ppm ($\Delta\nu_{\frac{1}{2}} = 3.7$ Hz).

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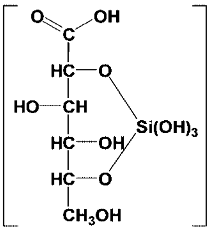
certainly arise from pentaoxosilicon complexes rather than from those containing either tetrahedral Si(OSi≡)$_4$ or (≡CO)$_n$Si(OSi≡)$_{4-n}$ sites.

The spectrum remains unchanged over time, indicating that the complexes are thermodynamically stable. Indeed, the complexes are so energetically favoured that they re-assemble within the time required to obtain an NMR spectrum if the sample constituents are broken down by heating the sample to boiling.

The actual molecular structure of these complexes cannot be deduced with certainty from our spectra. The low Si concentrations involved place these experiments at the very edge of the spectrometer detection limits, even using isotopically enriched materials. The spectrum shown in Fig. 1 required 8 days to acquire. Nevertheless, our work on concentrated alkaline samples[7] would suggest that pentavalent organosilicon complexes **1**, **2** and **3** occur when silicate anions combine with gluconate ligands. Based then on the chemical shifts of signals identified at higher pH, we tentatively assign the peak at −101.3 ppm in Fig. 1 to species **2** and that at −102.0 ppm to species **3**.



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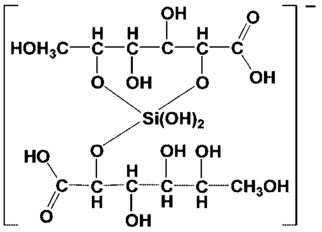

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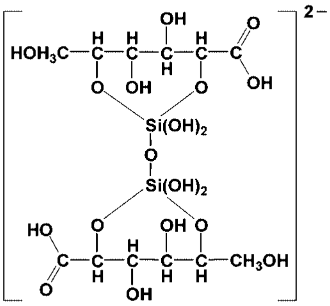

3

Evidence that gluconic acid is effective at sequestering silicate anions in dilute neutral solution suggests that simple sugar acids, or molecules containing structurally related subunits, could indeed play a role in isolating and trapping silicate anions in groundwater and biofluids, thus contributing to the functionality of silicon in nature.

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Notes and references

† pH measurements were performed on two non-isotopically enriched solutions prepared under conditions identical to those used for the ^{29}Si enriched sample in Fig. 1 (also yielding the same 1.4×10^{-3} mol kg^{-1} Si concentration), using an Orion ROSS glass pH electrode. The calculated pH for a 3.35 mol kg^{-1} gluconate ($K_b = 4.0 \times 10^{-11}$) solution is 9.0, which indicates that 4 weeks exposure to atmospheric CO$_2$ and amorphous silica had an appreciable neutralizing effect.

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