Synthesis and Structure of Isolated Silicon Clusters of Nine Atoms

Virginie Quéneau, Evgeny Todorov, and Slavi C. Sevov*

Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, Indiana 46556

Received January 5, 1998

We have discovered and structurally characterized the first "naked" silicon clusters larger than four atoms, Si_9^{4-}, in the compound $Rb_{12}Si_{17}$. Silicon is of unparalleled importance for many electronic applications, and the research associated with it spans over many different areas of science: chemistry, physics, surface science, materials processing, etc. In addition to the extensively studied silicon clusters in the gas phase,[1] much interest has been focused lately on silicon nanoparticles and porous silicon due to their valuable optical properties.[2] Recently, the first synthesis of such Si and Ge nanoparticles in liquid medium was reported.[3] This approach utilizes a metathesis reaction (comproportionation) between the negatively charged silicon or germanium in the solids KSi or NaGe, respectively, and the corresponding positively charged ions in the tetrachlorides. Perhaps a better approach to the synthesis of such nanoparticles is to use premade silicon clusters in the solid state, extract them intact into a solution, and then use a metathesis reaction. Unfortunately, the only known such species, Si_4^{4-} tetrahedra in A_4Si_4 (A = alkali metal)[4] and some lithium-stabilized planar silicon formations,[5] cannot be extracted, apparently due to the large charge per atom ratio.[6] The same is true for the tetrahedra of the other tetrels (tetrel = a group 14 element), Ge_4^{4-}, Sn_4^{4-}, and Pb_4^{4-}.[6] On the other hand, nine-atom clusters of germanium, tin, and lead have been identified in solutions made by dissolving the corresponding alkali-metal tetrelides in ethylenediamine or liquid ammonia.[7] Such clusters with different shapes and charges have also been crystallized from the corresponding solutions and have been structurally characterized.[6] It should be pointed out that in all reports the tetrelide precursors for such solutions have been labeled either "alloys" or "melts", i.e., substances with no particular structure and without defined cluster formations. Hence, the current understanding on the formations of the clusters in solution is that they do not exist in the precursors but are rather assembled somehow during the process of dissolution.[6] However, our recent studies of the systems alkali-metal−tetrel show that clusters of Ge_9^{4-} and Pb_9^{4-} exist in the compounds Cs_4Ge_9 and K_4Pb_9, respectively.[8] Similarly, recent Raman studies of these and other alkali-metal−tetrel systems also suggest the existence of such clusters.[9] The same clusters most likely existed in the precursors for the solution studies. The new compound, $Rb_{12}Si_{17}$, contains isolated nine-atom silicon clusters, Si_9^{4-}, and is a potential candidate for a precursor for silicon clusters in solution.

The compound is made at 900 °C (kept for 1 h at that temperature and then slowly cooled with a rate of 5°/h) by direct synthesis from the pure elements sealed in niobium containers and jacketed in evacuated ampules of fused-silica. The same approach also yields the isostructural $K_{12}Sn_{17}$ (the phase which most likely "produces" the Sn_9^{4-} in solution) and $(K_xRb_{1-x})_{12}Si_{17}$.[10] Furthermore, phases with the same or very similar structures and stoichiometries seem to exist in the systems Cs−Si, Cs−Sn, Rb−Sn, Cs−Pb, and Rb−Pb, according to their X-ray diffraction powder patterns.

The structure of $Rb_{12}Si_{17}$ was determined from single-crystal X-ray data collected from a crystal made by slow cooling of a mixture loaded as Rb_4Si_9.[11] Later, the compound was made in nearly 100% yield by quenching the stoichiometric melt (900 °C for 1 h) and then annealing it at 300 °C for 1 week. $Rb_{12}Si_{17}$ crystallizes in a structure with very low symmetry and a large unit cell, monoclinic with $V \approx 16000$ Å^3, and also diffracts extremely poorly. The compound is best described as ionic with isolated cluster-anions of silicon and countercations of rubidium. The unit cell contains 48 isolated clusters of two different sizes, nine- and four-atomed, in 12 crystallographically different types, four are the nine-atom clusters and eight are the tetrahedra (Figure 1). The clusters are well separated, 4.6−5.0 Å vertex-to-vertex, with the shortest distance of ca. 4.6 Å occurring between tetrahedra. The formula can be written as $(Rb)_{12}(Si_9)(Si_4)_2$ or $(Rb_4Si_9 + 2Rb_4Si_4)$. The compound is diamagnetic, and therefore electronically balanced (closed-shell).[12]

