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Complexes of pentaoxo and hexaoxo silicon with furanoidic vicinal *cis*-diols in aqueous solution †

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Addition of furanoidic sugars having vicinal *cis*-diol functionality to aqueous alkaline silicate solutions results in the spontaneous formation of a family of organosilicate complexes in which silicon is either penta- or hexacoordinated. Silicon complexation occurs with 1,4-anhydroerythritol, apiose and ribose, as well as with ribonucleosides (adenosine, cytidine, guanosine) and ribonucleotides (including ATP and NAD^+). Silicon-29 and carbon-13 NMR analysis indicates the occurrence of three main complexes containing pentacoordinated silicon. Two hexacoordinated silicon species are also observed in most instances, these being favoured over the pentacoordinated complexes as solution pH is increased, temperature decreased, or the sugar-to-silicon concentration ratio increased. Ribose, which has two vicinal *cis*-dihydroxy sites for binding silicon, yields a much wider array of complexes.

Introduction

Aqueous silicon chemistry plays a major role in a number of important and topical fields. Silicates in the Earth's crust interact with water on a massive scale to yield life-sustaining soils and mineral deposits. Dissolved silicon is ubiquitous throughout the hydrosphere and living organisms have evolved mechanisms to benefit from the element. Some plants cannot survive without it while others, including all the vital grain crops, require substantial amounts to defend against disease and other biological and physical stresses.[1] In mammals, silicon is a potent stimulator of bone and connective tissue growth and shows promise in the clinical treatment of osteoporosis.[2–4] There is, however, remarkably little known about the absorption, transport and underlying biochemistry of silicon in *any* organism. In fact, the very existence of organosilicate chemistry in Nature has been questioned.[3]

Nevertheless, we recently identified a series of stable organosilicate complexes which form in aqueous alkaline silicate solutions upon addition of certain aliphatic polyols (such as mannitol, xylitol and threitol),[5] and sugar acids (such as gluconic, saccharic and glucoheptonic acids).[6] In these complexes silicon is not four-coordinated, but exists instead as a hypervalent pentaoxo or hexaoxo centre. Only polyols which contain at least four adjacent hydroxy groups, with the centre pair in *threo* configuration, are capable of producing these hypervalent complexes. Although our original analysis of the ^{13}C NMR data suggested that silicon binds to the hydroxy groups adjacent to the *threo* pair, subsequent molecular orbital modeling studies[7,8] have shown that the likely bonding sites on the polyols are at the *threo* hydroxy groups themselves. The organosilicates thus formed contain five-membered chelate rings, consistent with a recent report by Benner *et al.*[9] who present crystallographic data for threitol, xylitol and mannitol silicate complexes. This structural configuration greatly enhances the complex's overall stability, since it allows the two hydroxy groups flanking the *threo* pair to form strong hydrogen bonds with ligating alkoxo functions.[9]

We report here that furanoidic sugars possessing vicinal *cis*-diol groups also form hypervalent organosilicate complexes upon addition to aqueous alkaline silicate solutions, and that the resulting penta- and hexaoxosilicon complexes are so stable that, under favourable conditions, they dominate the silicate anion equilibrium.

Experimental

NMR spectra were recorded at 99.36 MHz for ^{29}Si and 125.76 MHz for ^{13}C on a Varian Unity Inova 500, usually with ^1H-decoupling (gated to prevent nuclear Overhauser distortion). The temperature was calibrated (± 0.5 K) using the ^1H NMR spectrum of ethylene glycol.[10] Chemical shifts are reported relative to tetramethylsilane, employing the orthosilicate monomer peak, here set to −71.0 ppm, as a secondary reference. Spectral parameters are listed in the individual figure captions. Attention was paid to avoid sample contamination by contact with glass surfaces, and all samples were contained in custom made 10mm Kel-F NMR tubes (9 mm I.D.) or Teflon FEP lined glass NMR tubes (8 mm I.D.). Reported NMR spectra are those of freshly prepared solutions, and samples were stored frozen between individual experiments. Most samples exhibited yellowing soon after preparation, although ^{13}C NMR indicated no evidence of decomposition; nor did the ^{29}Si NMR spectra change over the course of the investigation.

