DALTON COMMUNICATION

Aqueous hypervalent silicon complexes with aliphatic sugar acids

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Received 19th December 2000, Accepted 19th February 2001
First published as an Advance Article on the web 8th March 2001

Silicon-29 and carbon-13 NMR spectroscopy is employed to determine the structures of stable five- and six-coordinated organosilicon complexes formed by the addition of certain aliphatic acid carbohydrates (such as gluconic acid, glucoheptonic acid and saccharic acid) to aqueous alkaline silicate solutions.

Until recently, the only known instances of aqueous silicate ions bonding directly with organic solutes were the six-coordinated Si complexes that form when $H_3SiO_4^-$ is chelated by catechol, 2-hydroxypyridine *N*-oxide, tropolone or their respective analogues.[1] However, it turns out that Si–O–C bonding is actually quite common in the aqueous environment. Many aliphatic mono- and poly-hydroxy alcohols combine with silicates to produce alkoxy-substituted tetraoxosilicon complexes.[2] The complexing affinity is greater for smaller alcohols and increases with the number of attached hydroxy groups.[2] Indeed, simple polyols such as threitol, xylitol and sorbitol–containing at least four adjacent hydroxy groups with the middle two being in *threo* configuration–strongly interact with silicate anions to produce stable complexes in which silicon is either penta- or hexa-coordinated to oxygens.[3] Silicon does not coordinate across the *threo* hydroxy pair as does boron under similar circumstances,[4] but instead binds to the two *flanking* hydroxy groups. The resulting polyolatosilicate structures are relatively short-lived on the NMR timescale, making them impossible to determine with certainty. Rapid inter- and intra-molecular chemical exchange obscures all ^{1}H–^{29}Si scalar coupling, even down to the solution's freezing point.

We report here that polyol chains which contain a terminal carboxylic acid group ("polyol acids" or "sugar acids"), along with the requisite *threo*-plus-flanking hydroxy group configuration, exhibit dramatically enhanced affinity for silicate complexation. For example, gluconic acid, saccharic acid and glucoheptonic acid all form five- and six-coordinated organosilicon complexes over much wider ranges of pH and concentration than their neutral polyol counterparts.[5] A corresponding increase in average chemical exchange lifetime of the hypervalent complexes (to values of $>10^{-1}$ s at 298 K) causes equilibria to shift significantly in their favour and, in many cases, leads to the appearance of well defined, ^{1}H-coupled ^{29}Si multiplets that arise from three-bond scalar coupling between silicon and aliphatic hydrogens on the sugar acid. (Rapid chemical exchange with water protons prevents detection of ^{1}H–^{29}Si *J*-coupling involving hydroxy groups.) The resolution of the coupling provides, for the first time, a way of determining the molecular structure of silicon–carbohydrate complexes, as we demonstrate below.

Fig. 1 shows the ^{1}H-coupled ^{29}Si NMR spectrum of a concentrated alkaline silicate solution to which saccharic acid has been added. As with solutions containing neutral polyols, three spectral regions are apparent and correspond, by comparison with model compounds of known structure,[3,6,7] to tetraoxosilicon[8] (*ca.* −71 to −110 ppm with respect to tetramethylsilane), pentaoxosilicon (*ca.* −98 to −110 ppm) and hexaoxosilicon (*ca.* −135 to −145 ppm) sites. Two well resolved

