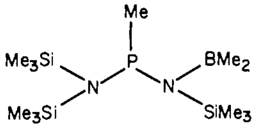
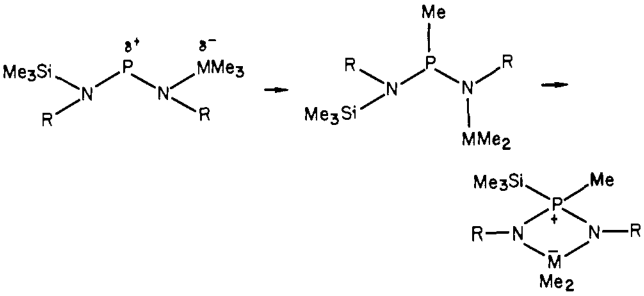
downfield from that of **9** and in the region expected for diamidoalkylphosphines.[10,11] The ^{1}H NMR of **8** (Figure 2) consists of four resonances assignable as follows: PMe (d, 3 H, δ 1.60, J_{PCH} = 11.3 Hz), BMe (d, 6 H, δ 0.63, J_{PNBCH} = 1.2 Hz), BNSiMe$_3$ (d, 9 H, δ 0.31, J_{PNSiCH} = 1.2 Hz), and N(SiMe$_3$)$_2$(d, 18 H, δ 0.30, J_{PNSiCH} = 1.5 Hz). The separation between the two BMe resonances remains constant at 1.5 Hz when the spectrometer frequency is increased from 90 to 200 MHz, thus indicating the BMe doublet is due to coupling with the phosphorus. It is clear that in **8** all Me$_3$Si groups are attached to nitrogen. This fact is confirmed by the ^{13}C{^{1}H}, (Me$_4$Si) spectrum of **8** which also gives no indication of a PSiMe$_3$ moiety. PMe (d, δ 25.6, J_{PC} = 32.8 Hz), BMe (br, δ 12–20.0), N(SiMe$_3$)$_2$ (d, δ 5.64, J_{PNSiC} = 8.1 Hz), and BNSiMe$_3$(d, δ 5.34, J_{PNSiC} = 4.0 Hz). The 70-eV mass spectrum of **8** exhibits no molecular ion; the 100% peak is at *m/e* 279, which corresponds to loss of NBMe$_2$. The foregoing data indicate that the structure of **8** is

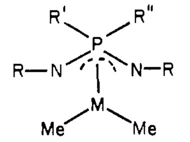


8

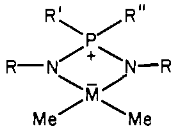
In turn, the isolation of **8** suggests that the most likely reaction pathway leading to the cyclic compounds **5**, **6**, and **9** is



Two canonical forms, **10** and **11**, can be written for the cyclic compounds **5**, **6**, and **9**.



10



11

In **10** a neutral (RN)$_2$PR'$_2$ ligand behaves in a trihapto manner toward an Me$_2$M moiety,[12] while **11** implies formation of a zwitterion via electron transfer from P to M. The ^{31}P chemical shifts of **5**, **6**, and **9** fall in the range of 30–60 observed for dialkylamino, alkyl-substituted phosphonium cations,[13] thus indicating considerable zwitterionic character. The possibility that (RN)$_2$PR'$_2$ ligands can coordinate to transition metals is under active investigation.

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[10] For example, MeP(NMe$_2$)$_2$ (+86.4),[11] EtP(NMe$_2$)$_2$ (+99.9),[11] C$_6$H$_{11}$P(NMe$_2$)$_2$ (+107.1).[11]

[11] Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van-Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 227–457 and references therein.

[12] R$_2$Al moieties are known to coordinate in a trihapto manner to cyclopentadiene and permethylcyclopentadiene rings. See: Schonberg, P. R.; Paine, R. T.; Campana, C. F. *J. Am. Chem. Soc.* **1979**, *100*, 7726–7728.

[13] For example: [Me$_2$P(NH$_2$)(NMe$_2$)]Cl (+39),[11] [MeP(NMe$_2$)$_3$]Cl (+44),[11] [(*n*-Bu)P(NMe$_2$)$_3$]Br (+62).[11]

Nature of Species Present in an Aqueous Solution of Potassium Silicate

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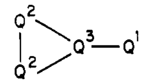
We wish to report definitive evidence for the structures of 11 species present in an aqueous solution of potassium silicate. These include five ions which involve a ring containing three siloxy units.

