Naked Deltahedral Silicon Clusters in Solution: Synthesis and Characterization of Si_9^{3-} and Si_5^{2-}

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Deltahedral Zintl anions of the group 14 elements have been known for over 100 years.[1] However, the examples isolated to date included only species of the three heaviest members of the group, i.e., Ge, Sn, or Pb.[2] These anions are ligand-free clusters of nine or five atoms, E_9^{n-} ($n = 2$, 3, or 4) and E_5^{2-}, respectively. They have been structurally characterized in solids crystallized from ethylenediamine or liquid ammonia solutions with alkali-metal countercations sequestered in various cryptands or crown ethers.[2] Recently, contrary to expectations, the same nine-atom clusters were found in simple binary compounds A_4E_9 where A = alkali metal and E = Ge, Sn, Pb.[3] Furthermore, the first nine-atom clusters Si_9^{4-} were characterized also in similar intermetallics, $Rb_{12}Si_{17}$,[4a] and later in $K_{12}Si_{17}$.[4b] These compounds, however, also contain the known tetrahedral species Si_4^{4-} ($Rb_{12}Si_{17} = 12Rb^+ + 2Si_4^{4-} + Si_9^{4-}$). The latter are also found in the compounds A_4E_4 that exist not only for Si but also for Ge, Sn, and Pb.[5] It is well-known that these tetrahedra cannot be extracted into solution from such compounds in all likelihood due to the high negative charge per atom. This, perhaps, is also the reason for the observed insolubility of $A_{12}Si_{17}$ in ethylenediamine, even at higher temperatures. Various other solvents with high dielectric constants and/or the use of soft oxidizing agents intended to oxidize the more reduced Si_4^{4-} were only partially successful and, judging from the color, extracted clusters into solution. However, the concentrations were apparently always too low to allow for crystallization. Finally, when all attempts to obtain these elusive clusters in common and easy to handle solvents failed, we turned back to the original solvent used for such work, liquid ammonia.[1] In addition to the inconvenience, our hesitation for using ammonia as a solvent was because of the belief that ammonia, H_2N-H, and ethylenediamine, $H_2N-CH_2CH_2NH_2$, have very similar solvating capabilities. However, as we have observed, ammonia is by far a better solvent for polar compounds (a good analogy is to compare the solubility of various salts in water, $HO-H$, and in ethylene glycol, $HO-CH_2CH_2OH$). Here we report the use of liquid ammonia as a solvent in extracting the first nine- and five-atom naked clusters of silicon in solution and the structural characterization of Si_9^{3-} and Si_5^{2-} in compounds crystallized from such solutions.[6]

Precursors of $K_{12}Si_{17}$ and $Rb_{12}Si_{17}$ dissolve readily in liquid ammonia upon addition of 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]-hexacosane), forming intensely colored dark red solutions. Such solutions were layered over THF, and dark orange to yellow crystals of (K-crypt)$_3$Si$_9$·8NH$_3$ (**1**) and (Rb-crypt)$_6$Si$_9$Si$_9$·6.3NH$_3$ (**2**) were recovered from them after several days.[7] Crystals of (Rb-crypt)$_2$Si$_5$·4NH$_3$ (**3**) containing five-atom clusters Si_5^{2-} were found in the product of a similar solution treated with triphenylphosphine.[7] Compounds **1** and **2** dissolve readily in pyridine (py), and the clusters can be recrystallized from such solutions. Crystals of (K-crypt)$_3$Si$_9$·2.5py (**4**) were recovered from a pyridine solution of **1**.[7] The structures of all four compounds were determined by single-crystal X-ray diffraction at 100 K.[8]
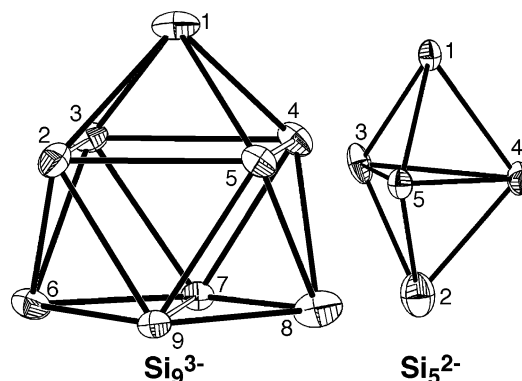
Figure 1. ORTEP drawings of the nine- and five-atom silicon clusters in **1** and **3**, respectively.

