

Silicon-29 2D NMR Evidence of Four Novel Doubly Germanium Substituted Silicate Cages in a Tetramethylammonium Germanosilicate Solution[†]

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Abstract: We have identified four novel, doubly germanium substituted silicate cages in an aqueous tetramethylammonium germanosilicate solution by means of high-field silicon-29 NMR spectroscopy, in conjunction with ²⁹Si isotopic enrichment. Three of the species are derivatives of the double four-membered silicate ring (cubic octameric cage) in which two silicon sites have been replaced by germanium, notably including the species in which two adjacent silicon sites have been replaced. Although all three anions may co-exist in solution, their relative concentrations indicate that germanium incorporation is site-selective, favoring maximum separation between germanate tetrahedra. The fourth germanosilicate species detected is a doubly germanium substituted double three-membered ring (prismatic hexameric cage). In this case we find no evidence of structures in which two adjacent silicon sites are replaced, perhaps because such cages are too strained. Two-dimensional ²⁹Si NMR homonuclear correlated spectroscopy (2D COSY) is used to determine the connectivities within the cages, and the results are supported by means of computer simulations.

Aqueous tetramethylammonium silicate solutions are receiving increasing attention, due in part to their role in zeolite synthesis,¹ and in part to their unique ability to provide a concentrated silicate solution, containing, under appropriate conditions, a mixture of two silicate cages,²⁻⁴ the cubic octamer (or double four-membered ring, [Si₈O₂₀]⁸⁻) and the prismatic hexamer (or double three-membered ring, [Si₆O₁₅]⁶⁻). (The terms “*n*-mer” and “*n*-membered” refer to the condensed species containing *n* SiO groups, together with the appropriate number of additional oxygen atoms. The extent of protonation of the species is ignored.) The relative concentration of these species is a function of the time elapsed after heating the sample to boiling. The cubic octamer is the more thermodynamically stable of the two, and after several weeks at room temperature, tetramethylammonium silicate solutions attain equilibrium, at which point only the cubic octamer and the monomer remain in solution.⁴ Such solutions form good model systems for studying many aspects of the solution chemistry of silica, from the weathering of minerals to the structures of zeolite precursors. We have recently shown⁵ that germanosilicate cages may be readily synthesized by the addition of GeO₂ to a hot tetramethylammonium silicate solution. Using high-field (11.7 T) ²⁹Si nuclear magnetic resonance spectroscopy and samples prepared with silica isotopically enriched in the magnetically active silicon-29 nucleus, we confirmed the presence of two symmetric silicate cages in solution, the cubic octamer and the prismatic hexamer, and demonstrated the simultaneous existence of their singly substituted germanium analogues, in which a single silicon site is replaced by germanium.

We now report evidence of germanosilicate cages in which two silicon sites are occupied by germanium. In the case of the cubic octamer, ²⁹Si NMR spectroscopy of isotopically enriched solutions provides evidence of all three possible doubly germanium substituted germanosilicate cages, present in approximately equal concentrations. Similarly, we provide evidence for the presence of one of the three possible doubly germanium substituted prismatic hexameric cages. In both cases, the observations are supported by connectivity data supplied by two-dimensional (2D) homonuclear correlated ²⁹Si NMR spectroscopy⁶ (COSY) and confirmed by first- and second-order spectral analysis. The observation of the co-existence of all three doubly germanium substituted cubic octameric cages is of particular interest, since

it implies the existence of stable anions containing a Ge-O-Ge linkage. This provides hints about isomorphous substituent ordering in zeolitic frameworks, a subject of some considerable debate.^{7,8} We note, however, a slight site selectivity for germanium substitution, with the species containing the Ge-O-Ge linkage being somewhat less stable than the two other doubly substituted cages.

Experimental Section

All samples were prepared and stored as described previously.⁵ NMR spectra were obtained at 99.3 MHz on a “homebuilt” 11.7 T NMR spectrometer, described in detail elsewhere.⁵ Individual spectral parameters are given in the appropriate figure captions.

