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Charged Si₉ Clusters in Neat Solids and Solution – A Combined NMR, Raman, Mass Spectrometric, and Quantum Chemical Investigation

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Abstract

Polyanionic silicon clusters are outstanding building blocks for tailor-made silicon-based materials. Such clusters are provided by the Zintl phases K₄Si₄, comprising [Si₄]⁴⁻ units, and K₁₂Si₁₇, consisting of [Si₄]⁴⁻ and [Si₉]⁴⁻ clusters. A combination of solid-state MAS and solution NMR, Raman and electrospray ionization mass spectrometry as well as quantum-chemical investigations was used to investigate fourand nine- atomic silicon Zintl clusters in neat solids and solution. The results are compared to ²⁹Si isotope-enriched samples. ²⁹Si-MAS NMR and Raman shifts of the phase-pure solids K₄Si₄ and K₁₂Si₁₇ are interpreted by state of the art quantum chemical calculations. Extraction of [Si₉]⁴⁻ clusters from K₁₂Si₁₇ with liquid ammonia/222crypt and their transfer to pyridine yields to (K-222crypt)₂K₂Si₉ (1). Compound 1 is characterized by elemental and EDX analyses as well as by ²⁹Si-MAS NMR and Raman spectroscopy. Within these investigations charged Si₉ clusters have also been detected for the first time by ²⁹Si NMR in the solid and in solution. According to the results of comprehensive quantum-chemical calculations, the NMR spectra reveal the presence of the [H₂Si₉]²⁻ cluster anion in solution. The dependency of the characteristic ²⁹Si-¹H coupling patterns on the isotope distribution in the Si₉ clusters is discussed. Furthermore, temperature-dependent NMR measurements establish a dynamic behavior of the protonated anionic Si₉ cluster species.

As silicon is an abundant, inexpensive and nontoxic semiconducting material, research on this element is of particular interest. Silicon compounds already play an important role in daily-life products as in electronic devices, solar cells, anode materials, micro- and optoelectronics.^[1] Nowadays, the field of silicon-based applications is constantly growing and of increasing importance. Low-valent nano-scaled silicon compounds can play a key-role by providing tailor-made building blocks for the design of welldefined materials. Promising candidates are so-called siliconoids^[2], best described as neutral silicon clusters with unsaturated silicon atoms.^[2-3] Further research also brought up a [20]silafullerane with a Si₂₀-core^[4] as well as a neutral triatomic silicon(0) cluster stabilized by three cyclic (alkyl)amino carbenes.^[5] However, the synthesis of silicon cluster compounds often requires multi-step reactions^[6] which still hamper technical applications. In this context Zintl phases consisting of silicon and alkali metals, which already contain polyatomic silicon clusters, can be employed as precursors. Such siliconrich phases can be directly obtained in quantitative yield from high-temperature reactions of the respective elements.^[7] Via these reactions binary phases of the compositions A_4Si_4 (A = Li-Cs) and $A_{12}Si_{17}$ (A = K-Cs), containing either solely $[Si_4]^{4-}$ or $[Si_4]^{4-}$ beside $[Si_9]^{4-}$ clusters in a 2:1 ratio, respectively, are easily accessible (Figure 1).

For further conversions solutions of well-defined silicon clusters are of fundamental interest. However, A_4E_9 phases (E = Si-Pb) that contain exclusively nine-atomic clusters, and which are soluble in aprotic solvents, are only known for the heavier tetrel homologues Ge–Pb, but not for Si. Since the A_4Si_4 phases are rather insoluble in any solvent, the focus lies on the $A_{12}Si_{17}$ phases that are sufficiently soluble in liquid ammonia. Here, solvate crystals containing $[Si_4]^{4-}$ and $[Si_9]^{4-}$ units could be obtained^[8] and the $[Si_9]^{4-}$ cluster units can further react to $[PhZn(Si_9)]^{3-}$,^[9] $[{Ni(CO)_2}_2(Si_9)_2]^{8-}$,^[10] and $[NHC^{Dipp}Cu(Si_9)]^{3-}$.^[11] in liquid ammonia. For the $[Si_4]^{4-}$ unit only the $[(MesCu)_2(Si_4)]^{4-}$ complex could be obtained.^[12]



Figure 1. Silicon cluster polyanions as they occur in binary phases or in solvates. The given point groups are used in the computational studies, and the atom numbers refer to the calculated NMR shifts (Table 1).