Results and discussion

Pentaoxosilicon containing complexes

We show in Fig. 1 the ^{29}Si-{^1H} NMR spectra of concentrated silicate solutions of varying alkalinity to which 1,4-anhydroerythritol, the prototypic Si-binding furanoidic structure, has been added. As with solutions containing acyclic polyols,[5,6] three spectral regions are apparent and correspond, in order of decreasing frequency, to tetraoxosilicon (***Q***-centres, *ca.* −70 to −105 ppm), pentaoxosilicon (***P***-centres; *ca.* −98 to −110 ppm) and hexaoxosilicon (***H***-centres; *ca.* −135 to −143 ppm) containing species.[11,12] Three strong signals appear in the pentaoxosilicon region. These exhibit evidence of long-range scalar coupling to protons as demonstrated in Fig. 2. Rapid ^1H–^1H chemical exchange with water prevents the emergence of ^{29}Si–O–^1H coupling. The observed ^{29}Si–^1H coupling must therefore involve protons on the furanose ring, indicating that Si is covalently bound to the hydroxy group oxygens. The multiplet structures cannot be resolved, even at temperatures down to the

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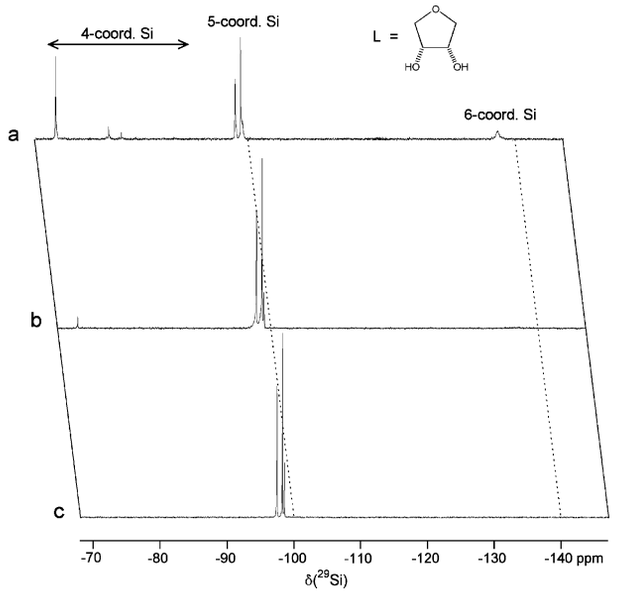

Fig. 1 Silicon-29 NMR (99.36 MHz) spectra of sodium silicate solutions containing 0.50 mol kg^{-1} SiO_2, 4.0 mol kg^{-1} 1,4-anhydroerythritol and (a) 3.1, (b) 1.8 or (c) 0.65 mol kg^{-1} NaOH (pH = 13.4, 13.1 and 12.7, respectively, at 298 K), recorded at 278 K using 1200 $\pi/2$ pulses, a 42 s inter-pulse delay and gated ^{1}H-decoupling. The longitudinal (T_1) relaxation times for the dominant signals in spectrum (a) are: −71.0 ppm, 8.3 s; −97.4 ppm, 10.5 s; and −98.2 ppm, 10.0 s. (Dotted lines are drawn at −100 and −140 ppm to help visually register the spectra.)

