Synthesis and Structure of Isolated Silicon Clusters of Nine Atoms

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

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

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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, much interest has been focused lately on silicon nanoparticles and porous silicon due to their valuable optical properties. Recently, the first synthesis of such Si and Ge nanoparticles in liquid medium was reported. This approach utilizes a metathesis reaction (compro- 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$_{9}$Si$_{17}$ (the phase which most likely “produces” the Sn$_{4}^{4-}$ in solution) and (K,Rb)$_{12}$Si$_{17}$. 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$_{5}$Si$_{6}$. 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$_{2}$Si$_{17}$ crystallizes in a structure with very low symmetry and a large unit cell, monoclinic with V = 16000 Å$^3$, and also diffraacts 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$_{2}$)$_{4}$Si$_{4}$, or (Rb$_{2}$- Si$_{4}$ + 2Rb$_{2}$Si). The compound is diamagnetic, and therefore electronically balanced (closed-shell).

Tetrahedra of silicon are not new. As mentioned above, they exist in A$_{4}$Si$_{4}$, for A = Na, K, Rb, or Cs. The average Si–Si distances in the eight crystallographically different tetrahedra in Rb$_{2}$Si$_{17}$ are virtually identical, 2.42(2) Å, and compare well with that of the tetrahedra in Rb$_{2}$Si$_{4}$, 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$_{2}$Si$_{17}$ (Figure 2, labeled A–D) do not have symmetry elements. In a first glance

(10) Lattice parameters for K$_{2}$_Si$_{4}$: a = 25.71(1) Å, b = 14.77(0) Å, c = 48.19(4) Å, β = 91.64(5)°. For (K$_{2}$_Rb$_{2}$)$_{1}$Si$_{17}$ loaded as K$_{2}$Rb$_{2}$Si$_{5}$ a = 24.58(2) Å, b = 13.85(1) Å, and c = 45.38(4) Å, β = 91.11(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$_{5}$Si$_{6}$ (0.12 ± 0.10 × 0.08 mm) with monochromated Mo Kα radiation. Since the crystals diffracts 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 26max = 40°. (Crystal data: monoclinic, P2$_{1}$/c; $Z = 16$, $a = 24.44(5)$ Å, $b = 14.01(7)$ Å, $c = 46.038(9)$ Å, $\beta = 91.32(3)$°. V = 15770(6) Å$^3$, $\mu = 152.66$ cm$^{-1}$, dcalc = 2.53 g cm$^{-3}$, R(F) = 9.81% for all reflections with I > 4σ(I).
(12) The magnetization of 25 mg of the sample with near 100% yield of Rb$_{5}$Si$_{6}$ 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 iron-core diamagnetism for 12 Rb$^+$ and 17 Si$^{4+}$ ions, are temperature independent and fluctuate within −8.358(5) × 10$^{-5}$ emu mol$^{-1}$. Correction for paramagnetism due to the paramagnetic contribution of the delocalized pairs of electrons on cluster orbitals is calculated according to the formula −0.792(10) × 10$^{-3}$ emu/mol (cluster)$^{-1}$ where Z is the number of such electrons (12 for Si$^{4+}$ and 22 for Si$^{2-}$), $r$ is the average radius of the cluster (calculated 1.5 and 2.3 Å for Si$^{4+}$ and Si$^{2-}$, respectively), and $a_0 = 0.529$ Å. This correction amounts to −4.81 × 10$^{-4}$ emu mol$^{-1}$, and when applied, the susceptibility becomes −2.54×10$^{-4}$ emu mol$^{-1}$. This is consistent with a closed-shell electronically balanced structure.
The clusters of Si\textsuperscript{9+} spheres are the rubidium cations.

All four are of deltahedral (borane or cage) type and apparently in shapes, angles, and distances, most likely due to packing effects. Nevertheless, they differ somewhat.

A.

Silicon. The atoms in all four are numbered in the order shown for cluster A.

The four crystallographically different nine-atom clusters of the unit cell (monoclinic, \( P2_1/c \)) of Rb\textsubscript{12}-Si\textsubscript{17}. The clusters of Si\textsuperscript{9+} and Si\textsuperscript{7+} are shown as polyhedra. The isolated spheres are the rubidium cations.

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\textsuperscript{−} which corresponds to 22 bonding electrons. The charge is characteristic for \textit{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 \textit{closo}-deltahedron, i.e., a deltahedron with no missing vertexes, and should require 20 bonding electrons. The only exceptions to this rule are Bi\textsubscript{9}\textsuperscript{5+} in Bi\textsubscript{16}Hf\textsubscript{18}Cl\textsubscript{18} and Bi\textsubscript{12}Cl\textsubscript{18}, and the recently characterized Pb\textsubscript{9}\textsuperscript{2+} in K\textsubscript{2}Pb\textsubscript{9}.\textsuperscript{30} 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\textsubscript{12}Si\textsubscript{17} seem to belong to the same geometry and electron count, and therefore carry a charge of 4\textsuperscript{−}. 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\textsubscript{9}\textsuperscript{5+} and Pb\textsubscript{9}\textsuperscript{2+}, the HOMO in clusters B, C and D is an orbital of type \( a_{2u}^\prime \) (assuming \( D_{3d} \) symmetry).\textsuperscript{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.\textsuperscript{15} The first example, Sn\textsubscript{9}\textsuperscript{4+}, was structurally characterized 50 years later,\textsuperscript{16} and the last, that of Ge\textsubscript{5}\textsuperscript{2−}, only a few months ago.\textsuperscript{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\textsubscript{9}\textsuperscript{4+} cluster described here completes the series of E\textsubscript{9}\textsuperscript{4+} in this group (carbon excluded). Work on its extraction into solution is in progress.

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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, 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.

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