Inorg. Chem. **2005**, *44*, 2654–2658

Ligand-Free Deltahedral Clusters of Silicon in Solution: Synthesis, Structure, and Electrochemistry of Si_9^{2-}

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Received January 20, 2005

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_3GeCl 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)]$_2Si_9 \cdot C_5H_5N$ (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 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_5^{2-} in (K-2,2,2-crypt)$_3Si_9 \cdot 8NH_3$, (Rb-2,2,2-crypt)$_6Si_9Si_9 \cdot 6.3NH_3$, and (Rb-2,2,2-crypt)$_2Si_5 \cdot 4NH_3$ (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)$_3Si_9 \cdot 2.5$py, 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 can be similarly crystallized from ethylenediamine or liquid ammonia solutions of the corresponding intermetallic compounds with the alkali metals using sequestering agents such as 2,2,2-crypt and 18-crown-6 polyether (1,4,7,10,13,16-hexaoxacyclooctadecane).[3] It should be mentioned that the main phases in the intermetallic precursors are the Zintl compounds A_4E_9 and $A_{12}E_{17}$ which contain the same nine-atom clusters.[4] The compounds $A_{12}E_{17}$ contain also the more reduced E_4^{4-} tetrahedra which cannot be extracted into solution, most likely because of their high negative charge per atom.

All of the structurally characterized nine-atom clusters of Ge, Sn, and Pb carry charges of either 4− or 3− and correspond to *nido*- (22 cluster-bonding electrons) or *intermediate*-clusters (21 cluster-bonding electrons), respectively,

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10.1021/ic0500964 CCC: $30.25
Published on Web 03/15/2005

i.e., E_9^{4-} and E_9^{3-} (E = Ge, Sn, Pb).[3] In addition to these monomeric species, oligomers and chains of nine-atom germanium clusters with formal charge of 2− per cluster (*closo*-, 20 cluster-bonding electrons), $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$, $[Ge_9{=}Ge_9{=}Ge_9{=}Ge_9]^{8-}$, and $(-Ge_9^{2--})_\infty$, have been recently isolated as well.[5−7] However, despite their formal charge of 2−, the nine-atom clusters in these formations are actually *nido*-species with 22 cluster-bonding electrons and would exist as Ge_9^{4-} 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 Ge_9^{2-} clusters, but all attempts to resolve its crystal structure have been unsuccessful. The compound crystallizes in a hexagonal cell with two crypt-sequestered countercations 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 Ge_{10}^{2-}.[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 countercations sequestered by 2,2,2-crypt, i.e., $[K(2,2,2\text{-crypt})]_2Si_9$. 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 Si_9^{2-} in $[K(18\text{-crown-6})]_2Si_9{\cdot}$py 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 Si_9^{2-}/Si_9^{3-} 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. Ethylenediamine (Acros) was distilled over A_4Pb_9 and/or A_4Sn_9 intermetallics (A = alkali metal) and stored in gastight ampules under argon. Triphenylgermanium chloride (99%, Aldrich) and 18-crown-6 (99%, Acros) were used as received after carefully drying them under vacuum.

Precursor Synthesis. The precursor of $K_{12}Si_{17}$ 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 $[K(18\text{-crown-6})]_2Si_9{\cdot}$py

formula	$C_{29}H_{53}K_2NO_{12}Si_9$
fw	938.73
space group, *Z*	*Pnma*, 4
unit cell dimens	
a	18.320(1) Å
b	14.013(1) Å
c	18.104(1) Å
V	4647.6(7) Å^3
d_{calc}	1.342 g cm^{-3}
radiatn, λ	Mo Kα, 0.710 73 Å
T	100 K
m	4.88 cm^{-1}
R1/wR2 ($I \geq 2\sigma_I$)[a]	6.18/14.93%
R1/wR2 (all data)[a]	11.27/16.23%