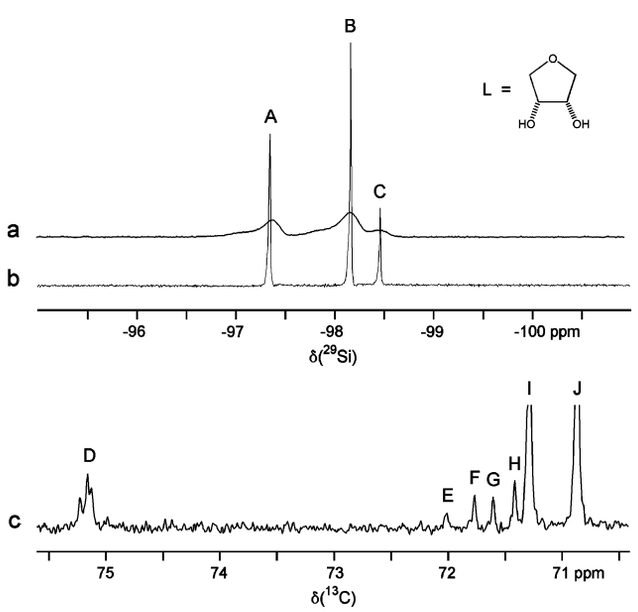

Fig. 2 (a) Silicon-29 NMR spectrum of a sodium silicate solution containing 0.50 mol kg^{-1} SiO_2, 0.65 mol kg^{-1} NaOH and 4.0 mol kg^{-1} 1,4-anhydroerythritol, recorded at 278 K without ^{1}H-decoupling. (b) The equivalent spectrum acquired using ^{1}H-decoupling gated on during acquisition only. (c) The corresponding ^{13}C NMR spectrum (125.76 MHz) acquired using gated ^{1}H-decoupling. Refer to Table 1 for peak assignments.

freezing point of the solutions, owing to the small value of $^3J(^{29}Si–O–C–^1H)$ (generally, 5–8 Hz[6,13]) and the lability of the complexes. No $^{29}Si–^{29}Si$ scalar *J*-coupling can be detected for solutions enriched in ^{29}Si, which indicates that the Si centres in each complex are either magnetically equivalent or else separated by at least five bonds. The area of each resonance varies independently with silicon concentration, sugar concentration and pH, suggesting that they correspond to different complexes. Variable-temperature NMR line broadening studies show that the three species have similar lability in solution. Other furanose compounds with *cis*-2,3-diol functionality exhibit the same triad of signals in the five-coordinate region of the spectrum, with roughly the same intensity ratio. We investigated solutions containing apiose, ribose (see below), ribonucleosides (adenosine, cytidine, guanosine) and ribonucleotides (ATP and NAD^+). Silicon-29 NMR spectra of solutions containing furanoidic molecules which lack the vicinal *cis*-diols (*e.g.* 2-deoxyribose, deoxyribonucleosides, deoxyribonucleotides) appear almost identical to those of the parent alkaline silicate solution, indicating that silicon does not bind to these sugars.

All the silicon in the solution represented by Fig. 1(c) is pentacoordinated, presumably as a result of complexation by 1,4-anhydroerythritol. The lower trace of Fig. 2 illustrates the corresponding ^{13}C NMR spectrum. Consistent with ^{13}C NMR spectra of aliphatic polyolatosilicon complexes,[5,9] the signal of carbons 2 and 3, which are directly bound to the pentaoxosilicon centre, is shifted only slightly (<1 ppm) upon complexation, whereas that of the adjacent carbons ($C_{1,4}$, labelled "D" in Fig. 2) moves by more than 4 ppm. Four well resolved $C_{2,3}$ signals (labelled E, F, G and H in Fig. 2) result from complexation. A careful comparison of the integrated ^{29}Si and ^{13}C NMR spectra of several different silicate–furanose *cis*-diol solutions, obtained under conditions which yield quantitative peak areas, reveals that, for each of the three complexes, the ligand concentration is exactly twice that of the silicon concentration. The area of the lowest frequency ^{13}C NMR signal consistently correlates with the highest frequency ^{29}Si peak, and *vice versa*, and the two intermediate frequency ^{13}C NMR peaks, F and G, are equivalent in area and each correlate with the middle ^{29}Si peak.