Results

We show in Figure 1 the 99.3-MHz ²⁹Si NMR spectrum of a freshly prepared tetramethylammonium germanosilicate solution, 1 M in SiO₂, 0.25 M in GeO₂, and with an N:Si ratio of 2:1, prepared with silica isotopically enriched in ²⁹Si to the 95.28% level. Under such conditions, ²J_{Si-O-Si} spin-spin coupling ensures that all resonances from molecules containing more than one silicon site appear as spin-multiplets. Conversely, silicate species which contain only a single silicon chemical site, such as the symmetric silicate cages, give rise to a single resonance peak. It is clear that at least two of the peaks in Figure 1 are singlets and may be readily assigned to the prismatic hexamer and to the cubic octamer by comparison with previous work.^{5,9} In silicate cages in which a single silicon site is replaced by germanium, the chemical shift degeneracy of the remaining sites is lifted, giving rise to a series of characteristic spin multiplets in the ²⁹Si NMR spectra of isotopically enriched germanosilicate solutions. Thus the resonances of both the single germanium substituted analogues of the prismatic hexameric and of the cubic octameric cages appear on either side of the signals of the parent anions.⁵ The remaining sharp peaks arise from species in which two silicon sites have been

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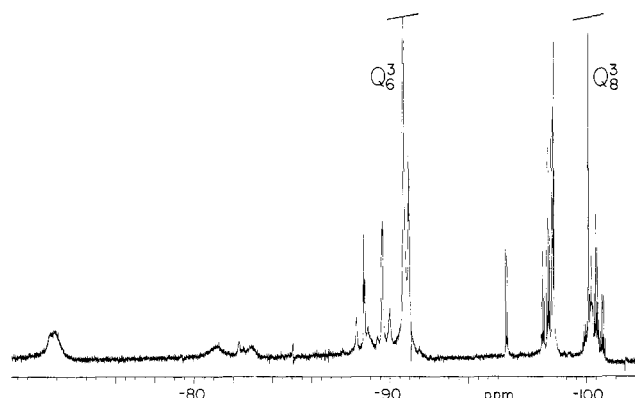


Figure 1. The 99.3-MHz (11.7 T) ²⁹Si NMR spectrum of a freshly prepared tetramethylammonium germanosilicate solution, 1 M in ²⁹SiO₂, 0.25 M in GeO₂, and 2 M in tetramethylammonium hydroxide, at 22 °C. Approximately 20% (v/v) CD₃OD was added to provide a field lock signal. The signals of the prismatic hexamer, Q₆³, and the cubic octamer, Q₈³, have been truncated at ca. 5% and ca. 40% of their total intensity, respectively. The spectrum was recorded with use of a sweep width of 4000 Hz and 600 10-μs (50°) pulse with an interpulse delay of 20 s. 32K points were acquired, giving an acquisition time of 4.1 s. An exponential line-broadening function of 0.3 Hz was applied. The chemical shift scale is referenced to an external sample of Me₄Si (50% (v/v) in acetone-*d*₆), signals resonating to low frequency of this being denoted negative.

Table I. Silicon-29 Isotropic Chemical Shifts and Coupling Constants for Doubly Germanium Substituted Cubic Octameric and Prismatic Hexameric Cages^a

species		chemical shift (ppm) ^b δ _i	coupling constant (Hz) ² J
II	A	-98.37 ₆	—
III	A	-95.94 ₂	7.42
	M	-97.79 ₉	7.42
	X	-100.85 ₃	7.42
IV	A	-98.29 ₉	7.27
	X	-100.28 ₁	7.27
VI	A	-88.28 ₁	—
	X	-88.99 ₇	—

^aData from a freshly prepared tetramethylammonium germanosilicate solution at 22 °C, prepared with silica enriched to 95.28% in ²⁹Si, nominally 1 M in ²⁹SiO₂, 0.25M in GeO₂, and 2 M in tetramethylammonium hydroxide. The solution contained ca. 20% (v/v) CD₃OD. ^bIn parts per million relative to an external standard of tetramethylsilane, adopting the "high frequency positive" convention.

replaced by germanium, and their assignment is treated in detail below. The chemical shifts and coupling constants of the species concerned are listed in Table I.

