Ligand-Free Deltahedral Clusters of Silicon in Solution: Synthesis, Structure, and Electrochemistry of Si$_9^{2−}$

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Deltahedral nine-atom clusters of silicon, Si$_9^{2−}$, were synthesized by mild oxidation of a liquid ammonia solution of K$_{12}$Si$_{17}$ with Ph$_3$GeCl in the presence of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) or 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane). The clusters were structurally characterized in [K(18-crown-6)]$_3$Si$_9$C$_5$H$_5$N (yellow; orthorhombic, $Pnma$; $a = 14.013(1)$, $b = 18.108 (1)$, $c = 18.320 (1)$ Å; $Z = 4$) crystallized from a pyridine solution of the product of the aforementioned reaction in liquid ammonia. Si$_9^{2−}$ is the first unequivocally characterized nine-atom cluster of group 14 with a charge of 2−. In addition to pyridine, the product from the reaction in liquid ammonia is also soluble in DMF, and the Si$_9^{2−}$ clusters were characterized by mass spectrometry in such a solution. The more reduced clusters Si$_9^{3−}$ have also been crystallized from pyridine solution. Cyclic voltammetry in both pyridine and DMF solutions clearly shows the Si$_9^{2−}$/Si$_9^{3−}$ redox couple as a one-electron reversible process. The structural similarities and differences between Si$_9^{3−}$ and Si$_9^{2−}$ are discussed herein.

Introduction

We reported recently the isolation and structural characterization of the first ligand-free deltahedral clusters of silicon obtained from solution.1 These are Si$_9^{3−}$ and Si$_9^{2−}$ in (K-2,2,2-crypt)$_3$Si$_9$8NH$_3$ (Rb-2,2,2-crypt)$_6$Si$_9$6.3NH$_3$, and (Rb-2,2,2-crypt)$_2$Si$_9$4NH$_3$ (2,2,2-crypt stands for 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) crystallized from liquid ammonia solutions of the intermetallic precursors K$_{12}$Si$_{17}$ and Rb$_{12}$Si$_{17}$. Si$_9^{3−}$ was also characterized in (K-2,2,2-crypt)$_3$Si$_9$2.5py, which was crystallized from a pyridine solution of the solid obtained from liquid ammonia solution of K$_{12}$Si$_{17}$ after removal of the solvent.1 Analogous examples of these clusters have been well-known and extensively studied for the heavier elements of this group ever since their discovery in 1890.2 Compounds with these clusters have been well-known and extensively studied for the heavier elements of this group ever since their discovery in 1890.2 Compounds with these clusters have also been crystallized from pyridine solution. Cyclic voltammetry in both pyridine and DMF solutions clearly shows the Si$_9^{2−}$/Si$_9^{3−}$ redox couple as a one-electron reversible process. The structural similarities and differences between Si$_9^{3−}$ and Si$_9^{2−}$ are discussed herein.


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clusers of Ge102 of atoms in the cluster is difficult to assess. In fact, the two crypt-sequestered cations per cluster. The cluster, cationic agents that could potentially induce crystallization of the compound, prompted exploration of other solvents and sequestering solutions by cyclic voltammetry and observed the Si92 species with 22 cluster-bonding electrons and would exist as Ge94+ when monomeric. Their charges are reduced to 2− due to intercluster bonding. Thus, no true closo-cluster of group 14 with 20 cluster-bonding electrons has been structurally characterized to date. As a result, the geometry of the species has remained a mystery until now. At the same time, on numerous occasions, we and others have crystallized a compound that clearly contains Ge92 clusters, but all attempts to resolve its crystal structure have been unsuccessful. The compound crystallizes in a hexagonal cell with two crypt-sequestered counterions per cluster. The cluster, however, takes different orientations in its position and shows very pronounced disorder, so much so that even the number of atoms in the cluster is difficult to assess. In fact, the structure was reported at one time as containing 10-atom clusters of Ge102.8