The simplest interpretation of the NMR data is that three diastereomers of the monomeric bis(diolato)-hydroxo complex, $[(L=)_2SiOH]^-$ (where L represents the furanose *cis*-diol ligand), coexist in solution. Benner and Klüfers[14] crystallized such a complex from a potassium silicate solution containing 1,4-anhydroerythritol (species **1** in Fig. 3). It has square-pyramidal

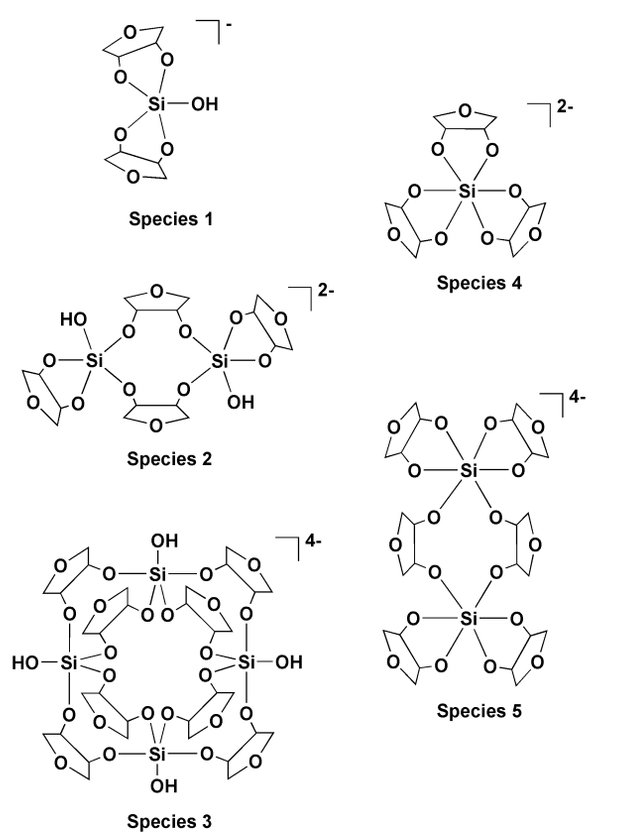

Fig. 3 Schematic representation of the five furanato silicate complexes tentatively characterized in this study.

Table 1 Silicon-29 and carbon-13 NMR assignments for three pentaoxosilicon complexes in an aqueous silicate solution containing 0.50 mol kg^{-1} SiO_2, 0.65 mol kg^{-1} NaOH and 4.0 mol kg^{-1} 1,4-anhydroerythritol at 278 K. (Refer to the spectra in Fig. 2)

		^{29}Si		^{13}C ($C_{2,3}$)		^{13}C ($C_{1,4}$)	
Species [a]	Conc./mol kg^{-1}	Label	δ/ppm	Label	δ/ppm	Label	δ/ppm
Free anhydroerythritol ligand (L)	3.0			I	71.29	J	70.87
$[(L=)_2SiOH]^-$, **1**	0.17	A	−97.37	H [b]	71.42	D	75.2
$[(L=)SiOH(–L–)_2SiOH(=L)]^{2-}$, **2**	0.13	B	−98.19	G [b]	71.61	D	75.2
				F [c]	71.77	D	75.2
$[(–L–)_2SiOH]_n^{n-}$ ($n \geq 4$), **3**	0.02 [d]	C	−98.48	E [c]	72.02	D	75.2

[a] Tentative assignments, shown in the fully protonated state. See structural representations in Fig. 3. [b] Corresponding to non-bridging ligand. [c] Corresponding to bridging ligand. [d] Assuming $n = 4$.

