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Two substituted cubic octameric silicate cages in aqueous solution

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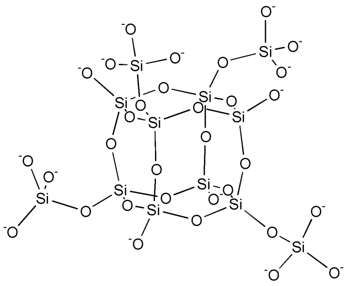
Two novel silicate anions, a singly-substituted cubic octamer (double four-ring cage with a pendant ortho-silicate group) and its dimeric counterpart (two octameric cages linked by a single siloxane bridge), are detected by ^{29}Si NMR spectroscopy in concentrated tetraalkylammonium silicate solutions at the low alkalinity and high SiO_2 concentration typical of zeolite synthesis slurries.

Aqueous alkaline silicate solutions are widely used in the chemical industry, and are of particular importance in zeolite synthesis. Over the past two decades, the structures of the twenty-three most common dissolved silicate anions have been determined with varying degrees of certainty using ^{29}Si NMR spectroscopy in conjunction with ^{29}Si enriched materials.[1] These assignments were generally made using highly alkaline solutions, with concentration ratio $[OH^-] : [SiO_2] > 1 : 1$, so as to limit the number of species present and thus simplify the resulting ^{29}Si NMR spectra. As solution pH is decreased, however, the number of silicate anions increases dramatically. Consequently, spectra of industrially important mixtures with $[OH^-] : [SiO_2] \leq 1 : 1$, such as those used in zeolite synthesis, exhibit so many resonances that individual signals become difficult to resolve.[1]

In 1997, Harris *et al.*[2] reported the presence of a novel silicate anion (**1**) in solutions prepared using a diquaternary ammonium base. This species is a four-fold symmetrically-substituted cubic octameric cage, and is the first reported example of an aqueous silicate anion containing the Q^4 structural unit.† Since zeolites are composed primarily of Q^4 centres joined in a three dimensional array, Harris *et al.*'s observation has important implications in terms of understanding the mechanism of zeolite formation. The work described here presents direct evidence of two different Q^4 containing silicate anions, species **2** and **3**, that are similarly derived from the cubic octameric cage structure.

We show in Fig. 1A the ^{29}Si NMR spectrum of a tetramethylammonium silicate solution with an SiO_2 concentration of 0.8 mol kg^{-1} and a nominal $[OH^-] : [SiO_2]$ ratio of 0.7 : 1. The spectrum is similar to those of concentrated organic base silicate solutions published elsewhere[3–6] and exhibits a series of sharp NMR signals, the most intense of which at −27.14 ppm is that of the well characterized[4] cubic octameric cage, Q^3_8. The majority of signals lying to high frequency of this resonance correspond to the other previously characterized silicate species.[1] On the low frequency side of the Q^3_8 peak, in a spectral region associated with Q^4 units, two new signals appear at −34.91 and −35.73 ppm.

The spectrum in Fig. 1B is of a similar solution, with ratio $[OH^-] : [SiO_2] = 0.9 : 1$, that has been isotopically enriched to 95 atom% in ^{29}Si. Because of ^{29}Si–^{29}Si scalar coupling, all signals from silicate anions containing more than one silicon chemical environment will occur as multiplets. Conversely, all peaks which remain unsplit upon ^{29}Si enrichment must arise from single site species such as the monomer, dimer, and all rings and symmetric cages. Seven such singlets are apparent and are assigned to the monomer Q^0 (0 ppm), dimer Q^1_2 (−8.79 ppm), cyclic trimer Q^2_3 (−10.13 ppm), cyclic tetramer Q^2_4 (−16.52 ppm), prismatic hexamer Q^3_6 (−17.02 ppm), cubic octamer Q^3_8 (−27.14 ppm) and singly protonated cubic octamer (−27.56 ppm).[6]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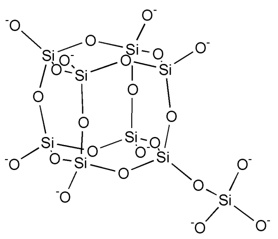
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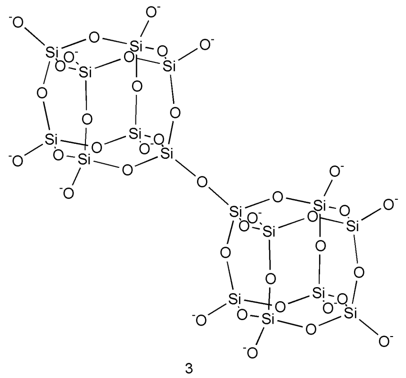
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We show as insets expansions of the ^{29}Si NMR spectra for the regions of interest. For the ^{29}Si enriched solution a clear doublet is apparent in the Q^1 region at −9.57 ppm. Both Q^4 peaks are also multiplets and consequently cannot arise from rings or symmetric cage structures. Additional multiplets appear on either side of the Q^3_8 signal at −27.01 and −27.32 ppm. Selective homonuclear ^{29}Si–{^{29}Si} decoupling experiments show that irradiation of the doublet at −9.57 ppm causes the quintet at −35.73 ppm to collapse into a quartet. (See Fig. 1B'.) The latter resonance is also coupled to the quartet at −27.01 ppm. This signal is in turn coupled to the quartet at −27.32 ppm, which is itself coupled to a resonance directly coincident with the Q^3_8 signal. Silicon-29 2D-INADEQUATE spectra yield independent confirmation of the peak connectivities. In the absence of overlapping resonances from species **3** (refer below to the effect organic cations have on silicate equilibria), the intensity ratio $Q^1(a) : Q^3(b) : Q^3(d) : Q^4(e)$ (referring to the peak labels in Fig. 1) is always 1 : 3 : 3 : 1. This particular ensemble of NMR signals is therefore inconsistent with species **1** and is assigned instead to species **2**, the *singly-substituted* cubic octamer. (See Table 1.)