Several broad signals appear to high frequency. These lie in the spectral region normally associated with signals from the monomer (Q⁰), dimer (Q₂¹), various Q¹ end-groups, the cyclic trimer (Q₃²), and substituted cyclic trimeric species.⁹ Their unusual line widths must arise from the presence of the germanium, but it is not clear whether it is the result of a kinetic effect, such as chemical exchange, or whether it arises from a distribution of chemical sites. Investigations in this direction are in progress.

Species Based on the Cubic Octameric Structure. Figure 2A shows an expanded scale plot of the spectrum shown in Figure 1, in the region of the resonance signal of the cubic octamer. Three multiplets arise from the three chemically distinct silicon sites of the singly germanium substituted cubic octamer, structure I (the oxygen atoms have been omitted from the diagram). They are

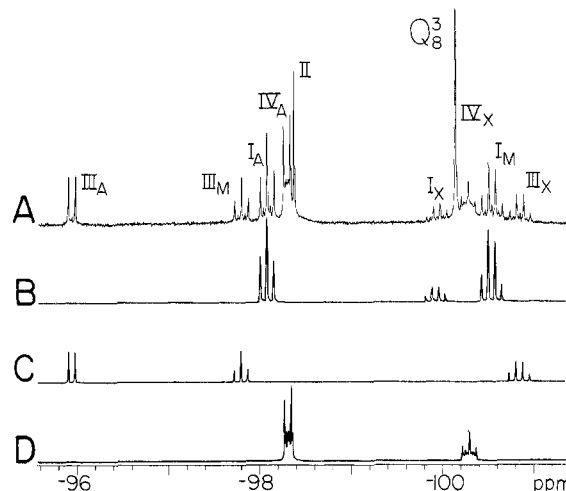
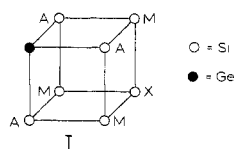
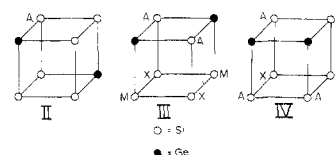


Figure 2. (A) Expansion of the 99.3-MHz ²⁹Si NMR spectrum shown in Figure 1, in the region characteristic of signals from germanium substituted cubic octameric cages. (B-D) Simulations of the ²⁹Si NMR spectra of species II-IV, respectively, performed on the data given in Table I using the Nicolet NMRSIM routine.

helpful in assigning spectral regions to characteristic silicate groups. Three regions are apparent, those characteristic of silicate tetrahedra with a germanate tetrahedron as (1) the first nearest neighbor, ≡Ge—O—Si≡ (multiplet A), (2) the second nearest neighbor, ≡Ge—O—Si—O—Si≡ (multiplet M), and (3) the third nearest neighbor, ≡Ge—O—Si—O—Si—O—Si≡ (multiplet X). For clarity, the computer simulated spectrum of structure I is shown in Figure 2B. These chemical shift ranges provide the groundwork for assigning signals from the three possible doubly germanium substituted silicate cages, structures II-IV.



In structure II, in which the germanate tetrahedra occupy sites at diagonally opposed apices of the cube, the six silicon sites are chemically equivalent and will consequently yield a single resonance signal, even for the fully isotopically enriched case. This is expected in the spectral region around multiplet A of structure I, since the silicate tetrahedra all have a germanate tetrahedron as first nearest neighbor, and we assign the singlet at δ = -98.38 ppm to structure II.