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0807P)^2]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Important Si−Si Distances for Si_9^{2-} in $[K(18\text{-crown-6})]_2Si_9{\cdot}{\bullet}_p$y and Si_9^{3-} in $[K(2,2,2\text{-crypt})]_3Si_9{\cdot}2.5$py

atoms	Si_9^{2-}	Si_9^{3-}
Si1−Si2	2.458(2)	2.435(1), 2.441(1)
Si1−Si3	2.459(2)	2.443(1), 2.434(1)
Si2−Si3	2.774(1)	2.648(1), 2.638(1)
Si2−Si2A	2.530(3)	2.642(2)
Si3−Si3A	2.518(2)	2.625(1)
Si2−Si5	2.494(2)	2.490(2), 2.427(1)
Si2−Si6	2.407(1)	2.425(2), 2.444(1)
Si3−Si4	2.491(2)	2.433(1), 2.467(2)
Si3−Si6	2.412(1)	2.475(1), 2.467(1)
Si4−Si6	2.391(2)	2.354(2), 2.463(2)
Si5−Si6	2.383(2)	2.410(2), 2.496(1)
Si6−Si6A	3.035(2)	3.418(2)

Synthesis of $[K(18\text{-crown-6})]_2Si_9{\cdot}$py. $K_{12}Si_{17}$ (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 NH_3(l) was condensed over the solid at −70 °C. The resulting orange solution/suspension was allowed to stir for 30 min after which Ph_3GeCl (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 Me_3SnCl and *t*-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 $[K(18\text{-crown-6})]_2Si_9{\cdot}$py 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 F^2 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 Si_9^{3-} in $[K(2,2,2\text{-crypt})]_3Si_9{\cdot}2.5$py).

Electrospray Mass Spectrometry. The Si_9^{2-} 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

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dissolving $[K(2,2,2\text{-crypt})]_2Si_9$ in DMF (10−20 μM solutions), were introduced by direct infusion with a Harvard syringe pump at 10 μL/min.

Cyclic Voltametry. 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 $Ag/AgBF_4$ reference electrode. Sodium tetraphenylborate (Acros, 0.1 M) was used as a supporting electrolyte. Cyclic voltammograms were run at 100 mV/s at room temperature under a N_2 atmosphere in a glovebox.

Results and Discussion

Liquid ammonia solutions of $A_{12}Si_{17}$ (A = alkali metal) seem to produce exclusively nine-atom clusters of charge 3−, i.e., Si_9^{3-}. We have already characterized these species in three different compounds with 2,2,2-crypt as the sequestering agent of the alkali-metal countercations: $(K\text{-}2,2,2\text{-crypt})_3Si_9\cdot 8NH_3$; $(Rb\text{-}2,2,2\text{-crypt})_6Si_9Si_9\cdot 6.3NH_3$; $(K\text{-}2,2,2\text{-crypt})_6Si_9Si_9\cdot 5NH_3$.[1] It is worth noting that the precursor $A_{12}Si_{17}$ contains the more reduced nine-atom cluster Si_9^{4-} and the tetrahedral Si_4^{4-}.[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 Si_9^{3-} in addition to *closo*-Si_5^{2-} (trigonal bipyramids) characterized in $(Rb\text{-}2,2,2\text{-crypt})_2Si_5\cdot 4NH_3$.[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 Si_9^{2-} nor Si_9^{4-} 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., Ge_9^{4-}, Ge_9^{3-}, and Ge_9^{2-}, coexist in ethylenediamine solutions in equilibria with solvated free electrons.[10] Furthermore, using appropriate mild oxidizing agents such as Ph_3P and Ph_3As, these equilibria can be shifted toward the most oxidized species Ge_9^{2-}.[5,6] Such oxidation facilitates formation of oligomers such as the observed trimers and tetramers of clusters, $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$ and $[Ge_9{=}Ge_9{=}Ge_9{=}Ge_9]^{8-}$, respectively.[5,6] Also, oxidizing agents such as R_3ECl for R = Me and Ph and E = Ge and Sn not only oxidize the mixtures to exclusively Ge_9^{2-} but also add to the clusters the nucleophilic anions R_3E^- and form mono- and disubstituted species such as $[Ge_9ER_3]^{3-}$ and $[R_3EGe_9ER_3]^{2-}$.[10] (We have already shown that, during the process, the R_3ECl species are reduced to R_3E^- and Cl^- by the solvated free electrons from the cluster equilibria.[10]) After the recent discovery of Si_9^{3-}, the analogous reactions with these species were explored. Thus, liquid ammonia solutions of $K_{12}Si_{17}$ were treated with Ph_3GeCl and later with Me_3SnCl and *t*-BuCl. All these resulted in simple oxidation of Si_9^{3-} (orange-red) to Si_9^{2-} (yellow), and no oligomerization or functionalization was observed. The solubility of Si_9^{2-} seems to be lower than that of Si_9^{3-}, and yellow precipitation of $(K\text{-}2,2,2\text{-crypt})_2Si_9$ forms during the reactions. Nevertheless, the concentration of Si_9^{2-} 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 Ge_9^{2-} clusters in $(K\text{-}2,2,2\text{-crypt})_2Ge_9$ (see above); i.e., they crystallize in a similar hexagonal cell with highly disordered clusters that cannot be resolved.

