Two-Dimensional Silicon-29/Tin-117 NMR Evidence of Aqueous Stannosilicate Anions

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We report the first definitive evidence for the existence of stannosilicate anions in aqueous solution. Three singly Sn-substituted derivatives of silicate anions have so far been determined by two-dimensional heterocorrelated $^{29}Si-^{117}Sn$ NMR spectroscopy. They are the dimer $(HO)_3SiOSn(OH)_5^{2-}$, the symmetric acyclic trimer $(HO)_3SiOSn(OH)_4OSi(OH)_3^{2-}$, and the cyclic trimer $\overline{\mathrm{OSi(OH)_2OSn(OH)_4OSi}}\mathrm{(OH)_2}^{2-}$.[1] In each case, the tin is coordinated octahedrally. These are the least labile heterosubstituted silicate anions reported to date.

It has long been appreciated that the tetrahedral framework silicon sites in zeolites and other crystalline silicates may be replaced by a wide variety of elements.[2] More recently, NMR spectroscopy has demonstrated that the aqueous solutions from which zeolites are grown contain a complex equilibrium mixture of oligomeric silicate anions.[3−5] These too may undergo isomorphic replacement of Si, with germano-,[6] alumino-,[7−9] boro-,[8] and gallosilicate[10] species having been reported thus far. Knowledge of the structure of dissolved anions is held to be vital to understanding mechanisms of zeolite synthesis.[11,12] At the very least, knowledge of the thermodynamics and kinetics of silicate anion interactions in the bulk solution should provide a clearer picture of the analogous molecular events associated with zeolite nucleation and growth. Two distinct classes of aqueous, metal-substituted silicate species have so far been proposed:[6−10] (a) relatively long-lived, cubic octameric and prismatic hexameric cage structures that occur in solutions containing quaternary ammonium ions; (b) highly labile anions that are noted under much wider-ranging solution conditions. The former species, because of their kinetic stability, yield sharp ^{29}Si resonances and, therefore, have been unambiguously characterized using standard NMR techniques.[6,9] Structural identification of the latter species has proved more elusive, with tentative assignments based exclusively on ^{29}Si chemical shift grounds.[7−10] This is because the ^{29}Si signals are significantly broadened, sometimes to the extent that they are virtually invisible (for example, with boro- and germanosilicates), obscuring any scalar coupling and often resulting in spectral overlap. Kinrade and Swaddle[7] have shown that for aluminosilicates this broadening is predominantly a kinetic effect, the lifetimes of the Al-substituted species being 2−3 orders of magnitude less than those of their unsubstituted counterparts. Indeed, since ^{29}Si NMR signals from long-lived Ge-substituted cages are as sharp as those from unsubstituted species,[6] the broadening is not due to interaction with the nuclear quadrupole moment of the heteroatom substituent. To date, NMR observation of the heteroatom nuclei has been of little help toward making structural assignments since the quadrupolar moment of the metals investigated obscures any potential structural information.[6−10] We have sought to illuminate the situation by substituting a spin-$^1/_2$ nucleus into silicon sites, thereby providing a probe amenable to NMR structural analysis, and to this end we have succeeded in preparing a series of stannosilicate solutions.

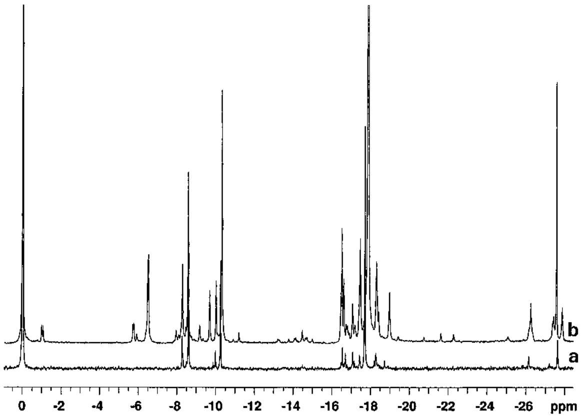

Figure 1. Vertically expanded ^{29}Si spectra (99.36 MHz) at 264 K of solutions containing (a) 0.8 mol kg^{-1} SiO_2 and 1.6 mol kg^{-1} TMAOH and (b) 0.6 mol kg^{-1} SiO_2 (22.5 atom % ^{29}Si), 0.2 mol kg^{-1} Sn (92.8 atom % ^{117}Sn), 2.4 mol kg^{-1} TMAOH, and 0.8 mol kg^{-1} HCl. The spectra are normalized to give equal areas of the orthosilicate resonance (0 ppm) and include 0.6 Hz artificial line broadening. They were generated with 1000 $\pi/2$ pulses of 20 μs with a 22 s repetition time.