Table 2 Silicon-29 and carbon-13 NMR assignments for two hexaoxosilicon complexes in an aqueous silicate solution containing 0.43 mol kg^{-1} SiO_2, 1.7 mol kg^{-1} NaOH and 0.86 mol kg^{-1} guanosine at 278 K. (Refer to the spectrum in Fig. 4(c))

Species [a]	Conc./mol kg^{-1}	^{29}Si δ/ppm	^{13}C (C_8) [b,c] δ/ppm		
Free guanosine ligand (L)	0.57			150.70	
$[(L=)_3Si]^{2-}$, **4**	0.095	−137.3	151.0	151.7_6	151.7_9
$[(L=)_2Si(–L–)_2Si(=L)_2]^{4-}$, **5**	0.001	−138.3		[d]	

[a] Tentative assignments, shown in the fully protonated state. See structural representations in Fig. 3. [b] Peak assignments for C_8, located on the imidazole ring adjacent to the guanine–ribose link. [c] For species **4**, this site yields three peaks with approx. equal area. [d] Peaks for species **5** are hidden beneath other signals.

geometry at the Si centre, with both furanose ligands oriented towards the terminal silanol group. Two other diastereomers potentially exist for this complex: one with a single furanose ring facing away from the silanol group; and the other with both rings oriented away. In the former case, carbons 2 and 3 become spatially non-equivalent, which could account for the observed ^{13}C peak splitting. A problem with this simple interpretation, however, is that outward-facing furanose ligands are, in effect, no different from non-Si-complexing polyols such as ethylene glycol or erythritol. They impart no additional stability through intramolecular H-bonding, nor protect the reactive silanol group through their hydrophobic character.

An alternate interpretation of the NMR data involves the presence of two oligomers, both with L : Si = 2 : 1, as shown in Fig. 3. Species **2**, $[(L=)SiOH(–L–)_2SiOH(=L)]^{2-}$, consists of a pair of doubly bridged pentaoxosilicons and species **3**, $[(–L–)_2SiOH]_n^{n-}$, is a ring of n doubly-bridged Si centres. In each case, furanoid rings face inwards towards the non-bonding silanol groups as in the monomeric complex, species **1**. Modelling analysis suggests that the cyclic complex is most stable when composed of four bridged pentaoxosilicon centres. Based solely on the NMR data, no distinction can be made with any degree of confidence between the validity of these two structural interpretations. For the aforementioned reasons, however, the NMR signals are tentatively assigned to the three pentaoxosilicon structures we show in Fig. 3. (See Table 1.)

Hexaoxosilicon containing complexes

An increase in either pH or the furanose *cis*-diol concentration yields at least one NMR signal in the hexaoxosilicon region, as shown in Fig. 1 for 1,4-anhydroerythritol (top trace) and in Fig. 4 (lower traces) for adenosine and guanosine. For 1,4-anhydroerythritol a new resonance at −137.1 ppm appears only at very high alkalinity and exhibits significant exchange broadening, indicative of relatively high molecular lability. (Line width calculations indicate an average lifetime ≤1 ms at 298 K.) Ribonucleosides and ribonucleotides tend to yield substantially more hexaoxosilicon complex than 1,4-anhydroerythritol under similar solution conditions.

The ^{13}C NMR signals of guanosine all shift upon silicon binding. Those arising from the five ribose carbons shift to lower frequency, but the complexity of this spectral region precludes their assignment. The guanine spectral region is straightforward by comparison, with Si-complexation producing the largest chemical shift change for C_4 and C_8, which are situated on either side of the nitrogen linked to the ribose ring. Three new C_8 signals, each with equal area, are easily resolved. Individual NMR parameters are listed in Table 2. Spectral integration reveals that there are exactly three guanosine ligands for every Si centre in this hexaoxosilicon complex. Based on the similarity with NMR spectra obtained for the analogous acyclic polyol–silicate complex[6] and recent crystallographic confirmation of that structure by Benner *et al.*,[9] the structure is assigned to species **4** in Fig. 3, the monomeric tris(diolato) complex $[(L=)_3Si]^{2-}$, in which each ligand has a slightly different spatial orientation.