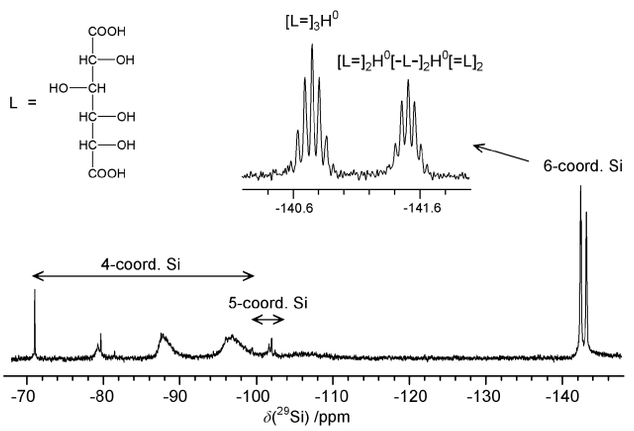

Fig. 1 Silicon-29 NMR ^{1}H-coupled spectrum (99.36 MHz) at 270 K of a solution containing 1.2 mol kg^{-1} SiO_2, 2.9 mol kg^{-1} NaOH and 1.7 mol kg^{-1} monopotassium D-saccharic acid (Fischer projection shown; $K_{a1} = 1.0 \times 10^{-5}$ at 298 K). It was recorded with 1250 π/2 pulses and an interpulse delay of 62 s, using a Si-free probehead and sample tube. Artificial line broadening = 1 Hz. Inset: the two well resolved septets at −140.8 and −141.5 ppm have measured *J*-splitting of 5.7 and 5.0 Hz, respectively. Both correspond to complexes containing a hexaoxosilicon centre coupled, *via* stable Si–O–C–H linkages, to six protons. The equilibrium shift towards five- and six-coordinated Si species caused by the addition of potassium saccharate is far greater than that caused under equivalent conditions by the neutral analogue, threitol, as shown by comparison with Fig. 2(a) of ref. 3.

binomial septets appear at −140.8 and −141.5 ppm, both of which collapse to singlets upon ^{1}H-decoupling. These resonances appear in the region characteristic of hexaoxosilicon centres and are ubiquitous in silicate–sugar acid solutions, appearing over a wide range of sample conditions. Their relative intensities depend upon the sample composition, however, indicating that they arise from two different hexaoxosilicon complexes.

Because the silicate complexes are in dynamic equilibrium with one another, it is possible to manipulate the solution parameters to achieve model systems containing relatively few species, and in this way facilitate structural analysis. Generally, an increase in polyol concentration, an increase in pH or a decrease in temperature favours hexa-coordinated species over both penta- and tetra-coordinated species. For example, Fig. 2(a) shows the ^{29}Si NMR spectrum of an alkaline silicate solution at 270 K in which the pH and gluconate concentration are both elevated to such an extent that only the two hexaoxosilicon complexes indicated are present. The ^{13}C NMR spectrum of the solution indicates that, as with the neutral polyols, silicon coordinates at the hydroxy groups flanking the *threo* pair. Unlike polyoxo anions of aluminium, gallium and indium under similar circumstances,[9] silicon shows no tendency whatsoever of binding to the carboxylate group. The carboxy region of the ^{13}C NMR spectrum is thus relatively simple [Fig. 2(b)]. Four signals are visible. By varying the solution conditions, it is

DOI: 10.1039/b010111g

Table 1 Representative ^{29}Si NMR peak assignments for the five- and six-coordinated silicon–carbohydrate species[a]

Species[b]	$\delta(^{29}Si)$/ppm[c]	Multiplicity [$^3J(^{29}Si–O–C–^1H)$/Hz]
[η²-2,5-(+)-glucoheptonato]silicate (L=P⁰)	−98.1	Triplet [5.8]
[η²-2,5-(+)-glucoheptonato],[η¹-2-(+)-glucoheptonato]silicate (L=P⁰–L)	−100.1	Quartet [7.0]
1,2-di[η²-2,5-(+)-glucoheptonato]disilicate (L=P¹P¹=L)	−102.1	Triplet [7.6]
Other P-species	−100.7	Indeterminate
	−101.0	Indeterminate
	−101.1	Indeterminate
	−101.5	Indeterminate
tri[η²-2,5-(+)-glucoheptonato]silicate ([L=]₃H⁰	−141.4	Septet [5.4]
di-μ-[η²-2,5-(+)-glucoheptonato]-bis([η²-2,5-(+)-glucoheptonato]silicate) ([L=]₂H⁰[–L–]₂H⁰[=L]₂)	−141.8	Septet [5.1]
Other H-species[d]	−140.8	Indeterminate
	−141.2	Indeterminate
	−141.7	Indeterminate
	−142.1	Indeterminate
	−142.7	Indeterminate

[a] Chemical shifts and coupling constants are dependent on solution conditions, and here correspond to a solution containing 0.95 mol kg^{-1} SiO_2, 0.95 mol kg^{-1} NaOH and 1.4 mol kg^{-1} sodium glucoheptonate at 300 K. [b] Refer to structures shown in Fig. 3; full names are given for the case where L = glucoheptonic acid. [c] Chemical shift from tetramethylsilane, employing the orthosilicate monomer peak (assigned here at −71 ppm) as a secondary reference. [d] Observed where L = glucoheptonic acid which has a second *threo* hydroxy pair and therefore two sets of Si bonding sites, but *not* for gluconic acid or saccharic acid.

