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A novel symmetric silicate anion

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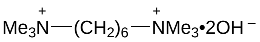
For the first time, a simple symmetrical silicate anion containing Q^4 sites has been detected in alkaline solution by the use of high-field ^{29}Si NMR spectroscopy involving isotopic enrichment.

Alkaline aqueous solutions of silicates contain a variety of anionic species in dynamic equilibrium. Silicon-29 NMR spectroscopy has proved to be the most valuable tool for obtaining information about the molecular structures, but isotopic enrichment in ^{29}Si is generally necessary in order to make diagnostic use of splitting patterns caused by (^{29}Si, ^{29}Si) scalar coupling.[1,2] To date some 23 anionic structures have been proposed.[1,3] The solutions are relevant to a number of industrial applications, including zeolite formation, though the solution conditions are generally far from those used in practice. As concentrations increase and the pH is lowered, many highly-condensed species are presumably formed, so that resonance bands overlap and information about individual anions is lost. In consequence, whereas oligomers containing Q^1, Q^2 and Q^3 silicon sites (where the superscript indicates the number of siloxane bridges) are well known, information on small Q^4-containing species is hard to come by. (The 'Q' notation carries no explicit implications regarding the protonation state of the ions.) However, the existence of the 'cubic octamer', Q^3_8, is well established, and it is known to be favoured by the presence of substituted ammonium species as the gegenions. Zeolitic species occur which incorporate 'four-membered' rings, such as are present in Q^3_8, so that zeolite synthesis involving the linking of Q^3_8 rings is conceivable, but such linking immediately implies the presence of Q^4 sites. The work described here presents the first clear demonstration, to our knowledge, of the existence of a symmetrical silicate anion based on addition of Q^1 units to the cubic octameric species.

Our investigations involved the use of an anion (**I**) containing two substituted ammonium sites, referred to as HMOH, as the gegenion. In our studies with this anion we examined an aqueous (D_2O) HMOH silicate solution with 5.7 wt % SiO_2 and a molar ratio SiO_2 : HMOH of 1 : 1, using the highest magnetic field available to us (14.1 T, ^{29}Si resonance 119.2 MHz, Varian VXR600). The pH of the solution is *ca.* 12. We observed a sharp ^{29}Si signal shifted 35.9 ppm to low frequency of the peak arising from Q^0 in the same solution, which places it in the middle of the Q^4 region (approximately at δ_{Si} −108 from the resonance of the usual reference standard, tetramethylsilane).



$\overset{+}{Me_3N}—(CH_2)_6—\overset{+}{N}Me_3 \cdot 2OH^-$

I HMOH

In order to structurally characterise the species responsible for this signal, we prepared an aqueous (D_2O) solution enriched to the 92% level in ^{29}Si and obtained 119.1 MHz ^{29}Si spectra. The Q^4 signal in question appeared as a 1 : 4 : 6 : 4 : 1 quintet of average spacing 9.2 Hz ($\equiv|^2J_{SiSi}|$), with interleaving signals with intensity ratio 1 : 3 : 3 : 1 [presumably arising from species with ^{28}Si ($I = 0$) rather than ^{29}Si at one of the coupled sites] (see Fig. 1). In order to ascertain the nature of the sites coupled to the −35.9 ppm signal, we recorded a two-dimensional correlation (COSY) spectrum at 35 °C (optimised to minimise exchange while avoiding unduly high viscosity), see Fig. 2. This showed clear cross peaks to a doublet ($|^2J_{SiSi}| = 9.9$ Hz) at −9.58 ppm from the Q^0 peak and a multiplet (probably 1 : 3 : 3 : 1) at *ca.* −27.36 ppm. Unfortunately there was significant overlap of the latter signal with an intense peak from Q^3_8 at −27.48 ppm. However, integration showed that bands at −35.92 and −9.58 ppm had equal intensity, and the multiplet patterns imply the band at −27.48 ppm also has this intensity.