Three chemically distinct silicon sites exist in structure III, in which the germanate tetrahedra lie diagonally across a face of the cube. For an enrichment of 100% in silicon-29, structure III represents an [AX]₂M₂ spin system. Assuming four-bond spin-spin coupling (⁴J_{Si-O-Si-O-Si}) to be negligible, first-order spectral analysis predicts a doublet in the A region, a triplet in the M region, and either a quartet (if J_{AX} = J_{MX}) or a doublet of triplets (if J_{AX} ≠ J_{MX}) in the X region. The A resonance is expected to lie appreciably to high frequency of the spectral region characteristic of silicate tetrahedra having a germanate tetrahedron as nearest neighbor, since here it is has two germanate groups as neighbors, and consequently we assign the high frequency doublet to site A, the triplet at δ = -97.80 ppm to site M (its chemical shift is consistent with a silicate tetrahedron having a single germanium tetrahedron as nearest neighbor), and the low frequency quartet to site X (it falls in the spectral region ascribed to silicate tetrahedra having a germanate tetrahedron as second nearest neighbor). The observation of a quartet for site X implies that J_{AX} = J_{XM} in this structure, indicating that incorporation of germanium into the cage has no effect on the coupling constants (as is the case for structure I), presumably because the cage geometry is unaffected. In Figure 2C we show the computer

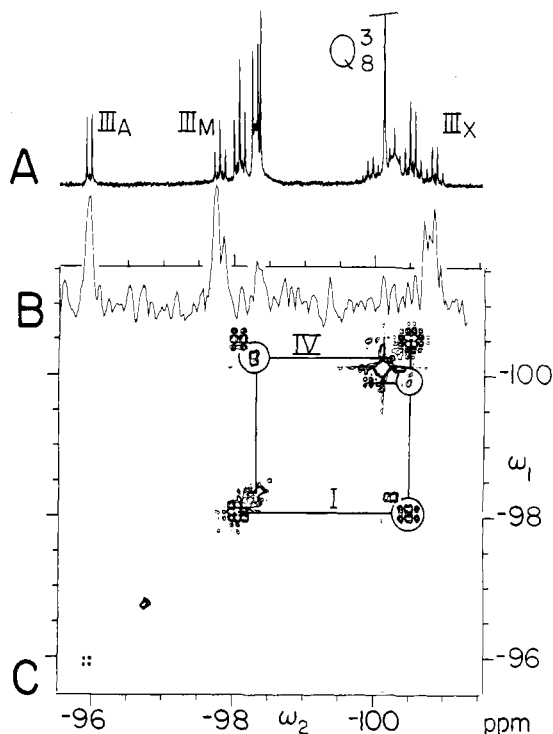


Figure 3. 99.3-MHz ^{29}Si NMR spectra of a freshly prepared tetramethylammonium germanosilicate solution, 1 M in $^{29}\text{SiO}_2$, 0.25 M in GeO_2 , and 2 M in tetramethylammonium hydroxide, at 22 $^\circ\text{C}$. Spectrum A is that shown in Figure 2A. Spectrum B is the sum of 4 cross sections in the f_2 dimension through a ^{29}Si NMR 2D homonuclear correlation (COSY) experiment at the frequency of the multiplet ascribed to site X of species III, and it indicates that the multiplets assigned to sites A and M of species III are both connected to site X, consistent with the proposed structure. The COSY experiment that generated these cross sections used four-step phase cycling and n -type peak selection. The spectral width in each dimension was 600 Hz, obtained from 256 t_1 points, using 36 transients for each point and a recycle time of 4 s. Part C shows the results of a similar 2D ^{29}Si NMR homonuclear correlation experiment on the same solution, in the form of a contour plot. Cross peaks between the signals of the two sites of structure IV are clearly visible, as are those of structure I, as noted elsewhere.⁵ The spectral conditions were as those for Figure 3B, except that 1K t_1 points were used, with 20 transients for each point and a recycle delay of 5 s. The diagonal peak at ca. -96.7 ppm results from the folded signal of the prismatic hexamer.

simulation of the ^{29}Si NMR spectrum of structure III.

The two remaining multiplets in Figure 2A are ascribed to the two silicon sites of structure IV, a cube in which two neighboring silicon sites have been replaced by germanium. This is an example of an $[\text{AX}]_2$ spin system, with the signal from the A sites expected in the spectral region characteristic of a silicate tetrahedron with a germanate tetrahedron as first nearest neighbor and the signal from the X sites expected in the region ascribed to silicate tetrahedra having a germanate tetrahedron as second nearest neighbor. In this case a second-order splitting pattern is expected, due to the finite coupling between the chemically equivalent A sites. Similarly, both X sites are coupled but are chemically equivalent. Figure 2D shows that the computer simulation of structure IV is in good agreement with the observed ^{29}Si NMR spectrum.