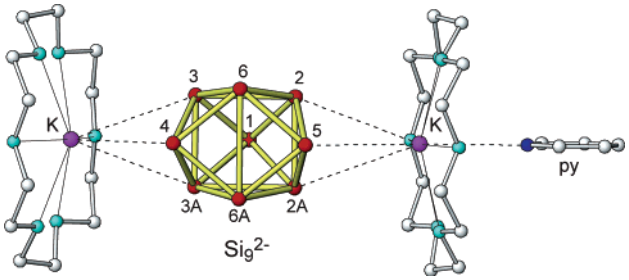

Figure 1. Interactions between Si_9^{2-} and the countercations of $K(18\text{-crown-6})^+$ in $[K(18\text{-crown-6})]_2Si_9\cdot py$. One of the cations interacts also with a solvent molecule of pyridine captured in the structure.

The disorder of the Ge_9^{2-} and Si_9^{2-} clusters in the isostructural compounds $(K\text{-}2,2,2\text{-crypt})_2E_9$ (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 Si_9^{2-} clusters were again generated by oxidation of liquid ammonia solution of $K_{12}Si_{17}$ with Ph_3GeCl 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 $[K(18\text{-crown-6})]_2Si_9\cdot py$ 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 countercations with the clusters eliminated the possibility of cluster disorder. It should be mentioned here that Si_9^{3-} clusters were similarly crystallized from pyridine solutions of the solid obtained from liquid ammonia solutions of $K_{12}Si_{17}$ and 2,2,2-crypt (without oxidation reaction) after removal of the solvent, and the structure of the corresponding compound $[K(2,2,2\text{-crypt})]_3Si_9\cdot 2.5py$ was already reported.[1] 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 Si_9^{2-} (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 $B_9H_9^{2-}$ and $B_7C_2H_9$, respectively, its geometry

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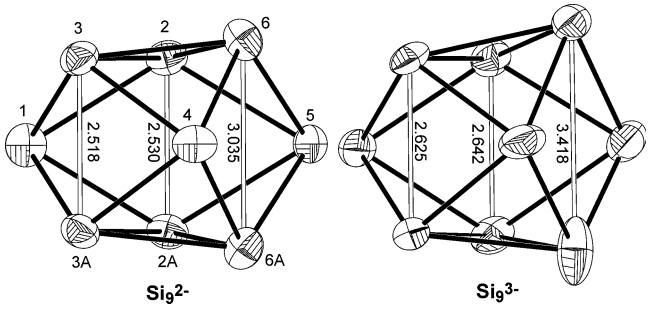

Figure 2. ORTEP drawings (50% thermal ellipsoids) of Si_9^{2-} in [K(18-crown-6)]$_2$Si$_9$·py and Si_9^{3-} in [K(2,2,2-crypt)]$_3$Si$_9$·2.5py. The latter is more elongated along the vertical semi-3-fold axis of the distorted tricapped trigonal prism.