Alkali-metal cations, we discovered, significantly lower stannosilicate solubility and therefore had to be either chelated (with cryptand or crown-ether macrocycles)[13] or replaced altogether with quaternary ammonium ions. Tetramethylammonium (TMA) stannosilicate solutions, for instance, were prepared by combining aliquots of aqueous TMA stannate and TMA silicate. Stock stannate solutions were made by adding either $SnCl_4 \cdot 5H_2O$, or ^{117}Sn metal (92.8 atom %, Isotec) dissolved in HCl to aqueous TMAOH; silicate solutions were made by dissolving amorphous SiO_2 (or $^{29}SiO_2$; 67.3 atom %, Isotec) in TMAOH. Homogeneous stannosilicate mixtures were heated to boiling and, owing to the slow evolution of TMA silicate equilibria,[6] were left standing at least 2 weeks at room temperature to ensure complete equilibration.

In Figure 1 we show the ^{29}Si NMR spectra of otherwise similar tetramethylammonium silicate solutions, with and without the addition of tin. The ^{117}Sn spectrum of the TMA

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(1) Aqueous silicate anions are deprotonated to varying degrees depending on solution pH. For convenience, the degree of protonation is not considered here.

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Table 1. NMR Assignments for the Principal Stannosilicate Anions in a Solution at 264 K with 0.60 mol kg^{-1} SiO_2 (22.5 atom % ^{29}Si), 0.20 mol kg^{-1} Sn (92.8 atom % ^{117}Sn), 2.45 mol kg^{-1} TMAOH, and 0.79 mol kg^{-1} HCl

δ (^{29}Si)^{a,b}/ppm	δ (^{117}Sn)^{b,c}/ppm	^2J ($^{29}Si-O-^{117}Sn$)^d/Hz	Sn-substituted species^e	concn/mol kg^{-1}
−1.08 (1.0)	−610.7 (1.0)	7.4	dimer $(HO)_3SiOSn(OH)_5^{2-}$	0.012
−5.75 (1.0)	−636.5 (0.52)	5.0	acyclic trimer $(HO)_3SiOSn(OH)_4OSi(OH)_3^{2-}$	0.006
−6.47 (4.8)	−625.9 (2.4)	4.6	cyclic trimer $\overline{OSi(OH)_2OSn(OH)_4OSi(OH)_2}^{2-}$	0.027

[a] ^{29}Si resonances are internally referenced (±0.01 ppm) to the orthosilicate monomer peak which resonantes −73 ppm from tetramethylsilane; $^{29}Si-^{117}Sn$ spin coupling splits each signal into a doublet. [b] Integrated peak areas relative to the highest frequency stannosilicate resonance are given in parentheses. [c] ^{117}Sn resonances are externally referenced (±0.1 ppm) to $Sn(CH_3)_4$; $^{29}Si-^{117}Sn$ spin coupling yields doublet (−610.7 ppm) and triplet (−636.5 and −625.9 ppm) line splitting. [d] Uncertainty is ±0.3 Hz. [e] See ref 1.

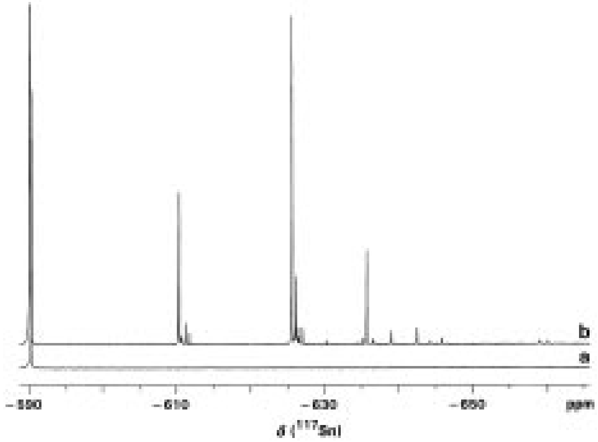

Figure 2. ^{117}Sn spectra (178.2 MHz) at 264 K: (a) a solution containing 0.38 mol kg^{-1} (92.8 atom % ^{117}Sn), 1.51 mol kg^{-1} HCl, and 3.21 mol kg^{-1} TMAOH; (b) the TMA stannosilicate solution described for Figure 1b. The spectra were obtained using *ca*. 3000 $\pi/2$ pulses of 12 μs with a repetition time of 1.8 s and include 2 Hz artificial line broadening.