We have observed that the analogous nine-atom silicon clusters of charge 2− form exactly the same problematic structure when crystallized with alkali-metal counterions sequestered by 2,2,2-crypt, i.e., [K(2,2,2-crypt)]2 Si9. The compound crystallizes in the same hexagonal cell, and the clusters show exactly the same disorder problems. This prompted exploration of other solvents and sequestering agents that could potentially induce crystallization of the clusters in a different structure, hopefully without disorder. Here we report one successful result of this exploration, the synthesis and unequivocal crystal structure of Si92− in [K(18-crown-6)]2 Si9-2py crystallized from pyridine. This is the first structurally characterized nine-atom closo-cluster of any of the elements of the carbon group. In addition, we also studied the electrochemistry of the species in pyridine and DMF solutions by cyclic voltammetry and observed the Si92−/Si93− redox pair.

Experimental Section

General Methods. All manipulations were carried out under argon or nitrogen using standard Schlenk-line and glovebox techniques. DMF (N,N-dimethylformamide), anhydrous, Acros) and pyridine (anhydrous, Acros) were used as received. Ethylene-diamine (Acros) was distilled over A4 Pb9 and/or A4 Sn9 intermetallics (A = alkali metal) and stored in gastight ampules under argon. Triphenylgermanium chloride (99%, Aldrich) and 18-crown-6 (99%, Acros) were used after carefully drying them under vacuum.

Precursor Synthesis. The precursor of K12 Si17 was prepared by heating a stoichiometric mixture of the elements (K, 99%, Strem; Si, 99.9999%, Alfa-Aesar) at 900 °C for 2 days in a sealed niobium container that was jacketed in an evacuated fused-silica ampule.

| Table 1. Crystallographic Data for [K(18-crown-6)]2 Si9-2py |
|----------|------------------|------------------|------------------|------------------|
| formula  | C39H53K2NO12Si9 |
| fw       | 938.73           |
| space group | Pmnn, 4        |
| unit cell dimens |              |
| a        | 18.320(1) Å     |
| b        | 14.013(1) Å     |
| c        | 18.104(1) Å     |
| V        | 4647.06(7) Å3   |
| dcalc    | 1.342 g cm−3    |
| radiat, λ | Mo Kα, 0.710 73 Å |
| T        | 100 K           |
| m        | 4.88 cm−1       |
| R1/wR2 (I ≥ 2σ) | 6.18/14.93%  |
| R1/wR2 (all data) | 11.27/16.23% |

w = 1/[σ2(Fo)2 + (0.0807P)2], P = (Fo)2 + 2(Fc)2/3.

Synthesis of [K(18-crown-6)]2 Si9-2py. K12 Si17 (54 mg, 0.06 mmol) and 18-crown-6 (145 mg, 0.55 mmol) were weighed out into a Schlenk tube under inert atmosphere inside a glovebox. The Schlenk tube was transferred to a vacuum line where approximately 5 mL of NH3(l) was condensed over the solid at −70 °C. The resulting orange solution/suspension was allowed to stir for 30 min after which Pb4GeCl (21 mg, 0.06 mmol) was added. This resulted in an immediate color change from orange to yellow. The solvent was subsequently evaporated and the resulting yellow powder dried under vacuum and collected. The reaction worked equally well with Me5SnCl and i-BuCl. The yellow powder was transferred to a glovebox and was dissolved in approximately 1 mL of pyridine. The resulting dark yellow/orange solution was filtered, and the filtrate was layered with toluene. Yellow, rodlike crystals of [K(18-crown-6)]2 Si9-2py were collected after 2 days.

Structure Determination. Single-crystal X-ray diffraction data were collected on a Bruker APEX diffractometer equipped with a CCD area detector using graphite-monochromated Mo Kα radiation. The structure was solved by direct methods and refined on F2 using the SHELXTL V5.1 package.9 Details of the data collection and refinement are given in Table 1 while important Si−Si distances are listed in Table 2 (together with the distances of Si93− in [K(2,2,2-crypt)]2 Si9-2py).