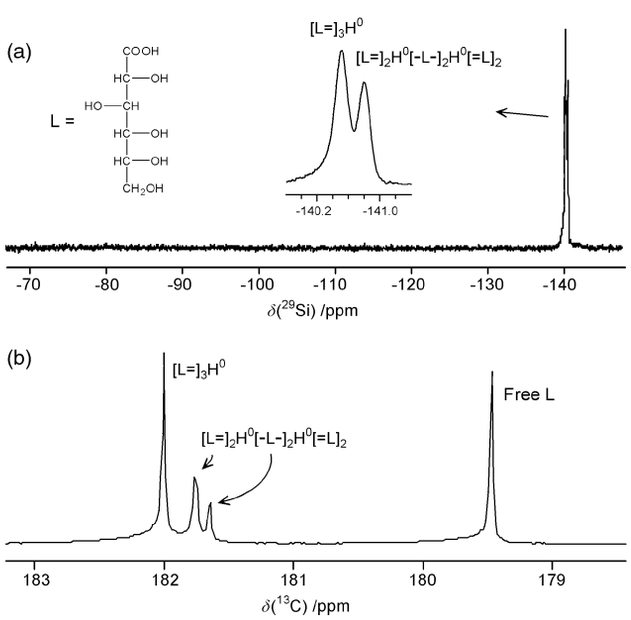

Fig. 2 (a) Silicon-29 (99.36 MHz) spectrum at 270 K of a solution containing 1.2 mol kg^{-1} SiO_2, 2.9 mol kg^{-1} NaOH and 4.9 mol kg^{-1} potassium D-gluconate (Fischer projection shown; $K_a = 2.5 \times 10^{-4}$ at 298 K). (b) Portion of the corresponding ^{13}C NMR spectrum (125.76 MHz) which contains the carboxylate signals. Both spectra were acquired using ^{1}H-decoupling, gated to prevent nuclear Overhauser distortion of signal intensities. They reveal that the solution contains just two six-coordinated silicon species, each having three gluconate ligands per Si centre.

clear that the low frequency signal arises from free gluconate. The two intermediate frequency signals always occur in a 2 : 1 intensity ratio and arise from the complex giving the low-frequency ^{29}Si NMR signal. The high-frequency ^{13}C NMR signal arises from the complex which gives the high-frequency ^{29}Si NMR signal. Spectral integration also shows that each organosilicon complex contains exactly three sugar acid molecules per silicon centre.

Given the NMR data, it is now possible to determine the structure of both complexes. The complex giving rise to the highest frequency ^{29}Si and ^{13}C NMR signals can only be the monomeric tri[η²-2,5-(+)-gluconato]silicate anion (represented as [L=]$_3$H^0 in Fig. 3). Here the silicon nucleus is coupled