Aqueous silicate solutions are important in the detergent industry[1] and geochemistry[2] and have some biochemical significance.[3] Stable solutions of moderate concentration can only be achieved at high pH. Although these solutions might appear to be simple, in practice they are complex because the orthosilicate ion polymerizes in such a fashion as to yield a variety of species in dynamic equilibrium. Until recently, information about the nature of these species was obtained only indirectly, for instance, by trimethylsilylation followed by chromatographic separation.[4] ^{29}Si NMR has given promise of more direct information,[5–9] since a variety of peaks can be resolved in the spectra, but unfortunately there has been no clear way of assigning the peaks to given structures. Rapid proton exchange ensures that no (Si,H) coupling can be observed, and the natural abundance of ^{29}Si (4.7%) means that (Si,Si) coupling is also absent. Limited progress has, however, been achieved, and bands due to the monomeric orthosilicate species (Q^0), end groups (Q^1), middle groups (Q^2), and branching positions (Q^3) have been recognized.[5,6] Two further bands are the subject of dispute but have been tentatively assigned to Q^2 and Q^3 units in three-membered rings.[7] The Q designation refers to silicons bonded to four oxygen atoms, and the superscript number indicates how many of these bonds are part of siloxy bridges. Assignments of individual lines have been very sparse, only the monomer (Q^0) and dimer (Q^1Q^1) peaks being recognized definitively.[8] [The designations *n*-mer and *n*-membered ring refer to the condensed species containing *n* siloxy (SiO) groups plus the appropriate number of additional oxygen atoms. Throughout this discussion the states of protonation of the species present are ignored.] A third peak has been assigned to the cyclic trimer ($Q^2{}_3$), and Harris and Newman[7] have also tentatively assigned peaks to the linear trimer ($Q^1Q^2Q^1$), the linear tetramer ($Q^1Q^2Q^2Q^1$), and a substituted cyclic trimer (I). Recently, we have begun



I

studies by using material enriched in ^{29}Si and have obtained some information from splitting patterns.[8] In particular, five peaks were found to be unsplit, including those assigned as Q^0, $Q^1{}_2$, and $Q^2{}_3$. Moreover, splitting evidence tended to confirm the existence of I but fell short of clear proof. Since the chemical likelihood of

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[1] Barby, D.; Griffiths, T.; Jaques, A.; Pawson, D. "Soluble Silicates and Their Derivatives" In "The Modern Inorganic Chemicals Industry", Thompson, R., Ed.; Chemical Society: London, 1977.

[2] Vail, J. G.; Wills, J. H. *ACS Monogr.* **1952**, No. **116**.

[3] Birchall, J. *New Trends Bio-Inorganic Chem.* **1978**, 209.

[4] (a) Dent-Glasser, L. S.; Lachowski, E. E. *J. Chem. Soc., Dalton Trans.* **1980**, 393–398. (b) Dent-Glasser, L. S.; Lachowski, E. E.; Cameron, G. G., *J. Appl. Chem. Biotechnol.* **1977**, *27*, 39–47.

[5] Engelhardt, G.; Jancke, H.; Hoebbel, D.; Wieker, W. *Z. Chem.* **1974**, *14*, 109–110.

[6] Marsmann, H. C. *Z. Naturforsch. B* **1974**, *29B*, 495–499.

[7] Harris, R. K.; Newman, R. H. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1204–1215.

[8] Harris, R. K.; Jones, J.; Knight, C. T. G.; Pawson, D. *J. Mol. Struct.* **1980**, *69*, 95–103.

[9] Engelhardt, G.; Zeigan, D.; Jancke, H.; Hoebbel, D.; Wieker, W. *Z. Anorg. Allg. Chem.* **1975**, *418*, 17–28.

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Table I. ^{29}Si NMR Chemical Shifts of Silicate Species[a]

system	Q^1Q^1	$Q^2{}_3{}^c$	$Q^2{}_4$	$Q^3{}_6{}^c$	$Q^3{}_8$
Δδ	−8.620	−10.186	−16.096	−17.210	−25.580

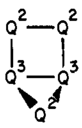
system	I	I	I	II	II	II
group	Q^1	$Q^{2\,c}$	$Q^{3\,c}$	Q^2	$Q^{2\,c}$	$Q^{3\,c}$
Δδ[b]	−8.072	−9.870	−18.234	−16.355	−9.863	−17.160

system	III[d]	III[d]	III[d]	III[d]	V	V	VI	VI
group	Q^2	Q^3	$Q^{3\,c}$ (M)	$Q^{3\,c}$ (X)	Q^2	Q^3	Q^2	Q^3
Δδ[b]	−16.048	−24.714	−17.436	−16.650	−14.222	−21.938	−14.511	−21.004

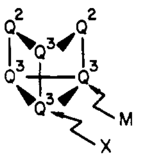
[a] Present in the aqueous solution described in the text. [b] Δδ is the shift from the resonance of the monomer Q^0, by using the high-frequency-positive convention. The monomer resonance is at δ −71 from TMS. [c] In a three-membered ring. [d] For the labeling M and X, see the molecular structure III.

systems involving three-membered rings has been questioned, this situation is unsatisfactory.