Electrospray Mass Spectrometry. The Si93− clusters were characterized in solution by electrospray mass spectrometry on a Micromass Quattro-LC triple quadrupole mass spectrometer (125 °C source temperature, 150 °C desolvation temperature, 3 kV capillary voltage, and 25 V cone voltage). Spectra were taken both in negative- and positive-ion modes. The samples, made by

[55x138]Precursor Synthesis. The precursor of K12 Si17 was prepared by heating a stoichiometric mixture of the elements (K, 99%, Strem; Si, 99.9999%, Alfa-Aesar) at 900 °C for 2 days in a sealed niobium container that was jacketed in an evacuated fused-silica ampule.

dissolving [K(2,2,2-crypt)]3 Si₉ in DMF (10−20 μM solutions), were introduced by direct infusion with a Harvard syringe pump at 10 μL/min.

**Cyclic Voltammetry.** Cyclic voltammetry studies were performed on a BAS Epsilon-EC potentiostat using a Pt working electrode, Pt-plate auxiliary electrode, and a 0.1 M Ag/AgBF₄ reference electrode. Sodium tetraphenylborate (Aeros, 0.1 M) was used as a supporting electrolyte. Cyclic voltammograms were run at 100 mV/s at room temperature under a N₂ atmosphere in a glovebox.

**Results and Discussion**

Liquid ammonia solutions of A₁₂Si₁₇ (A = alkali metal) seem to produce exclusively nine-atom clusters of charge 3−, i.e., Si₉³⁻. We have already characterized these species in three different compounds with 2,2,2-crypt as the sequestering agent of the alkali-metal counterions: (K-2,2,2-crypt)₃Si₉₈NH₃; (Rb-2,2,2-crypt)₆Si₉₆.3NH₃; (K-2,2,2-crypt)₃Si₉₅NH₃.⁵ It is worth noting that the precursor A₁₂Si₁₇ contains the more reduced nine-atom cluster Si₉₄⁻ and the tetrahedral Si₉₄⁻,⁴d,k Presumably, during dissolution, the former loses an electron while the latter most likely interacts with other clusters (accompanied by release of more electrons) to form Si₉³⁻ in addition to closo-Si₉³⁻ (trigonal bipyramids) characterized in (Rb-2,2,2-crypt)₃Si₉₄NH₃.¹ The extra electrons are most likely solvated by the liquid ammonia and slowly interact with the solvent to form amides. Interestingly, unlike germanium (below), neither Si₉³⁻ nor Si₉₄⁻ has been crystallized from these solutions so far. Therefore, these species are either in very small concentrations or do not form at all under such conditions.

We have already shown that nine-atom clusters of germanium with different charges, i.e., Ge₉⁴⁺, Ge₉³⁻, and Ge₉⁵⁻, coexist in ethylenediamine solutions in equilibria with solvated free electrons.⁴ Furthermore, using appropriate mild oxidizing agents such as Ph₃P and Ph₃As, these equilibria can be shifted toward the most oxidized species Ge₉⁴⁺.⁵ Such oxidation facilitates formation of oligomers such as the observed trimers and tetramers of clusters, [Ge₉⁺Ge₉⁻Ge₉⁶⁻]³⁻ and [Ge₉⁻Ge₉⁻Ge₉⁵⁻Ge₉⁵⁻]⁴⁻, respectively.⁶ Also, oxidizing agents such as R₃ECl for R = Me and Ph and E = Ge and Sn not only oxidize the mixtures to exclusively Ge₉⁵⁻ but also add to the clusters the nucleophilic anions R₃E⁻ and form mono- and disubstituted species such as [Ge₉R₃]⁻ and [R₃E₄Ge₉R₃]⁻.¹⁰ (We have already shown that, during the process, the R₃ECl species are reduced to R₃E⁻ and Cl⁻ by the solvated free electrons from the cluster equilibria.) After the recent discovery of Si₉³⁻, the analogous reactions with these species were explored. Thus, liquid ammonia solutions of K₁₂Si₁₇ were treated with Ph₃GeCl and later with Me₃SnCl and t-BuCl. All these resulted in simple oxidation of Si₉³⁻ (orange-red) to Si₉²⁻ (yellow), and no oligomerization or functionalization was observed. The solubility of Si₉²⁻ seems to be lower than that of Si₉³⁻, and yellow precipitation of (K-2,2,2-crypt)₃Si₉ forms during the reactions. Nevertheless, the concentration of Si₉²⁻ in solution remains high enough that crystals of this compound can be obtained upon layering the liquid ammonia solution over THF. These crystals, however, turned out to be isostructural with the problematic structure observed for Ge₉²⁻ clusters in (K-2,2,2-crypt)₃Ge₉ (see above); i.e., they crystallize in a similar hexagonal cell with highly disordered clusters that cannot be resolved.