Tetrahedra of silicon are not new. As mentioned above, they exist in A_4Si_4, for A = Na, K, Rb, or Cs.[4] The average Si−Si distances in the eight crystallographically different tetrahedra in $Rb_{12}Si_{17}$ are virtually identical, 2.42(±2) Å, and compare well with that of the tetrahedra in Rb_4Si_4, 2.43 Å.

It is the nine-atom clusters of silicon that makes this compound special. These clusters are the missing member in the family of such species of the heavier members of the carbon group. The four crystallographically different clusters in $Rb_{12}Si_{17}$ (Figure 2, labeled A−D) do not have symmetry elements. In a first glance

(1) Brown, W. L.; Freeman, R. R.; Raghavachari, K.; Schlüter, M. *Science* **1987**, *235*, 860 and references therein.

(2) (a) Canham, L. T. *Appl. Phys. Lett.* **1990**, *57*, 1046. (b) Brus, L. E.; Szajowski, P. F.; Wilson, W. L.; Harris, T. D.; Schuppler, S.; Citrin, P. H. *J. Am. Chem. Soc.* **1995**, *117*, 2915. (c) Brus, L. *J. Phys. Chem.* **1994**, *98*, 3575. (d) Heath, J. R. *Science* **1992**, *258*, 1131. (e) Heinrich, J. L.; Curtis, C. L.; Credo, G. M.; Kavanaugh, K. L.; Sailor, M. J. *Science* **1992**, *255*, 66. (f) Littau, K. A.; Szajowski, P. J.; Muller, A. J.; Kortan, A. R.; Brus, L. E. *J. Phys. Chem.* **1993**, *97*, 1224. (g) Fojtik, A.; Henglein, A. *Chem. Phys. Lett.* **1994**, *221*, 363.

(3) (a) Bley, R. A.; Kauzlarich, S. M. *J. Am. Chem. Soc.* **1996**, *118*, 12461. (b) Taylor, B. R.; Kauzlarich, S. M.; Lee, H. W. H.; Delgado, G. R. *Chem. Mater.* **1998**, *10*, 22.

(4) Schäfer, H. *Annu. Rev. Mater. Sci.* **1985**, *15*, 1.

(5) (a) von Schnering, H.-G.; Nesper, R.; Curda, J.; Tebbe, K.-F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1033. (b) Nesper, R.; Curda, J.; von Schnering, H.-G. *J. Solid State Chem.* **1986**, *62*, 199. (c) von Schnering, H.-G.; Bolle, U.; Curda, J.; Peters, K.; Carillo-Cabrera, W.; Somer, M.; Schultheiss, M.; Wedig, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 984.

(6) Corbett, J. D. *Struct. Bonding* **1997**, *87*, 157 and references therein.

(7) Wilson, W. L.; Rudolph, R. W.; Lohr, L. L.; Taylor, R. C.; Pyykkö, P. *Inorg. Chem.* **1986**, *25*, 1535.

(8) (a) Quenéau, V.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1754. (b) Quenéau, V.; Sevov, S. C. *Inorg. Chem.* **1998**, *37*, 1358. Published on the Web: http://pubs.acs.org/journals/inocaj/index.html, 3/3/98.

(9) von Schnering, H.-G.; Baitinger, M.; Bolle, U.; Cabrera, W. C.; Curda, J.; Grin, Y.; Heinemann, F.; Llanos, L.; Peters, K.; Schmeding, A.; Somer, M. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1037.

(10) Lattice parameters for $K_{12}Sn_{17}$: $a = 25.71(1)$, $b = 14.770(7)$, and $c = 48.19(4)$ Å, $\beta = 91.64(5)°$. For $(K_xRb_{1-x})_{12}Si_{17}$ loaded as $K_2Rb_2Si_9$: $a = 24.15(2)$, $b = 13.85(1)$, and $c = 45.35(4)$ Å, $\beta = 91.1(1)°$.