As expected, the two silicon clusters are exactly analogous to the corresponding species of Ge, Sn, and Pb (Figure 1).[2] Thus, Si_9^{3-} can be viewed as a tricapped trigonal prism (Figure 1: 3−4−7 and 2−5−9 are the triangular bases, while 1, 6, and 8 are the capping atoms) with variously elongated prismatic edges (7−9, 2−3, and 4−5, shown as open bonds). A cluster with one elongated edge such as that in **1** ($d_{7-9} = 3.245$ Å, $d_{2-3,4-5} = 2.690$, 2.685 Å) resembles also a monocapped square antiprism (Figure 1: 2−3−4−5 and 6−7−8−9 are the square bases, while 1 is the capping atom). One of the two clusters in **2** (two crystallographically different clusters are found in **2**), however, has three elongated edges with distances of 3.151, 2.952, and 2.896 Å. These elongations, as well as the rest of the distances in the clusters, resemble very closely those of the clusters in the $A_{12}Si_{17}$ precursors.[4]

It has been discussed in detail before that the nine-atom clusters have very flexible geometries and charges.[2,9] The latter can be 4−, 2−, and 3−, and correspond to *nido*-, *closo*-, and an intermediate species, respectively. It has been determined that the corresponding germanium species are in equilibria between themselves and solvated electrons,[9] and the availability of appropriate cations determines which species crystallize from solution. Specifically, the presence of only the large cryptated cations prevents crystallization of the clusters with a charge of 4−, as it seems the cluster cannot pack well with four large cations. Thus, with an excess of 2,2,2-crypt, as is the case reported here, the 3− species are obtained.[2] These clusters carry an odd number of cluster-bonding electrons, 21, and are paramagnetic. This was proven for Si_9^{3-} by the EPR spectrum of compound **1** in pyridine, which showed a very strong signal with a *g* value of 2.004.[10] The paramagnetism exhibited by these species prevented the observation of any resonance by ^{29}Si NMR spectroscopy. Despite extensive efforts and prolonged data collections on various NMR spectrometers, a highly concentrated and intensely colored solution of a crystalline sample of **1** in pyridine solution remained silent.

The five-atom cluster Si_5^{2-} is a trigonal bipyramid, as are the Ge, Sn, and Pb counterparts, and can be considered a *closo*-cluster

due to its 2− charge.[2] Also, as with the other species, the equatorial distances, d_{ave} = 2.535 Å, are longer than those to the apexes, d_{ave} = 2.350 Å. These species are generally very rarely observed, and their synthesis is not yet well rationalized. The same seems to be the case for silicon, as these clusters were found only in one crystal selected among many crystallized from a solution treated with triphenylphosphine (the rest of the crystals diffracted very poorly and could not be indexed). The role of the triphenylphosphine, if any, is not clear. It is known that with germanium systems, it oxidizes the clusters to $Ge_9{}^{2-}$ and, when at higher concentrations, the latter form trimers and tetramers, $[Ge_9=Ge_9=Ge_9]^{6-}$ and $[Ge_9=Ge_9=Ge_9=Ge_9]$,$^{8-}$ respectively.[9a,b] However, it is not clear in the silicon system whether triphenylphospine oxidized any existing species to generate $Si_5{}^{2-}$ or the latter are simply in equilibrium with the nine-atom clusters.

The fact that the same nine- and five-atom clusters known for Ge, Sn, and Pb exist for silicon confirms that, as expected, the chemistry of the latter is similar to that of the heavier elements of the group. The extensive knowledge accumulated in the past few years about oligomerization and functionalization of germanium clusters can be applied now directly to silicon clusters.[9] The solubility of the new compounds in pyridine provides a convenient medium for further reactions with them and allows for the study of their electrochemistry. Knowledge of the latter may be used for electrodeposition of thin layers of pure silicon from solution on various electrodes. After all, the solutions contain naked and charged species of silicon without "unwanted" substituents. Potential technology built on such deposition could be of great importance for the development of various novel microdevices of silicon, by far the most important element used in the electronic industry.