However, in solutions of $A_{12}Si_{17}$ not only $[Si_4]^{4-}$ and $[Si_9]^{4-}$, but also $[Si_9]^{3-}$, $^{[13]}$ $[Si_9]^{2-}$, $^{[14]}$ and $[Si_5]^{2-}$ [^{8e, 13]} clusters have been detected. Thus, the questions a) 'which species readily appear in solution' and b) 'what are their charges' remained unclear for many years. This triggered us to investigate $K_{12}Si_{17}$ and K_4Si_4 in the solid-state as well as solutions of $K_{12}Si_{17}$ by several spectroscopic methods combined with theoretical studies^[15] (details in Supporting Information) with the prerequisite of using well-defined single-phase intermetallic compounds. Of special interest was the NMR-spectroscopic detection of a nine-atomic cluster species, since so far only ²⁹Si NMR signals for $[Si_4]^{4-}$ clusters in A_4Si_4 ^[16] solid phases and in liquid ammonia solution, ^[17] arising from a solid phase of nominal composition "Rb₆K₆Si₁₇", have been reported.

The syntheses of K₄Si₄ and K₁₂Si₁₇ (including ²⁹Si enrichment for K₁₂Si₁₇) were optimized in order to obtain single-phase materials (for details see Supporting Information) of which the high purity and crystallinity could be shown by powder X-ray diffraction.^[18] The Raman spectra of the phases (Figure 2e and 2f) reveal the characteristic vibrations indicative for the polyanionic four- and nine-atomic silicon clusters. For K₄Si₄ four specific vibrations (*measd*.: 287, 337, 364, and 481 cm⁻¹) are observed. The calculated Raman vibrations (*calcd*.: 286, 344, 366, and 483 cm⁻¹; Figure 2g) are in accordance with the measurement, and thus, underline the accuracy of the applied synthesis and characterization methods. The Raman spectrum of K₁₂Si₁₇ reveals four vibrations of which three (at 281, 354 and 482 cm⁻¹) are assigned to the [Si₄]⁴⁻ cluster, whereas the fourth signal at 390 cm⁻¹ is allocated to the [Si₉]⁴⁻ unit by comparison with literature data of $A_{12}Si_{17}$ rever not feasible due to the large unit cell, and thus, the signal is compared to the calculated spectrum of an isolated [Si₉]⁴⁻ cluster (*calcd*.: 395 cm⁻¹; Figure 2c) which is in reasonable agreement with the experiment, but differs from the results of an earlier calculation (*calcd*.: 367 cm⁻¹).^[19]



Figure 2. Measured and calculated (DFT-PBE0) Raman spectra of nine- and four-atomic silicon clusters. The vibrations of the $[Si_9]^{4-}$ cluster anions are framed.



Figure 3. ²⁹Si-MAS NMR spectra: a) K₄Si₄; b) K₁₂Si₁₇ (²⁹Si-enriched); c) (K-222crypt)₂K₂Si₉ (**1**) (²⁹Si-enriched). Chemical shift values [ppm]: -323 (1a), -346 (2a), -316 (1b), -317 (2b), -320 (3b), -322 (4b), -326 (5b), -331 (6b), -344 (7b), -319 (1c) [full spectra in Supporting Information].

The recorded spectra and the calculated ²⁹Si-MAS NMR shifts of K_4Si_4 and $K_{12}Si_{17}$ are given in Figure 3a and 3b and Table 1. The spectrum of K_4Si_4 shows two signals (1a and 2a) with chemical shifts which agree well with previously reported values.^[16a] The calculated shifts (DFT-PBE) at -326 and -353 ppm

are in accordance with the signals 1a (-323 ppm) and 1b (-346 ppm), respectively, and are in agreement with two crystallographically different Si atoms building the $[Si_4]^{4-}$ clusters in K₄Si₄ (two Wyckoff positions). The ²⁹Si-MAS NMR spectrum of ²⁹Si-enriched K₁₂Si₁₇ reveals several signals within a similar shift range as those of K₄Si₄. Four main signals (1b–4b) are detected besides three broader ones with smaller intensities (5b–7b). Calculations on the ²⁹Si NMR shifts of the primitive unit cell result in 144 atom shifts for the [Si₉]^{4–}, and 128 atom shifts for the [Si₄]^{4–} cluster anions according to the 272 Si atoms in the unit cell of K₁₂Si₁₇.^[18b] This large number of signals (68 independent Si atoms are present if crystallographic symmetry is taken into account) enforces the application of an averaging method and a histogram plot of the calculated shifts of the respective cluster types allows a reliable comparison of the data sets.^[20] Thereby, we combined signal groups within 18 ppm resulting in 10 bins in a range from -281 to -398 ppm. The match with the measured intensities and the arrangement of the measured signals is satisfactory (details see Supporting Information), whereas the distribution range differs. The broader calculated distribution (measd. range: -316 to -344 ppm) is traced back to the circumstance that the calculations were carried out for 0 K, and the atoms were kept at the experimental X-ray positions without any thermal averaging. Finally, a qualitative comparison of the computational bins and the experimental data results in an assignment of three signals for the [Si₄]⁴⁻, and four signals for the $[Si_9]^{4-}$ cluster units (Table 1).