(11) A hemisphere of X-ray diffraction data was collected on a Siemens SMART system at −100 °C from a single crystal of $Rb_{12}Si_{17}$ (0.12 × 0.10 × 0.08 mm) with monochromated Mo Kα radiation. Since the crystals diffract extremely poorly and the unit cell is extremely large, data were collected with very long exposures of 120 s per frame, and only up to $2\theta_{max} = 40°$. (Crystal data: monoclinic, $P2_1/c$, $Z = 16$, $a = 24.445(5)$, $b = 14.017(3)$, and $c = 46.038(9)$ Å, $\beta = 91.32(3)°$, $V = 15770(6)$ Å^3, $\mu = 152.66$ cm^{-1}, $d_{calc} = 2.53$ g cm^{-3}, $R(F) = 9.81\%$ for all reflections with $I \geq 4\sigma I$).

(12) The magnetization of 25 mg of the sample with near 100% yield of $Rb_{12}Si_{17}$ was measured at field of 3 T over the range of 6−295 K on a Quantum Design MPMS SQUID magnetometer. The raw data, corrected for the holder and the ion-core diamagnetism for 12 Rb^+ and 17 Si^{4+} ions, are temperature independent and fluctuate within $-(8.35/8.10) \times 10^{-4}$ emu mol^{-1}. Correction for diamagnetism due to Larmor precession of the delocalized pairs of electrons on cluster orbitals is calculated according to the formula $-0.79Z(r/a_o)^2 \times 10^{-6}$ emu(mol cluster)$^{-1}$ where Z is the number of such electrons (12 for Si_4^{4-} and 22 for Si_9^{4-}), r is the average radius of the cluster (calculated 1.5 and 2.3 Å for Si_4^{4-} and Si_9^{4-}, respectively), and $a_o = 0.529$ Å. This correction amounts to -4.81×10^{-4} emu mol^{-1}, and when applied, the susceptibility becomes $-(2.54/2.29) \times 10^{-4}$ emu mol^{-1}. This is consistent with a closed-shell electronically balanced compound.

S0002-7863(98)00044-4 CCC: $15.00
Published on Web 03/21/1998

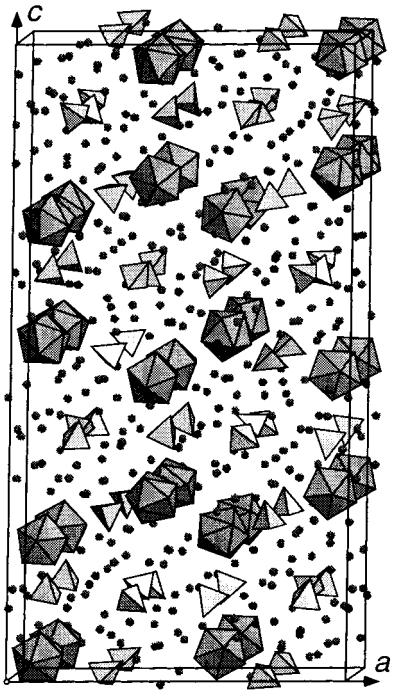

Figure 1. A view along *b* of the unit cell (monoclinic, $P2_1/c$) of $Rb_{12}Si_{17}$. The clusters of Si_9^{4-} and Si_4^{4-} are shown as polyhedra. The isolated spheres are the rubidium cations.

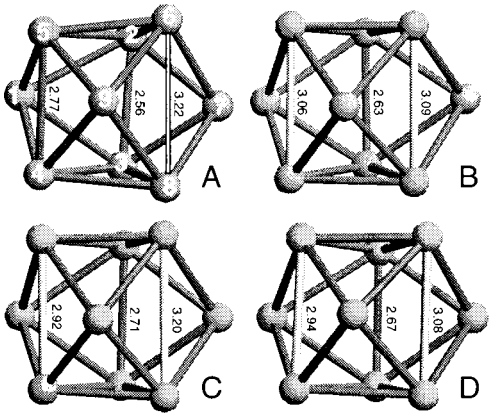

Figure 2. The four crystallographically different nine-atom clusters of silicon. The atoms in all four are numbered in the order shown for cluster A.