Note Added after ASAP: In the version published on the Web 5/5/2004, some of the crystal data in ref 8 was incorrect. The final version and the print version are correct.

Supporting Information Available: X-ray crystallographic file for the four structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) We found out recently that alkali-metal−silicon precursors were successfully dissolved in liquid ammonia and crypt before by J. D. Corbett's group. Crystals were grown from these solutions, but apparently they decomposed very easily and were not characterized structurally (Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383).
(7) All operations were carried out under an inert atmosphere or vacuum using standard Schlenk-line or glovebox techniques. The precursor compounds $Rb_{12}Si_{17}$ and $K_{12}Si_{17}$[4] were made from the elements heated at 850 °C for 60 h in sealed niobium containers that were jacketed in evacuated fused-silica ampules. In a typical reaction, 50 mg of precursor was placed in a Schlenk tube and 10 mL of ammonia was condensed over it using a dry ice−acetone bath. 2,2,2-Crypt (150 mg) was added, and the mixture was allowed to stir at −78 °C for 1 h. After 1 h, the color of the solution was dark brown-red and the precursor was completely dissolved. For the synthesis of **3**, 18 mg of triphenylphosphine was added to the aforementioned solutions of precursor and crypt. The solutions were then filtered, carefully layered over 25 mL of THF, and kept in a freezer at −40 °C for several days. Crystals of the compounds were recovered after evaporation of ammonia/THF (yields between 20 and 50% for **1** and **2**). Crystals of compound **4** were obtained by layering a pyridine solution of **1** with toluene.
(8) Single-crystal X-ray diffraction data sets for compounds **1**−**4** were collected on a Bruker APEX diffractometer with a CCD area detector and Kα radiation at 100 K. The crystals of **1**−**3** lose solvent very easily at room temperature. Therefore, they were selected at low temperatures from microscope slides cooled with either liquid nitrogen or acetone/dry ice mixtures and under Parathone-N oil. Nonetheless, even with all these precautions, some damage apparently occured as reflected in the relatively low quality of the data and the final *R*-factors. Also, one of the two crystallographically different $Si_9{}^{3-}$ clusters in **2** showed disorder among two positions. The crystals of **4** are stable at room temperature. The structures were solved by direct methods and refined on F^2 using the SHELXTL V5.1 package. Crystal data for **1**: triclinic, *P*-1, a = 14.077(3), b = 15.061(3), c = 22.745(5) Å, α = 80.518(4), β = 84.853(4), γ = 66.374(4)°, V = 4356(3) Å^3, Z = 2, R_1/wR_2 = 7.91/16.85% for the observed data ($I \geq 2\sigma_I$). Crystal data for **2**: triclinic, *P*-1, a = 18.127(3), b = 19.439(4), c = 23.320(4) Å, α = 86.515(3), β = 88.861(4), γ = 87.718(4)°, V = 8194(3) Å^3, Z = 2, R_1/wR_2 = 7.70/16.54% for the observed data ($I \geq 2\sigma_I$). Crystal data for **3**: triclinic, *P*1, a = 11.163(1), b = 11.863(3), c = 12.101(2) Å, α = 119.333(3), β = 100.859(3), γ = 91.662(4)°, V = 1358.2(5)(3) Å^3, Z = 1, R_1/wR_2 = 6.23/14.09% for the observed data ($I \geq 2\sigma_I$). Crystal data for **4**: triclinic, *P*-1, a = 13.639(1)(3), b = 14.851(1), c = 22.703(1) Å, α = 86.614(4), β = 79.222(3), γ = 79.168(3)°, V = 4435.7(6) Å^3, Z = 2, R_1/wR_2 = 6.53/13.50% for the observed data ($I \geq 2\sigma_I$).
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(10) EPR spectrum of a frozen pyridine solution of **1** in a 3 mm quartz tube was recorded on a Varian EC-1365E spectrometer at 77 K. A very strong single signal was observed.

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