It is clear that the only structure to be in accord with the evidence of chemical shifts and splitting patterns is the symmetrically substituted cubic octamer **II**, containing Q^1, Q^3 and Q^4 sites in equal numbers (and with no other inequivalences). The bridging and terminal oxygen atoms are omitted from the

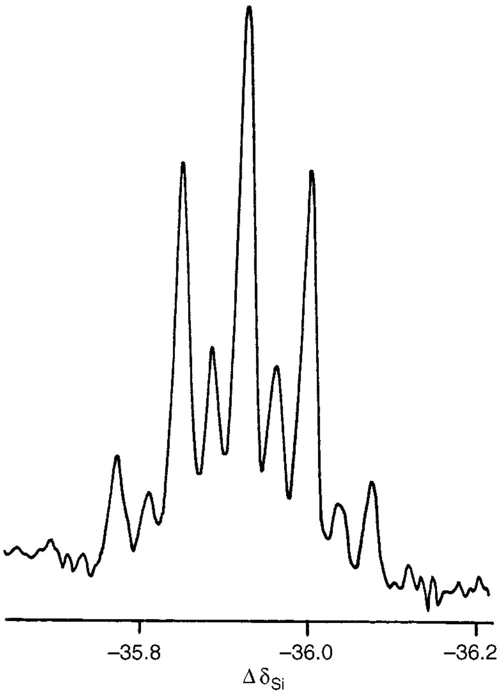


Fig. 1 The ^{29}Si NMR band at −35.92 ppm for the solution discussed in the text. Chemical shifts are quoted relative to the Q^0 peak in the same solution

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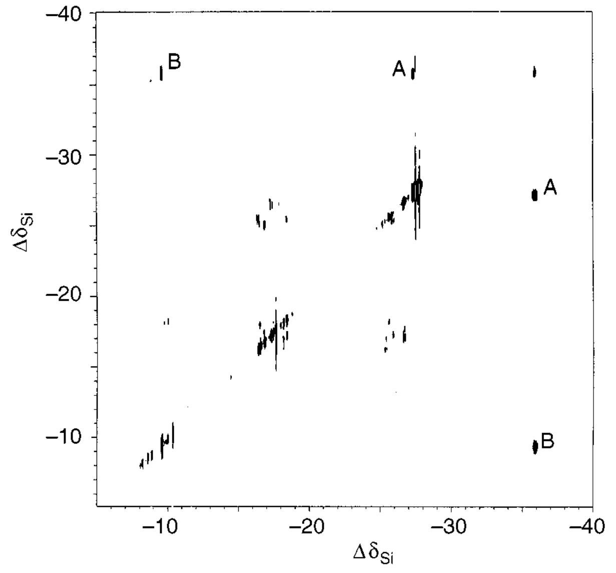
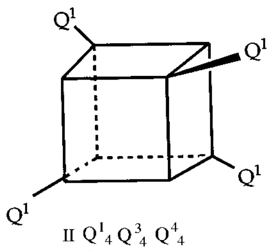


Fig. 2 The ^{29}Si COSY-90 spectrum discussed in the text. Cross-peaks marked A and B link the signals at −35.9/−27.4 and −35.9/−9.6 ppm respectively. There is no cross-peak linking the −27.4 and −9.6 ppm bands. Other cross-peaks shown correspond to species discussed earlier.[4] Chemical shifts are quoted relative to the Q^0 peak in the same solution. The total spectrometer time used to record the spectrum was 64 h, with 256 transients acquired for each of 256 t_1 points. The recycle delay was 3 s. Acquisition was in absolute value mode

diagram **II** for clarity. The shift for Q^1 in this species is highly unusual. It lies between ranges usually associated with Q^1 and Q^2 in 'three-membered' rings. It is unclear why species **II** is preferred over less-symmetrical substituted $Q^3{}_8$ anions, but there are some other, weak, peaks in the region −35.1 to −35.7 ppm which cannot be properly characterised.



II $Q^1{}_4\,Q^3{}_4\,Q^4{}_4$
(schematic)

Species **II** is the first example of an oligomeric anion containing a Q^4 unit bonded to Q^1; hitherto extreme connectivities in the same species have been considered to be disfavoured.

Acknowledgements

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