The assignments for both structures III and IV may be confirmed by observing the connectivities within each anion, determined with the help of a two-dimensional ^{29}Si NMR homonuclear correlation experiment. We show the results of this in Figure 3. Strong cross peaks appear between both multiplets of structure IV (Figure 3C), leaving no doubt that they arise from sites within the same molecule. Although not as obvious in the contour plot, cross peaks can be discerned for the three multiplets of structure III and indicate that site X is connected to both sites A and M, which in turn are not mutually coupled. Figure 3B illustrates this connectivity. The spectrum shown is the sum of four spectral cross

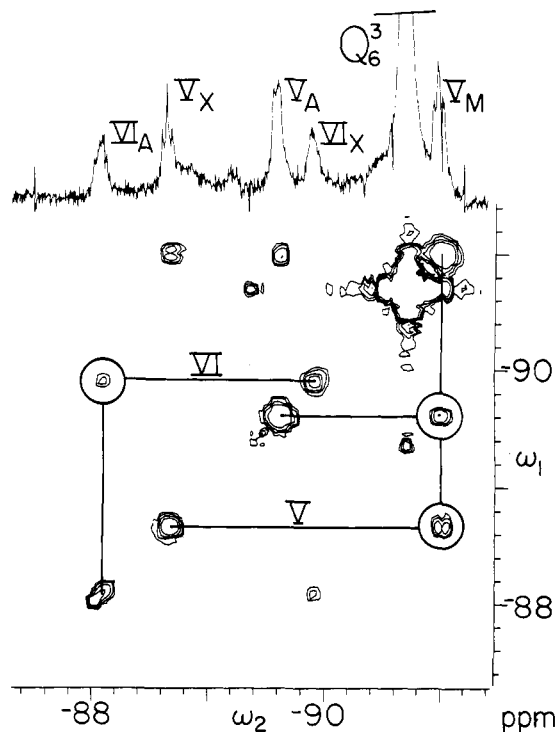
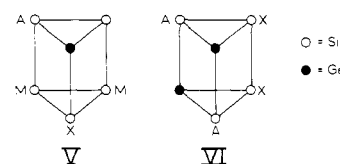


Figure 4. The 99.3-MHz ^{29}Si NMR spectrum of the sample described in the caption of Figure 1, in the region characteristic of the signals of the prismatic hexamer and related structures. The 1D spectrum was recorded with a sweep-width of 4000 Hz and 16K data points. 81 18- μs (90°) pulses were used, with an interpulse delay of 9 s. An exponential weighting function of 0.1 Hz has been applied. The 2D COSY spectrum was performed with four-step phase cycling and n -type peak selection. The spectral width in each dimension was 400 Hz, obtained from 512 t_1 points, using 4 transients per point and a recycle time of 9 s. The cross peaks coincident with the center of the spectrum are thought to be artifacts.

sections in the f_2 dimension, at the frequency of the quartet assigned to site X. If structure III is correct, then site X is coupled to both site A and site M, giving rise to signals at the resonance frequency of these sites in the 2D COSY spectral cross sections. Although the signal-to-noise ratio is low, it is clear that signals occur at the frequency of the multiplets ascribed to both site A and site M. Similarly (although not shown in the figure), spectral cross sections taken at the frequency of the multiplet ascribed to site A show a signal corresponding to the multiplet assigned to site X, as do those associated with the multiplet assigned to site M, supporting the assignment.