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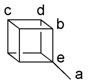
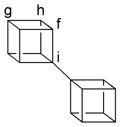
Table 1 Silicon-29 NMR peak assignments at 270 K for the spectrum in Fig. 1B

Species	Spin site	$\Delta\delta$/ppm[a]	Multiplicity	$^2J(^{29}Si–^{29}Si)$/Hz
	a (Q^1)	−9.57	Doublet (1 : 1)	10.2[b]
	b (Q^3)	−27.01	Quartet (1 : 3 : 3 : 1)	8.0
	c (Q^3)	−27.14[c]		
	d (Q^3)	−27.32	Quartet (1 : 3 : 3 : 1)	7.0
	e (Q^4)	−35.73	Quintet (1 : 4 : 6 : 4 : 1)	9.3[d]
	f (Q^3)	−27.01	Quartet (1 : 3 : 3 : 1)	8.0
	g (Q^3)	−27.14[c]		
	h (Q^3)	−27.32	Quartet (1 : 3 : 3 : 1)	7.0
	i (Q^4)	−34.91	Apparent quintet	≈5

[a] Chemical shift from monomer (Q^0) resonance. [b] Peak resolves into a singlet upon selective decoupling of site e. [c] Peak hidden under the large Q^3_8 resonance at −27.14 ppm. [d] Peak resolves into a quartet with ^2J(c–e) = 8.8 Hz upon selective decoupling of site a.