they look nearly identical. Nevertheless, they differ somewhat in shapes, angles, and distances, most likely due to packing effects. All four are of deltahedral (borane or cage) type and apparently of charge 4− which corresponds to 22 bonding electrons. The charge is characteristic for *nido*-species, i.e., clusters built of triangular faces where one of the vertexes is missing. Clusters A are the closest to the typical geometry for such clusters, a monocapped (atom 1) square antiprism (atoms 2−3−4−5 and 6−7−8−9). It is rather difficult to define such a geometry for the other three clusters, B, C, and D, since each has two open "square" bases, 6−7−8−9 and 1−4−5−9, and either one can be a base of a square antiprism. A somewhat better description is to look at them as an intermediate between a monocapped square antiprism and an elongated tricapped (atoms 1, 7, 9) trigonal prism (atoms 3−4−8 and 2−5−6). However, the tricapped trigonal prism is a *closo*-deltahedron, i.e., a deltahedron with no missing vertexes, and should require 20 bonding electrons. The only exceptions to this rule are Bi_9^{5+} in $Bi_{10}Hf_3Cl_{18}$ and $Bi_{12}Cl_{14}$[13] and the recently characterized Pb_9^{4-} in K_4Pb_9.[8b] They are tricapped trigonal prisms elongated along the 3-fold axes, and due to the elongation require 22 electrons instead. Clusters B−D in $Rb_{12}Si_{17}$ seem to belong to the same geometry and electron count, and therefore carry a charge of 4−. The average distance for the long vertical edges of the latter is 3.02 Å, while the averages of the remaining distances are between 2.37 and 2.53 Å.

Extended Hückel molecular orbital calculations carried out on all four clusters showed very similar HOMO−LUMO gaps of around 4.0 eV. Similarly to the "anomalous" tricapped trigonal prismatic Bi_9^{5+} and Pb_9^{4-}, the HOMO in clusters B, C and D is an orbital of type a_2'' (assuming D_{3h} symmetry).[6,14] It is antibonding between the two triangular bases and bonding within them. This is the "extra" orbital which is empty for "normal" tricapped trigonal prism but becomes bonding and filled for the elongated species since its antibonding character is reduced upon the elongation.

The existence of clusters of the elements of the carbon group in solutions was proposed three-quarters of a century ago.[15] The first example, Sn_9^{4-}, was structurally characterized 50 years later,[16] and the last, that of Ge_5^{2-}, only a few months ago.[17] The fact that nine-atom clusters exist in the precursors suggests that the process of cluster extraction into solution may turn out to be a dissolution of an "ionic" compound composed of single-atom cations and polyatomic cage-like anions. It seems feasible that deltahedral clusters may exist in solution if there is a precursor containing discrete species with the same or larger nuclearity and similar shape. The family of deltahedral clusters in solution included about a dozen of structurally characterized species, but none of them was of silicon. The Si_9^{4-} cluster described here completes the series of E_9^{4-} in this group (carbon excluded). Work on its extraction into solution is in progress.

Acknowledgment. We thank V. Young (University of Minnesota) for the X-ray data collection, J. Ostenson (Iowa State University) for the magnetic measurements, and the Camille and Henry Dreyfus Foundation for the financial support.

Supporting Information Available: Tables of data collection and refinement details, positional and thermal parameters, anisotropic displacement parameters, important interatomic distances, and a table with the dihedral angles of the clusters (8 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available through the Web only. See any current masthead page for ordering and information and Web access instructions.

JA980044W

(13) (a) Friedman, R. M.; Corbett, J. D. *Inorg. Chem.* **1973**, *12*, 1134. (b) Hershaft, A.; Corbett. J. D. *Inorg. Chem.* **1963**, *2*, 979.
(14) Corbett, J. D.; Rundle, R. E. *Inorg. Chem.* **1964**, *3*, 1408.
(15) (a) Kraus, C. A. *J. Am. Chem. Soc.* **1922**, *44*, 1229. (b) Zintl, E.; Goubeau, J.; Dullenkopf, W. *Z. Phys. Chem., Abt. A* **1931**, *154*, 1.
(16) Corbett, J. D.; Edwards, P. A. *J. Am. Chem. Soc.* **1977**, *99*, 3313.
(17) Campbell, J.; Schrobilgen, G. J. *Inorg. Chem.* **1997**, *36*, 4078.