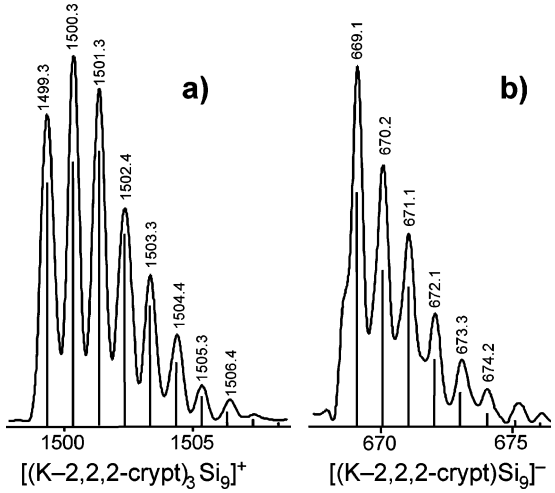

Figure 3. Observed and simulated electrospray mass spectra in positive- (a) and negative-ion (b) modes of a DMF solution of (K-2,2,2-crypt)$_2$Si$_9$. The solute was obtained from oxidized (with Me_3SnCl) solutions of "K_4Si_9" in liquid ammonia after removal of the solvent.

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 (4−5−6−6A), and the cluster resembles also a monocapped square antiprism (the antiprism is made of squares 2−2A−3A−3 and 4−6−5−6A, 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^{3-}, 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 5−2−2A, 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^{3-}) is very sensitive to changes in these lengths.[10,11] This molecular orbital is predominantly made of p_z orbitals (z is along the 3-fold axis of the prism) and is π-bonding within the two triangular bases of the trigonal prism but is σ-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 σ-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, that of {[K(2,2,2-crypt)$^+$]$_3$Si$_9^{2-}$}$^+$ and {[K(2,2,2-crypt)$^+$]Si$_9^{2-}$}$^-$, 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 sequestered 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.[12]

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

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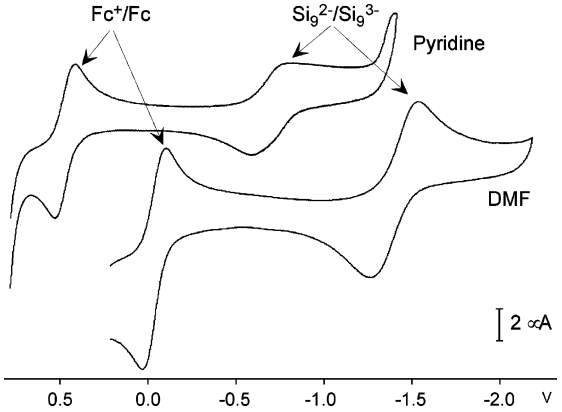

Figure 4. Cyclic voltammograms of 1 mM solutions of $[K(2,2,2\text{-crypt})]_3Si_9$ in pyridine and DMF with ferrocene as an internal standard (1 mM).

mM pyridine solutions of $[K(2,2,2\text{-crypt})]_3Si_9{\cdot}xNH_3$ 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 Si_9^{2-}/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 Si_9^{2-}/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 Fc^+/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 Si_9^{2-}/Si_9^{3-} in the two solvents with respect to Fc^+/Fc. Converted into standard potentials, i.e., with respect to H^+/H by using the standard values for Ag^+/Ag in DMF and pyridine, $+0.812$ and $+0.551$ V, respectively,[13] the numbers for Si_9^{2-}/Si_9^{3-} become -0.608 in DMF and -0.129 V in pyridine. The attempts to reduce Si_9^{3-} further to Si_9^{4-} failed in all tested solvents because the Si_9^{4-} species is too reduced and the Si_9^{3-}/Si_9^{4-} pair lies below the potential at which these solvents are reduced; i.e., the solvent is reduced before Si_9^{3-}. This may explain why the isolation of Si_9^{4-} clusters has been unsuccessful so far. Similarly elusive is further oxidation of Si_9^{2-} to, perhaps, elemental silicon; i.e., 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_9^{3-}, Sn_9^{3-}, and Pb_9^{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 E_9^{2-}/E_9^{3-} redox pairs. Their positions with respect to Ag/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 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 Si_4^{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 $^{19}Si\{^1H\}$ NMR spectra. We are currently involved in a series of such experiments attempting to obtain such functionalized nine-atom Si clusters.

Acknowledgment. We thank the National Science Foundation (Grant CHE-0098004 continued as 0446131) and the Petroleum Research Fund (Grant 37301-AC5,3), administered by the American Chemical Society, for the financial support of this research. We also thank Ivaylo Petrov and Iliya Todorov for the synthesis of the precursors, Dr. William Boggess for help with mass spectrometry, and Jieying Jiao for help with the electrochemical measurements.

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.

IC0500964

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