Table 1. Calculated ²⁹ Si NMR shifts [ppm] of the nine- and four-atomic silicon clusters shown in Figure 1 [(a)
labeling according to Figure 1, (b) Wyckoff position, (c) signals within a range of 18 ppm are collected in bins.
Shifts of [Si ₉] ⁴⁻ , [H ₂ Si ₉] ²⁻ , [Si ₉] ²⁻ , and [Si ₄] ⁴⁻ are calculated with CCSD(T)/cc-pVTZ, shifts of solid-state K ₄ Si ₄ and
K ₁₂ Si ₁₇ with DFT-PBE (details in Supporting Information).

	Calculated			Measured		
Cluster system	Atoms/ Clusters	Shift for each atom	Weighted average shifts	Details	Atoms/ Clusters	Shifts
[Si ₄] ^{4–} (<i>T_d</i>)	1 ^(a)	-484	-484	-	-	-
[Si9]⁴- (C₄v)	1 ^(a) 2 ^(a) 3 ^(a)	-405 -374 -431	-403	-	-	-
[H₂Si9]²- (C2v)	1 ^(a) 2 ^(a) 3 ^(a) 4 ^(a) 5 ^(a)	-395 -361 -185 -462 -1.3 (¹ H)	−348 (²ºSi) −1.3 (¹H)	py- <i>d5/</i> thf- <i>d8</i>	²⁹ Si ¹ H	-346 -0.71
[Si ₉]²− (D _{3h})	1 ^(a) 2 ^(a)	-342 -239	-308	py- <i>d5/</i> thf- <i>d8</i>	²⁹ Si	-309
K₄Si₄ (solid)	24 <i>i</i> ^(b) 8e ^(b)	-326 -353	-	Solid- state	[Si ₄] ^{4–} [Si ₄] ^{4–}	-323 -346
K ₁₂ Si ₁₇ (solid)	[Si ₄] ^{4–} [Si ₄] ^{4–}	Supporting	-281 ^(c) -300 ^(c)	Solid- state	[Si ₄] ^{4–} [Si ₄] ^{4–}	-316 -317
	[Si ₉] ^{4–} [Si ₄] ^{4–}	Information	-308 ^(c)		[Si ₉] ^{4–}	-320
	[Si ₉] ^{4–}		-326 ^(c)		[Si ₉] ^{4–}	-322

[Si ₄] ^{4–}	-337 ^(c)	[Si ₄] ^{4–}	-326
[Si ₉] ^{4–}	-344 ^(c)	[Si ₉] ^{4–}	-331
[Si ₉] ^{4–}	-362 ^(c)	[Si ₉] ^{4–}	-344
[Si ₉]4-	-380 ^(c)	-	-
[Si ₉] ^{4–}	-398 ^(c)	-	-

Concerning the solubility of the silicon clusters obtained from K₁₂Si₁₇ in liquid ammonia, the number of known solvate structures and reaction products indicates a better solubility of the nine-atomic versus four-atomic clusters. Moreover, the nine-atomic clusters could be initially transferred to the organic solvents pyridine (py) and dimethylformamide (dmf).^[13-14] Herein, this transfer was optimized by dissolving single-phase $K_{12}Si_{17}$ in a Schlenk tube in liquid ammonia at -78 °C in the presence of 222crypt. After two hours of stirring, the liquid ammonia was evaporated, and a brown solid ($K_{12}Si_{17}$ pre-extracted) remained. Subsequent extraction with py and filtration lead to a red-brown filtrate which yielded a brown-blueish solid after removal of the volatiles. In previous investigations we found^[21] that the blue color originates from the 4,4'-bipyridinyl radical mono-anion $[C_{10}H_8N_2]^{\bullet-}$ which is formed from py by reduction through the cluster anions. The radical unit could be removed by washing with fluorobenzene, and a red solid was obtained. Elemental and EDX analyses suggest a chemical composition of $(K-222 crypt)_2 K_2 Si_9$ (1) for the extraction product. The Raman spectrum of 1 (Figure 2d) reveals one dominating vibration at 386 cm⁻¹ which is indicative for $[Si_9]^{4-}$ clusters as this value is comparable to that of the $[Si_9]^{4-}$ clusters in $K_{12}Si_{17}$ (Figure 2e: 390 cm⁻¹) and to the calculated value (Figure 2c: 395 cm⁻¹). ²⁹Si-MAS NMR investigation of solid **1** (Figure 3c) reveals a broad signal 1c (signal range: 65 ppm) within the range of the [Si₉]⁴⁻ clusters in the K₁₂Si₁₇ solid phase, indicative of a strong disorder or a glass-like behavior of the sample.