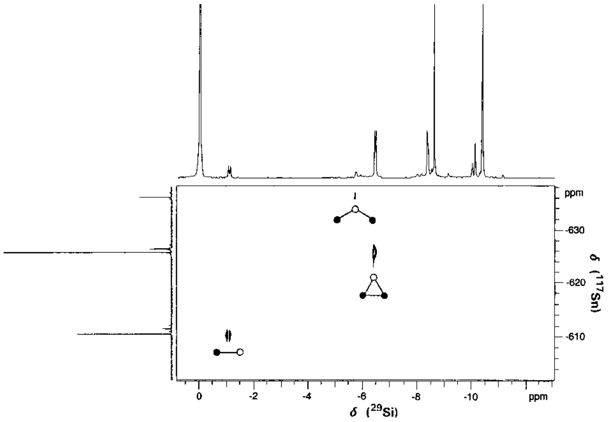

Figure 3. Expanded $^{29}Si-^{117}Sn$ NMR 2D correlation spectrum at 280 K of the stannosilicate solution described for Figure 1b. The assigned stannosilicate structures are shown with filled circles representing tetrahedral silicate centers, solid circles representing octahedral stannate centers, and lines representing the shared oxygen linkages.

stannate/silicate solution is shown in Figure 2, along with that of the parent stannate solution. The latter spectrum contains one principal resonance at −590.8 ppm (from the external reference $Sn(CH_3)_4$) that has been previously assigned[14] to the six-coordinate monomer, $Sn(OH)_6^{2-}$, on the basis of chemical shift along with the anion's Raman spectrum. For the stannate/silicate solution, the appearance of new peaks in both the ^{29}Si and ^{117}Sn spectra would suggest formation of discrete stannosilicate anions but falls short of definitive proof. We therefore acquired a two-dimensional $^{29}Si-^{117}Sn$ heterocorrelated NMR spectrum of the solution—isotopically enriched in both ^{29}Si and ^{117}Sn—to obtain certain evidence of connectivity. This spectrum, shown in Figure 3, represents the first reported use of silicon−tin NMR correlation spectroscopy. It contains three major cross peaks. The splitting patterns, relative intensities, and chemical shifts of the correlated ^{29}Si and ^{117}Sn resonances dictate peak assignments to the following singly Sn-substituted species: (a) silicate dimer; (b) acyclic trimer; (c) cyclic trimer (see Table 1). The major stannosilicate species in this particular solution is evidently the Sn-substituted cyclic trimer, which is consistent with observations of analogous gallosilicate solutions[10] and attests to the surprising stability of the heterosubstituted "three-ring" anion. As solution alkalinity is decreased, the number of ^{29}Si and ^{117}Sn peaks attributable to stannosilicate oligomers increases significantly. Work is underway to identify further species.

That tin occupies octahedral sites is further supported, though not entirely proven, by comparison of the ^{117}Sn chemical shifts in Table 1 with those reported for crystalline solids in which tin exhibits 6-fold coordination, *e.g.*, $Sn(OSn)_6$ (−450 to −680 ppm)[15] or $Sn(OSi)_6$ (−787 to −789 ppm)[16] coordination. Pentacoordinate and tetracoordinate tin centers resonate at substantially higher frequencies,[17] *e.g.*, −313 ppm for the square pyramidal $Sn(OSn)_5$ sites of K_2SnO_3.[15] The present data are therefore the first apparent evidence of hexacoordinated metal substitution into dissolved silicate polyanions. Remarkably, although tin is also the largest heteroatom shown to substitute into aqueous silicates, the long-term stability of stannosilicate solutions and the sharpness of the corresponding NMR peaks indicate that stannosilicates are some 2−3 orders of magnitude less labile than other metal-substituted silicate anions characterized to date. Indeed, the observation of stable, discrete stannosilicate species may well portend the synthesis of novel stannosilicate microporous materials.

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