The disorder of the Ge₉²⁻ and Si₉²⁻ clusters in the isostructural compounds (K-2,2,2-crypt)₃E₉ (E = Ge, Si) is clearly a result of the ability of the lower symmetry clusters to take more than one equivalent position within the higher symmetry cavity formed by the cryptated cations in the hexagonal structure. Furthermore, the 2,2,2-crypt molecules envelope the alkali-metal cations completely and prevent them from interacting with the clusters to eventually “pin” the clusters at a particular position. This suggested that a different solvent and/or a more open sequestering agent should be used. For example, crown ethers typically occupy only part of the coordination spheres of the alkali-metal cations and allow them to participate in additional interactions. The combination of pyridine as the solvent and 18-crown-6 as the sequestering agent worked exactly as hoped. The Si₉²⁻ clusters were again generated by oxidation of liquid ammonia solution of K₁₂Si₁₇ with Ph₃GeCl but this time in the presence of 18-crown-6. The solid product that was isolated after the removal of the solvent was then dissolved in pyridine, and the new compound [K(18-crown-6)]₃Si₉py was crystallized upon layering with toluene (Figure 1). Apparently, the capture of a solvent molecule in the structure and the interactions of the more open counterions with the clusters eliminated the possibility of cluster disorder. It should be mentioned here that Si₉³⁻ clusters were similarly crystallized from pyridine solutions of the solid obtained from liquid ammonia solutions of K₁₂Si₁₇ and 2,2,2-crypt (without oxidation reaction) after removal of the solvent, and the structure of the corresponding compound [K(2,2,2-crypt)]₃Si₉py was already reported.³ Clearly, the benefits of working in pyridine are simpler manipulations at ambient temperatures and the stability of the crystals obtained from such solutions in contrast to the typical rapid decomposition of crystals obtained from liquid ammonia due to loss of solvent above ca. −50 °C.

The geometry of the new cluster Si₉²⁻ (Figure 2) is somewhat unexpected. According to its electron count of 20 cluster-bonding electrons it is a closo-cluster of nine vertexes and, in analogy with the corresponding closo-borane and carborane B₉H₉²⁻ and B₁₂C₇H₉, respectively, its geometry