The ESI-MS spectra of **1** in py reveal the presence of the di-protonated cluster species $[H_2Si_9]^{2-}$ by detection of {(K-222crypt)[H_2Si_9]}⁻ (m/z = 670) in the negative ion mode, and of {(K-222crypt)_3[H_2Si_9]}⁺ (m/z = 1501) in the positive ion mode (Figure 4a). The corresponding ESI-MS spectrum of a ²⁹Si-enriched sample shows the typical isotope distribution of a sample with approximately 15% enrichment (Figure 4b) and confirms also the presence of the doubly-protonated species. An addition of two protons at the $[Si_9]^{4-}$ cluster units was also observed for $[Cu(NHC^{Dipp})Si_9]^{3-}$ after its transfer from liquid ammonia to py, resulting in the mass peak of {(NHC^{Dipp}Cu)[H_2Si_9]}⁻.^[11]

The ²⁹Si NMR measurement of a ²⁹Si-enriched sample of **1** in solution at ambient temperature shows a broad signal around –305 to –310 ppm (Figure 4). Upon cooling to –20 °C the pattern changes to a broad main signal at –346 ppm and a smaller broad resonance at –309 ppm. Quantum-chemical calculations on the NMR shifts of $[Si_4]^{4-}$, $[Si_9]^{4-}$, $[H_2Si_9]^{2-}$, and $[Si_9]^{2-}$ (Figure 1/Table 1) show a good match with the weighted average signal shifts of $[H_2Si_9]^{2-}$ (*calcd.:* –348 ppm; *measd.:* –346 ppm) and $[Si_9]^{2-}$ (*calcd.:* –308 ppm; *measd.:* –309 ppm), respectively.^[22] Thus, these signals represent the first ever detected ²⁹Si NMR resonances for a nine-atomic silicon cage in solution. Conclusively, the diprotonated majority species $[H_2Si_9]^{2-}$ is also observed in the ESI-MS measurements of **1**. Small amounts of $[Si_9]^{2-}$ are probably formed in py solution through an oxidation of the clusters under formation of the 4,4'-bipyridinyl radical mono-anion. Besides the discussed signals, all spectra show rather sharp

signals between -327 and -330 ppm of lower intensity (Supporting Information) which could not be assigned to a known species yet.



Figure 4. The ²⁹Si NMR spectra of (K-222crypt)₂K₂Si₉ (**1**) (²⁹Si-enriched) in solution at different temperatures [py-*d5*/thf-*d8* (1:1) solvent mixture for measurements at lower temperatures; full spectra in Supporting Information].

At -40 °C the intensity of the main signal at -346 ppm increases under sharping to smaller line width. The coalescence of this ²⁹Si NMR signal indicates dynamic processes: the Si atoms of the cage very likely undergo a fast exchange, and the H atoms are assumed to scramble over the cluster surface. The dynamic behavior of the Si cluster core is supported by calculations on their rigidity which have shown that the energy surface of such clusters is indeed rather flat with an energy difference of less than 2 kJ/mol between $C_{4\nu}$ and D_{3h} -symmetric $[Si_9]^{4-}$ anions at 0 K (Figure 1). Thus, a rigid cluster framework, which has to result in a NMR spectrum with discrete signals in dependence of the symmetry, cannot be expected (Figure1/Table 1). Further, the dynamic behavior of nine-atomic tetrel clusters is well known for the heavier homologue $[Sn_9]^{4-}$ for which also a single averaged ¹¹⁹Sn-NMR signal is observed.^[17, 23] Investigations of the endohedrally filled cluster [Cu@Sn₉]³⁻ also show a single ¹¹⁹Sn resonance and a typical splitting in the ⁶³Cu NMR experiment due to ^{117/119}Sn coupling is reported.^[24] Further proof of the presence of a protonated species provides the ¹H NMR spectra. The spectrum of a 29 Si-enriched sample shows a multiplet in the range of -0.6 to -0.8 ppm (Figure 5d) beside signals for the potassium-complexed 222crypt units. This shift is in reasonable agreement with the calculated ¹H NMR shift of the $[H_2Si_9]^{2-}$ cluster species at -1.3 ppm (Table 1), and also here signal coalescence is observed upon lowering of the temperature (full spectra see Supporting Information). The respective spectrum of a sample with natural-abundant ²⁹Si content (4.68%) shows the same chemical shifts, but with a different splitting pattern (Figure 5f).