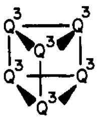
The difficulties in the way of more definitive work have been (a) the complexity of spectra, which show that many species are present over a wide range of pH and concentration, (b) the low S/N and poor dispersion provided by first-generation Fourier transform NMR spectrometers, and (c) the lack of evidence linking peaks due to the same species. We have, therefore, decided to make use of two further techniques which are well-known in other areas of NMR but have not, to our knowledge, been hitherto employed for ^{29}Si, in addition to the concept of ^{29}Si enrichment. These techniques are (a) use of a very high-field spectrometer system (operating at ca. 100 MHz for ^{29}Si) and (b) (^{29}Si,^{29}Si) homonuclear decoupling. Splitting patterns have provided essential additional evidence for particular species, and we have been able to definitively confirm the existence of I, which shows a first-order AMX_2 pattern for the per ^{29}Si isotopomer. This assignment also allows us to be reasonably certain of the existence of the cyclic trimer. Spectral analysis and homonuclear decoupling also show the existence of two other species involving the three-membered ring, viz., II and III, which give $(AM)_2X$ and $(AM)_2RX$ spin systems, respectively. Moreover, the chemical shifts of the latter make it reasonably certain that one of the unsplit peaks (the singlet Y mentioned in our previous work)[8] is due to the cage structure IV (double three-membered ring $Q^3{}_6$).



II

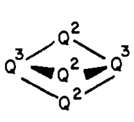


III

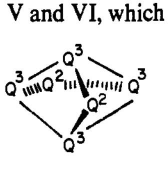


IV

It proved to be possible to recognize and assign the splitting patterns due to two further species, V and VI, which have not been postulated previously. The former gives a first-order A_3X_2 pattern and the latter forms an $(AX_2)_2$ spin system. The spectra of V and VI are illustrated in Figure 1. These two species give chemical shifts clear of the previously recognized bands. The Q^2 groups of V are responsible for the triplet (designated W) observed[8] in our earlier study with ^{29}Si-enriched material.



V



VI

Two further possible assignments may be made. The singlet X observed in our earlier work[8] is probably the cyclic tetramer $Q^2{}_4$. Finally, a sixth singlet, seen for the first time in the present work, may be tentatively assigned to the "cubic" cage compound (i.e., double four-membered ring), $Q^3{}_8$, on the grounds that it has been previously postulated to exist in solution[9] (the corresponding trimethylsilylated species certainly does),[10] the chemical shift is reasonable, and there are few other remaining structures that could be responsible for a singlet for the ^{29}Si-enriched situation.

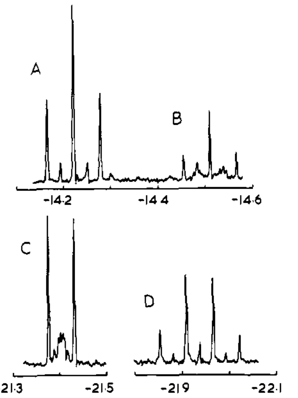
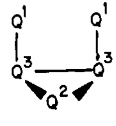


Figure 1. ^{29}Si NMR spectra of the silicate species V and VI (see the text) fully enriched in ^{29}Si. (A) Q^2 units of V, (B) Q^2 units of VI, (C) Q^3 units of VI, and (D) Q^3 units of V. The small peaks in A and D are due to species with one ^{28}Si replacing ^{29}Si. The frequency scale is in ppm with respect to the peak for Q^0.

Thus we have evidence for 11 separate species; our confidence in the structures range from ca. 70% to 100%. Apart from the monomer and dimer, these involve cyclic or cage compounds. Five species include three-membered rings, which therefore (contrary to expectation) must be particularly stable under the high pH conditions used. The remaining three species (as well as II, III, and IV) involve four-membered rings. The structures V and VI are clearly related. It is of interest that no species VII could be detected—presumably cyclization of the cis isomer to II occurs readily.



VII

All this work has been carried out for a particular solution of KOH/SiO_2 which was 0.65 M in Si, with a ratio K:Si = 1:1. The solution was prepared by dissolving SiO_2, enriched to the 95.3% level and obtained from the Electromagnetic Separation Group, A.E.R.E., Harwell, in a medium consisting of KOH, H_2O, and D_2O. The spectrum shows a number of additional peaks for which assignment is not yet possible. The chemical shifts for the assigned species are given in Table I. The spectral analysis has assumed that only two-bond (Si,Si) coupling constants are large enough to be resolved. The way is now open for exploiting the techniques described here by the study of solutions with a variety of pH's and concentrations. We shall report fully on such work later.

The spectra were obtained at 298 K by using a Bruker WM-500 spectrometer with a 10-mm multinuclear probe head, operating at 99.36 MHz for ^{29}Si. Homonuclear decoupling was achieved by gating a synthesizer frequency source (which can be set in 1-Hz steps) synchronously with the A–D converter dwell clock, amplifying it to ca. 2 W, and coupling it to the observe coil of the probehead via a directional coupler with ca. 25 dB loss at 99 MHz.

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(10) Dent-Glasser, L. S.; Harris, R. K.; Jones, J.; Lachowski, E. E. *J. Mol. Struct.* **1979**, *51*, 239–245.