![Figure 1](image-url)
should be that of an ideal tricapped trigonal prism. The structure of Si$_9^{2-}$, however, clearly deviates from this geometry. The cluster is rather a distorted tricapped trigonal prism (the prism is made of triangular bases of atoms 2–3–6 and 2A–3A–6A, and the rectangular faces of the prism are capped by atoms 1, 4, and 5) where one of the vertical edges of the prism, the edge 6–6A (Figure 2a), is considerably longer, 3.035(2) Å, than the other two edges, 2–2A and 3–3A, 2.529(2) and 2.518(2) Å, respectively. Such an elongation translates into an open four-atom face (4–3–6A, and atom 1 is capping). Such geometry is rather characteristic for the observed nido- and intermediate-clusters of germanium, tin and lead, i.e., E$_9$$^{4-}$ and E$_9$$^{5-}$, as well as for Si$_9^{3-}$ (Figure 2b). The elongation in these species, however, is more pronounced, and also, often the elongation is not only along one edge but along two or all three vertical edges of the trigonal prism. This is clearly evident when comparing Si$_9^{2-}$ and Si$_9^{3-}$ (Figure 2). The three edges in Si$_9^{2-}$ are 2.518, 2.529, and 3.035 Å, while they are longer in Si$_9^{3-}$, 2.625, 2.642, and 3.418 Å. It is very likely that the shape of Si$_9^{2-}$ deviates from ideal due to the interactions with the cations in the solid state as shown in Figure 1. The latter cap two triangular faces of the cluster, those made of atoms 4–3–3A and 2–2–2A, and interact with the lone pairs at these atoms (one of them interacts additionally with the nitrogen of a pyridine molecule). It can be speculated that the vertical edges of the corresponding idealized cluster, i.e., without such interactions, would be equal to the average of the observed distances, i.e., about 2.694 Å. Therefore, this distance can be considered as the length of a normal edge of an ideal tricapped trigonal prism of silicon. This distance compares well with the two shorter edges in Si$_9^{3-}$, 2.625 and 2.642 Å, and indicates that they are normal while the long edge of 3.418 Å is a truly elongated edge, by about 27%.

The differences in the lengths of the vertical edges in Si$_9^{2-}$ and Si$_9^{3-}$ are directly related to the electronic structures of the two clusters. As previously argued, the energy of the LUMO of the closo-E$_9$$^{2-}$ clusters (half-filled HOMO for E$_9$$^{1+}$) is very sensitive to changes in these lengths. This molecular orbital is predominantly made of p$_z$ orbitals ($z$ is along the 3-fold axis of the prism) and is $\pi$-bonding within the two triangular bases of the trigonal prism but is $\sigma$-antibonding between them. The interaction of the triangular bases with the capping atoms is independent of the lengths of the vertical edges and therefore irrelevant in the discussion. Elongation of one or more of the vertical prismatic edges stabilizes this orbital because of reduced $\sigma$-antibonding character. The orbital becomes occupied, either half or fully for E$_9$$^{3-}$ and E$_9$$^{4-}$, respectively, and becomes the HOMO for these charges. Therefore, the process of oxidation of Si$_9^{3-}$ should be viewed as a removal of one electron from this particular orbital and its destabilization from a half-filled HOMO for Si$_9^{3-}$ to a LUMO for Si$_9^{2-}$ accompanied with shortening of the vertical prismatic edges.

The electrospray mass spectra of [K(2,2,2-crypt)]$_2$Si$_9$ in DMF taken in positive- and negative-ion modes showed only one cluster-containing peak each, of [K(2,2,2-crypt)]$_2$Si$_9^{2-}$ and [K(2,2,2-crypt)]$_2$Si$_9^{3-}$, respectively (Figure 3). They both fit perfectly the corresponding calculated isotopic distributions. Several other peaks at much lower m/z values were also observed, but judging from the isotopic distribution patterns, they do not contain Si$_9$ clusters (most likely they are due to fragmented DMF). In addition, the positive-ion mode showed the sequesetered cation K(2,2,2-crypt)$^+$. The extensive ion pairing is quite typical for Zintl ions in electrospray mass spectrometry, although often the alkali-metal cation is found extracted from the crypt.

All compounds containing Si$_9^{3-}$ or Si$_9^{2-}$ are soluble in pyridine, ethylenediamine, liquid ammonia, and DMF, and this solubility has enabled us to electrochemically study the redox chemistry of these two species. Cyclic voltammetry measurements were carried out on 1 mM DMF and on 1