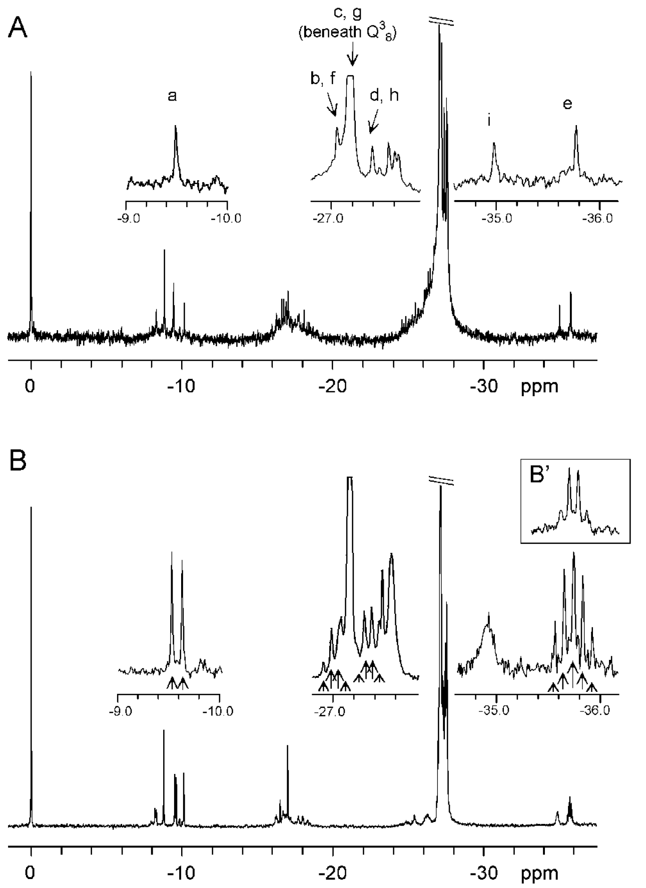


Fig. 1 A) Silicon-29 NMR (99.36 MHz) spectrum at 276 K of a sodium silicate solution containing 0.79 mol kg^{-1} SiO_2, 0.79 mol kg^{-1} tetramethylammonium hydroxide (TMAOH) and 0.23 mol kg^{-1} HCl, recorded using 2388 π/2 pulses and a 61 s interpulse delay. B) Silicon-29 NMR spectrum at 270 K of a comparable solution with 0.99 mol kg^{-1} SiO_2, *now 95 atom% enriched in* ^{29}*Si*, 0.99 mol kg^{-1} TMAOH and 0.12 mol kg^{-1} HCl. The solution has a measured pH of 12. The spectrum was acquired with 2000 π/2 pulses and a 61 s interpulse delay. Selective decoupling of the −9.57 ppm resonance caused that at −35.73 ppm to collapse into a quartet as shown in the boxed insert, B'. Both spectra were acquired using a silicon-free NMR probe and tubes, thus obviating any ^{29}Si background signal. The ^{29}Si chemical shift axis is internally referenced to the silicate monomer peak at 0 ppm (−71 ppm from $SiMe_4$).

Table 2 Occurrence of substituted-Q^3_8 species in solutions containing *ca.* 1.3 mol% SiO_2, 1.3 mol% MOH,[a] 0.3 mol% HCl and 10.0 mol% methanol. No evidence was found for species **1**

Quaternary ammonium ion[b]	Species **2**	Species **3**
$[(Me)_4N]^+$	√	√
$[HOCH_2CH_2N(Me)_3]^+$	√	√
$[(Ph)N(Me)_3]^+$	√	
$[–(CH_2)_3N(Me)_3]^+{}_2$[a]	√	
$[CH_3(CH_2)_{11}N(Me)_3]^+$		
$[CH_3(CH_2)_{15}N(Et)(Me)_2]^+$		
$[(n\text{-}Bu)_4N]^+$		
$[–(CH_2)_3N(n\text{-}Bu)_3]^+{}_2$[a]		

[a] For bis-quaternary ammonium solutions, the $M(OH)_2$ concentration was 0.7 mol%. [b] Me = methyl, Et = ethyl, *n*-Bu = *n*-butyl.

The other Q^4 signal at −34.91 ppm is coupled to Q^3 multiplets that almost perfectly coincide with those of species **2**, indicating that there must be a second Q^4 containing structure which contains Q^3 units with nearly identical chemical environments to those of the singly-substituted cubic octamer. No other NMR peaks are coupled to this series of signals which we therefore assign to species **3**, the dimer of the singly-substituted octamer. (See Table 1.) Increasing the sample temperature causes the ^{29}Si multiplets from species **3** to coalesce by 324 K while those of species **2** remain relatively sharp, indicating that the former species is the more labile of the two.

Signals from both species are evident for concentrated tetramethylammonium silicate solutions with pH values between 11.6 and 13.2, although they are strongest between pH 12 and 12.5. For the solution represented in Fig. 1B, 9 ± 1% of the dissolved silicon exists as species **2** and 5.1 ± 0.5% as species **3**.

As noted in Table 2, these species can also be detected in solutions prepared with different quaternary ammonium bases. In general, they exhibit a similar dependence on cation structure as does the cubic octamer, or more specifically the protonated cubic octamer,[6,7] indicating that they too are stabilized by a hydrated alkylammonium clathrate shell.[7] Thus, their relative concentration is increased by increasing the number of methyl groups on the quaternary ammonium cation, or by decreasing the size of substitute alkyl groups. The species are also favoured by the addition of methanol to the solution. Under the conditions of this study, however, only tetramethylammonium and choline–the most strongly clathrating organocations–yield species **3**. No evidence of species **1** could be found.

Low alkalinity tetraalkylammonium silicate solutions exhibit distinctive ^{29}Si NMR spectra which, with the exception of the usual array of smaller oligomers, can be interpreted solely in terms of the presence of cubic octamer, protonated cubic octamer, singly-substituted cubic octamer and dimeric cubic octamer. No other anions are apparent in appreciable quantity, contrary to previous claims of large rings and double-ring cages.

Acknowledgements

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Notes and references

† By convention, the Q^y_z symbol is used to denote a quadrifunctional Si centre with *y*-coordinated SiO_4^{4-} tetrahedra and, when applicable, *z* indicates the number of equivalent centres in a totally symmetric anion. Thus, the monomer ($H_{4-q}SiO_4^{q-}$), dimer ($H_{6-q}Si_2O_7^{q-}$), cyclic trimer ($H_{6-q}Si_3O_9^{q-}$), cyclic tetramer ($H_{8-q}Si_4O_{12}^{q-}$), prismatic hexamer ($H_{6-q}Si_6O_{15}^{q-}$), and cubic octamer ($H_{8-q}Si_8O_{20}^{q-}$) are respectively, and more conveniently, represented by Q^0, Q^1_2, Q^2_3, Q^2_4, Q^3_6 and Q^3_8.

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