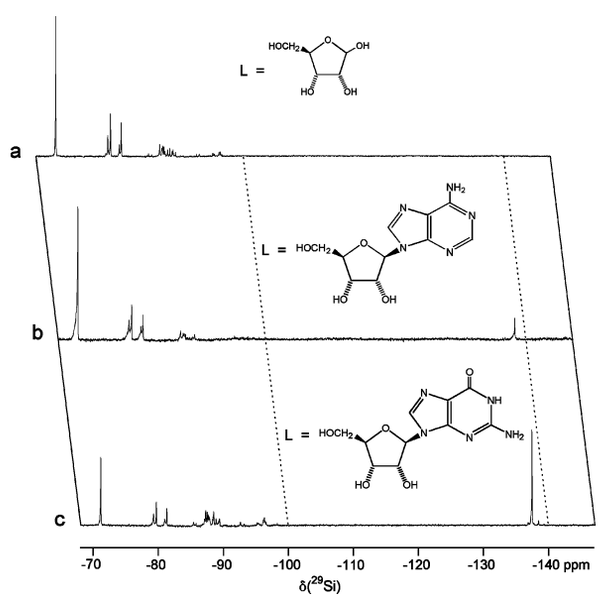

Fig. 4 Silicon-29 NMR spectra of sodium silicate solutions containing 0.43 mol kg^{-1} SiO_2, 1.7 mol kg^{-1} NaOH and 0.86 mol kg^{-1}: (a) D-ribose, (b) adenosine or (c) guanosine, recorded as in Fig. 1.

One other hexaoxosilicon resonance appears at high pH in solutions containing ribonucleosides or ribonucleotides. It is located approximately 1 ppm to low frequency of the dominant tris complex signal (Table 2) and is tentatively assigned to species **5** in Fig. 3, again by virtue of the close similarity with the aliphatic polyol–silicate system.[6]

Silicon–ribose complexes

Although ribose has an intermediate affinity for silicon complexation (falling between that of 1,4-anhydroerythritol and adenosine), it is unique among all the furanoidic *cis*-diol molecules we surveyed in that alkaline silicate solutions to which it is added yield highly complicated ^{29}Si NMR spectra, particularly in the hexaoxosilicon region. In ribose the C_1 hydroxy group shares the same ring face as the $C_{2,3}$ hydroxy pair, thus providing not one but two bonding sites, and opening the door to the existence of a wide variety of organosilicate complexes. We show in Fig. 5 the ^{29}Si NMR spectra of three ribose containing silicate solutions, prepared with different NaOH concentration. Fig. 6 shows the effects of varying the ribose concentration. In both cases a large number of signals are seen in the hexaoxosilicon region, with some 32 signals being apparent in more concentrated solutions, as shown in Fig. 7. Although the same three peaks we noted previously still dominate the pentaoxosilicon spectral region, four smaller signals are also apparent. The hexaoxosilicon region is so complex that it precludes

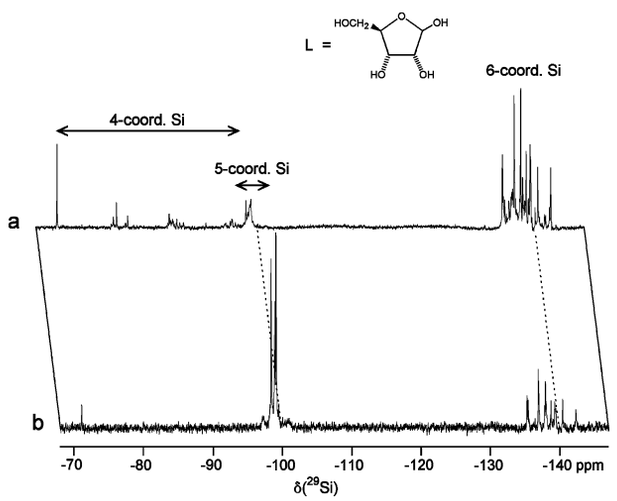

Fig. 5 Silicon-29 NMR spectra of sodium silicate solutions containing 1.2 mol kg^{-1} SiO_2, 5.0 mol kg^{-1} D-ribose and (a) 3.1 or (b) 1.2 mol kg^{-1} NaOH, recorded as in Fig. 1.