mM pyridine solutions of [K(2,2,2-crypt)]\(2\)\(\text{Si}_9\) obtained from liquid ammonia solution after removal of the solvent (Figure 4). Ferrocene was added as internal standard (1 mM solution). Both voltammograms show a quasi-reversible single-electron oxidation/reduction process corresponding to the \(\text{Si}_9^{2-}/\text{Si}_9^{3-}\) redox pair. Blank experiments with only solvent/electrolyte did not show any redox active impurities in the solvents and/or electrolyte. The voltammograms of the sample without ferrocene were also recorded in both solvents. They appeared very similar to those recorded with ferrocene and indicated, therefore, that the observed process is reduction/oxidation of \(\text{Si}_9^{2-}/\text{Si}_9^{3-}\) and not due to interactions of the silicon clusters with the ferrocene. The corresponding redox potentials with respect to the Ag\(^+/Ag\) reference electrode are \(-1.42\) V \((\Delta E = 0.26\) V) in DMF and \(-0.68\) V \((\Delta E = 0.18\) V) in pyridine (Figure 4). The ferrocene pair \(\text{Fc}^+/\text{Fc}\) appears at \(-0.05\) V \((\Delta E = 0.13\) V) in DMF and at \(+0.49\) V \((\Delta E = 0.11\) V) in pyridine. This gives potentials of \(-1.37\) and \(-1.17\) V for \(\text{Si}_9^{2-}/\text{Si}_9^{3-}\) in the two solvents with respect to \(\text{Fc}^+/\text{Fc}\). Converted into standard potentials, i.e., with respect to \(\text{H}^+/\text{H}\) by using the standard values for \(\text{Ag}^+/\text{Ag}\) in DMF and pyridine, \(+0.812\) and \(+0.551\) V, respectively,\(^{13}\) the numbers for \(\text{Si}_9^{2-}/\text{Si}_9^{3-}\) become \(-0.608\) in DMF and \(-0.129\) V in pyridine. The attempts to reduce \(\text{Si}_9^{3-}\) further to \(\text{Si}_9^{4-}\) failed in all tested solvents because the \(\text{Si}_9^{5-}\) species is too reduced and the \(\text{Si}_9^{3-}/\text{Si}_9^{4-}\) pair lies below the potential at which these solvents are reduced; i.e., the solvent is reduced before \(\text{Si}_9^{3-}\). This may explain why the isolation of \(\text{Si}_9^{4-}\) clusters has been unsuccessful so far.

Similarly elusive is further oxidation of \(\text{Si}_9^{2-}\) to, perhaps, elemental silicon; i.e., \(\text{Si}_9^{2-}\) seems to be more stable to oxidation than the corresponding solvents according to the electrochemistry of these systems. This result seems to be in agreement with similar measurements performed for Ge\(^{3+}\), Sn\(^{3+}\), and Pb\(^{3+}\) in acetonitrile which showed very strong and irreversible oxidation peaks (most likely to the corresponding elements) at about \(-0.19\) V for lead and \(+0.04\) V for tin and with no peak observed for germanium.\(^{14}\) This seems to indicate that the corresponding oxidation to elemental germanium is also outside the electrochemical window of the solvent, as is the case for silicon. It should be pointed out that the tin and lead solutions in acetonitrile show additional peaks that can be interpreted also as due to the corresponding \(\text{E}_9^{2-}/\text{E}_9^{3-}\) redox pairs. Their positions with respect to \(\text{Ag}/\text{Ag}^+\) in acetonitrile are at approximately \(-1.29\) and \(-1.00\) V for Pb and Sn, respectively.\(^{14}\)

All our attempts to obtain \(^{19}\)Si NMR spectra of the \(\text{Si}_9^{2-}\)-clusters have proven unsuccessful to date, despite numerous attempts at a variety of different temperatures using various acquisition times. The most likely reason for the failure is the prohibitively long relaxation time expected for a naked Si cluster. A similar failure was reported previously in the measurement of solid-state NMR spectra for comparable \(\text{Si}_9^{4-}\) clusters present in clathrates.\(^{15}\) Addition of exo-groups to the clusters in analogy with the germanium counterparts will very likely result in reduced relaxation times and in the opportunity to record \(^{19}\)Si{\(^1\)H} NMR spectra. We are currently involved in a series of such experiments attempting to obtain such functionalized nine-atom Si clusters.

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

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