Species Based Upon the Prismatic Hexamer. In Figure 4A we show the region of the ^{29}Si NMR spectrum characteristic of the signals of the prismatic hexameric cage, labeled as such, and the three multiplets arising from its singly germanium substituted derivative, structure V, as noted in our previous report.⁵ Two other major signals are observed, and we tentatively attribute them to the two inequivalent silicon sites of structure VI, a doubly germanium substituted prismatic hexameric cage. This provides an



example of an $[\text{AX}]_2$ spin system, giving two second-order multiplets in the ^{29}Si NMR spectrum. We have shown⁵ that four-bond spin-spin coupling cannot be neglected in these substituted prismatic hexameric cages. However, the poor resolution and signal to noise of the experimental spectrum precludes the observation of any coupling constants for structure VI and prevents a definitive structural assignment. Nevertheless, as with the species

based upon the cubic octameric cage, these assignments are consistent with the results of a two-dimensional ²⁹Si NMR homonuclear correlated (COSY) experiment on this region of the spectrum. The resulting spectrum is shown in Figure 4 and is entirely consistent with the postulated structures of both the singly and doubly germanium substituted prismatic hexameric cages. Thus both A and X sites of structure VI are connected to each other alone, and site M of structure V is connected to both sites A and X, which are not mutually coupled.

Discussion

The simultaneous presence of all three possible doubly substituted cubic octameric species in solution is interesting for several reasons. First, it implies that two adjacent silicon sites may be replaced by germanium, giving a stable $\equiv\text{Ge}-\text{O}-\text{Ge}\equiv$ linkage. This is in marked contrast to the situation with aluminum(III) distribution in zeolitic frameworks (Lowenstein's rule¹⁰) and attests to the remarkable isomorphism of germanates with silicates.¹¹ Nevertheless, our spectra do show that germanium distribution in the silicate cages is not completely random, and a clear site preference exists for germanium substitution. In the case of a totally random germanium substitution (no site preference), a statistical distribution of 1:3:3 is expected for structures II, III, and IV, respectively. Our spectra were obtained with use of an equilibrium recycle time value¹² and yield experimental ratios of 1:2.1:1.9. Germanium substitution must therefore be site selective, with the most favored structures being those in which the germanium separation is maximized.

It should be noted here, however, that all the NMR experiments reported in this work were performed on freshly prepared germanosilicate solutions. Unlike alkali-metal silicate solutions, the anions present in such tetramethylammonium silicate and germanosilicate solutions do not reach dynamic equilibrium rapidly, and the species described in this work are long-lived intermediates undergoing slow rearrangement, their relative concentrations being governed by several simultaneous kinetic pathways. All the silicate

and germano silicate anions, with the exception of the monomer, are ultimately unstable with respect to the cubic octameric cage.⁴ This gives a complex overall time-dependent anion distribution prior to thermodynamic equilibrium, which is reached only after several weeks at room temperature. However, the anion rearrangement is sufficiently slow to allow NMR experiments to be performed without a significant change occurring in the anion distribution during the course of the experiment. Moreover, the situation appears to be reversible, since heating a solution at equilibrium to boiling breaks up the cubic octamer, regenerating the smaller silicate oligomers as well as the singly and doubly substituted germanosilicate cages. Indeed, both the latter are only produced when germanosilicate solutions are held at or near their boiling point; adding GeO₂ to a cold tetramethylammonium silicate solution does not result in the formation of germanosilicate cages.

We should also note that solid-state ²⁹Si "magic-angle" sample spinning (MASS) NMR experiments performed on crystals taken from aged tetramethylammonium germanosilicate solutions yield only a single resonance at $\delta = -99.9$ ppm, indicating that germanium is not incorporated into the crystal lattice, which is comprised of the unsubstituted cubic octameric cage. A similar situation has been noted elsewhere¹³ for tetramethylammonium aluminosilicate solutions. It thus appears that all germanosilicate cages are ultimately unstable with respect to the unsubstituted species, and their formation requires an activation energy, brought about by heating the sample to boiling, after which point they slowly depolymerize, via singly substituted species, to yield the parent cages.

Finally, it is interesting to note in this context that we see no evidence of any triply substituted species, and in the case of the prismatic hexameric cage, there is no evidence for either of the two possible structures in which two adjacent silicon sites are replaced. This is perhaps not surprising in view of the stability of the cubic octamer over the prismatic hexamer in tetramethylammonium silicate solutions, and indeed the ratio of substituted to unsubstituted structures is always smaller for the prismatic hexamer than it is for the cubic octamer.

Registry No. II, 106569-58-8; III, 106569-59-9; IV, 106569-60-2; VI, 106569-61-3; Si, 7440-21-3.

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