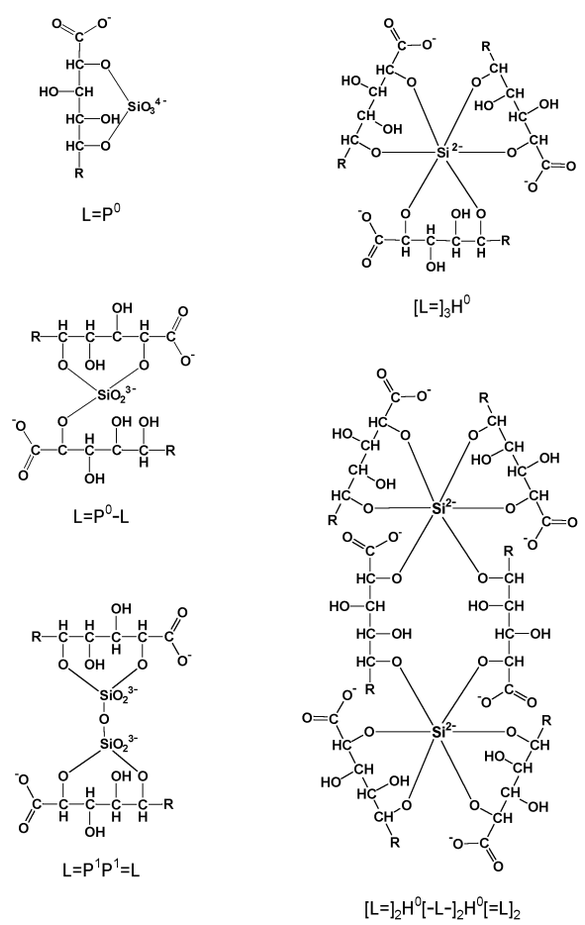

Fig. 3 Structures of the five carboxypolyolato silicate complexes characterized in this study. Here, R and R′ represent polyol chain ends. The pentaoxo Si centres are represented by the symbol P, and hexaoxo Si centres by H.[3] A superscript is used to denote the number of siloxane linkages at the corresponding Si centre.

to three identical pairs of inequivalent –OCH protons, yielding a binomial quartet, each line of which is further split into a quartet with similar *J*-coupling, and ultimately, therefore, a septet. The carboxy groups are all equivalent and consequently yield a single ^{13}C NMR signal.

Similarly, the complex giving rise to the low frequency ^{29}Si NMR signal is almost certainly the dimeric di-μ-[η^2-2,5-(+)-gluconato]-bis([η^2-2,5-(+)-gluconato]silicate) anion (represented as $[L=]_2H^0[-L-]_2H^0[=L]_2$ in Fig. 3). Here each silicon nucleus is coupled to two pairs of inequivalent protons on non-bridging ligands and to two inequivalent protons on bridging ligands, once again resulting in a septet (*i.e.*, a triplet of triplets of doublets of doublets, all with like *J*-coupling). The carboxy carbons will give two signals in a 2 : 1 ratio, arising from the two shared and four unshared sugar acid molecules. Neither the monomeric complex nor the dimer has been proposed previously. The respective ^{29}Si NMR assignments are summarized in Table 1. We note that an increase in either pH or silicon concentration shifts the equilibrium in favour of the dimeric complex.

As with neutral polyols, decreasing the alkalinity of the solution favours pentaoxo coordination over hexaoxo coordination. Up to seven pentaoxo ^{29}Si NMR signals are detected, as noted in Table 1. They are usually exchange-broadened, indicating that the corresponding complexes are not as long lived as the hexaoxosilicon species, and thus they provide less structural information. However, three equally spaced ^{1}H-coupled multiplets are sometimes observed (Table 1). Since their intensities vary independently with solution conditions, they must arise from separate species. Unfortunately, ^{13}C NMR spectra are relatively complicated at this pH and do not permit easy stoichiometric analysis. Assignment of NMR signals to individual complexes is consequently more tentative. Nevertheless, the splitting patterns and relative chemical shifts of the three multiplets are consistent with: the monomeric [η^2-2,5-(+)-gluconato]silicate complex ($L=P^0$; where L = gluconic acid); the monomeric [η^2-2,5-(+)-gluconato],[η^1-2-(+)-gluconato]silicate complex ($L=P^0-L$); and the dimeric 1,2-di[η^2-2,5-(+)-gluconato]-disilicate) complex ($L=P^1P^1=L$). The structures are illustrated in Fig. 3.

Sugar acids are common constituents of extracellular matter (being particularly common in plant rhizospheres[10] and throughout the gastrointestinal tract of animals[11]), cell membranes, most biofluids and soil solutions. Indeed, just as silicates constitute the bulk of the Earth's crust, carbohydrates are the most abundant class of compounds in the biosphere. It is tempting to conclude that their apparent readiness to combine in aqueous solution indicates that sugar acids, or biomolecules containing sugar acid substructures, play an important and hitherto unrecognized role in the geochemistry and biochemistry of silicon.

Acknowledgements

We thank R. J. Kirkpatrick (University of Illinois at Urbana-Champaign) for the generous loan of isotopically enriched silica and D. Aue (University of California at Santa Barbara) for helpful discussions. This work was supported in part by the National Institutes of Health (USA) and the Natural Sciences and Engineering Research Council of Canada.

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