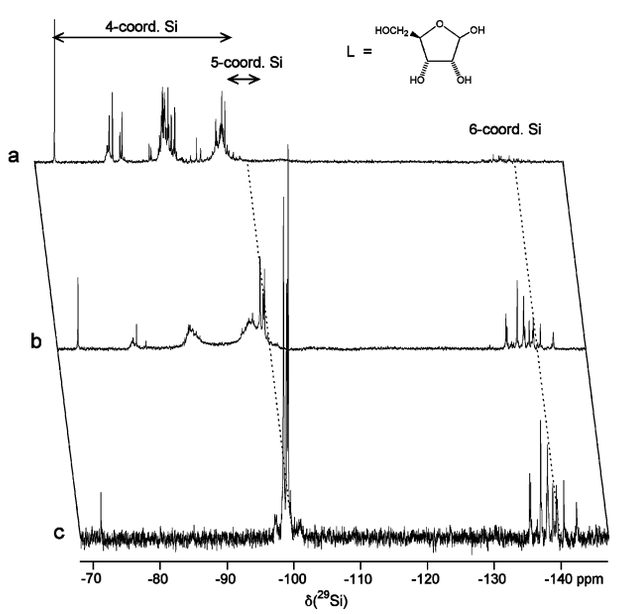

Fig. 6 Silicon-29 NMR spectra of sodium silicate solutions containing 1.2 mol kg^{-1} SiO_2, 1.2 mol kg^{-1} NaOH and (a) 0.57, (b) 2.4 or (c) 5.0 mol kg^{-1} D-ribose, recorded as in Fig. 1.

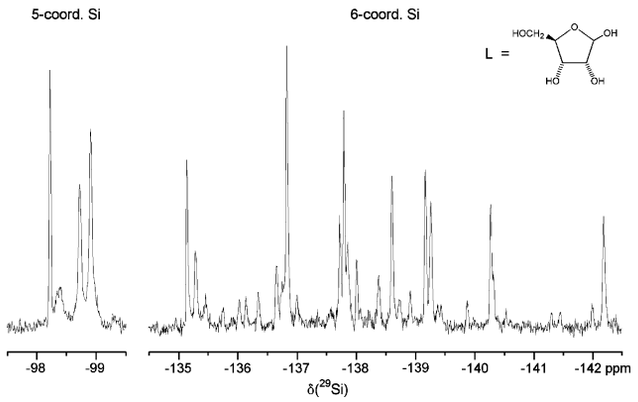

Fig. 7 Spectral regions corresponding to five- and six-coordinated silicon in a ^{29}Si NMR spectrum of a sodium silicate solution containing 0.96 mol kg^{-1} SiO_2, 1.9 mol kg^{-1} NaOH and 3.2 mol kg^{-1} D-ribose. The spectrum was acquired at 278 K using 1700 π/2 pulses, a 42 s inter-pulse delay and gated ^{1}H-decoupling.

further structural assignment, although we note that the chemical shift range of the six-coordinate signals extends further to high frequency than with acyclic sugars, starting at approximately −135 ppm. As with the other furanoidic *cis*-diol sugars, increasing the pH favours hexaoxo over pentaoxosilicon complexes.

Furanoidic sugars having *cis*-diol functionality such as ribose play an important role in living organisms. The ease with which these molecules associate with aqueous silicates to form hypervalent organosilicates suggests that such complexes may play an active role in the biological world.

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