Figure 5. a) ESI-MS spectrum of **1** without ²⁹Si enrichment (line: measurement, bars: simulated pattern); b) ESI-MS spectrum of **1** with ²⁹Si enrichment (line: measurement, bars: simulated pattern); c) ²⁹Si inverse gated decoupled ¹H NMR spectrum of **1** with ²⁹Si enrichment; d) coupled ¹H NMR spectrum of **1** with ²⁹Si enrichment (bars: simulated coupling pattern); e) ²⁹Si inverse gated decoupled ¹H NMR spectrum of **1** without ²⁹Si enrichment; d) coupled ¹H NMR spectrum of **1** without ²⁹Si enrichment; f) coupled ¹H NMR spectrum of **1** without ²⁹Si enrichment; f) coupled ¹H NMR spectrum of **1** without ²⁹Si enrichment; bars: simulated coupling pattern). Full spectra are shown in the Supporting Information.

The occurrence of the detected multiplets indicates that the protons are in contact with more than one Si atom. The signal patterns in Figures 5d und 5f arise from different $[H_2^{29}Si_n/Si_{9-n}]^{2-}$ isotopomers in which a variable amount of ²⁹Si atoms (²⁹Si: I = 1/2; ²⁸Si/³⁰Si: I = 0) couples with the H atoms. The intensity distributions of the observed peaks are consistent with the simulated patterns (bars in Figure 5d and 5f) for Si₉ cluster cores with a ²⁹Si isotope abundance of 15% (enriched) and 4.68% (natural abundance), respectively. As presented above, the amount of ²⁹Si in the samples matches also the corresponding isotope ratio obtained from the ESI-MS experiment of **1**. Even though a higher amount of ²⁹Si enrichment was used for the solid-state synthesis of K₁₂Si₁₇ (see Supporting Information), the intensity distribution of our experiments shows an enrichment of 15%. This discrepancy most probably arises from a lower ²⁹Si content in the enriched starting material and from an unknown amount of contained carbon impurity therein.

In the ¹H NMR splitting pattern of $[H_2Si_9]^{2-}$ we find a remarkably small $J(^{29}Si^{-1}H)$ coupling constant of 19.7 Hz, verified by ²⁹Si inverse gated decoupling ¹H NMR experiments, which result in the corresponding singlets (Figure 5c and 5e, respectively). This small value must originate from an increased electronic density at the attached protons due to the strong electronic influence of the electron-rich cluster core. Thus, shielded cluster protons are present with a stronger upfield shift and a smaller coupling constant than in common organo-silane compounds (TMS₃SiH: $J(^{29}Si^{-1}H) = 154$ Hz, $\delta = 2.55$ ppm; CltBu₂SiH: $J(^{29}Si^{-1}H) = 212$ Hz $\delta = 4.34$ ppm; C₆D₆). The delocalized nature of the protons in $[H_2Si_9]^{2-}$ is further comparable to the situation in borane compounds which also undergo hydrogen scrambling and show negative resonances in the ¹H NMR spectra.^[25] Moreover, also the ¹H NMR coupling pattern of the protonated cluster species $[HSn_9]^{3-}$ displays a very small ¹H-¹¹⁹Sn coupling

constant of 21 Hz, and also here a scrambling of the attached proton is observed supporting a comparable dynamic behavior in $[H_2Si_9]^{2-.[26]}$

The investigations here identify the step-wise transformation of the Zintl phase K₁₂Si₁₇, comprising two different anions, to solutions that contain solely nine-atom silicon clusters. For the first time deltahedral Si₉ clusters are detected in solution by ²⁹Si NMR establishing also the doubly-protonation of these clusters. Temperature dependent NMR measurements confirm their dynamic behavior at ambient temperatures and a coalescence by lowering of the temperature. Thereto, details on the dynamic process such as the correlation of proton scrambling and the Si atom rearrangement in the framework will be investigated in forthcoming studies.

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