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The Cluster Anion Si_9^{4-}

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Dedicated to Professor Achim Müller
on the occasion of his 60th birthday

The 40 valence electron cluster anions E_9^{4-} of the Group 14 (E14) elements Ge, Sn, and Pb have been known for many years. These anions form monocapped square antiprisms (SAPRS-9)—that is, the framework of a 22e *nido*-E_{10} Wade cluster—as shown by the investigations of Kummer et al.,[1] Corbett et al.,[2] and Fässler et al.[3] Until recently, it appeared certain that these cluster anions are only formed by the reactions of intermetallic phases with suitable solvents.[4] However, the existence of the isolated anions in these binary phases of the alkali metals M = Na, K, Rb, Cs was then established.[5, 6] Besides X-ray structure analyses, the successful stepwise thermal decomposition of the alkali metal tetrahedranides ME (M_4E_4), the quantitative analysis of the vibrational spectra, and the quantum chemical calculation of these spectra proved be essential tools in our investigations.[5] The binary compounds $M_{12}E_{17} = M_{12}[(E_4)_2E_9] = ME_{1.42}$ and $M_4E_9 = ME_{2.25}$, which contain the cluster anions E_4^{4-} and E_9^{4-}, were identified as well as clathrates of the types $M_6E_{25} = ME_{4.17}$,[7] $M_8E_{44}\square_2 = ME_{5.50}$, and M_xE_{136} $(5 \leq x \leq 12) \approx ME_{11-27}$. These results also suggested a route to the elusive Si_9^{4-}, for which no evidence for its existence was available.

The thermal decomposition of the alkali metal monosilicides MSi (M_4Si_4) by Schäfer and Klemm[8] 40 years ago only led to the clathrates $M_8Si_{44}\square_2$ in steep thermogravimetric (TG) steps, as was also observed for the germanides. We have now reinvestigated these reactions in a Knudsen cell under dynamic vacuum[9] and found the following:

1. In the thermal decomposition of NaSi, a distinct step appears for $NaSi_{2.3}$ (Na_4Si_9 ?), followed very quickly by the steps for the clathrates Na_6Si_{25} and $Na_8Si_{44}\square_2$, and then by that of Na_xSi_{136}.
2. According to DTG investigations, the thermal decomposition of KSi and RbSi passes through two steps close to KSi_2 and $RbSi_2$. However, only the later formed clathrates M_6Si_{25}, $M_8Si_{44}\square_2$, and M_xSi_{136} can be characterized unambiguously.
3. The thermal decomposition of CsSi (Cs_4Si_4) starts at 500 K and passes through three distinct steps at 630, 690, and 850 K (Figure 1). These steps represent the formation and decomposition of several phases, and these processes overlap over appreciable temperature intervals. The quantitative analysis of the DTG curves show that the mass loss at A corresponds to the formation and decomposition of the cluster phase $CsSi_{1.3}$ and the formation of the phase cluster $CsSi_{2.2}$. Before the formation of the latter is complete, its decomposition into the clathrate phases $CsSi_{4.2}$ and $CsSi_{5.5}$ commences (at B). The slightly declining TG plateau between 690 and 800 K indicates that the transformation into $CsSi_{5.5}$ needs a longer period of time. The mass loss at C corresponds to the formation of the clathrate phase Cs_xSi_{136} ($x \approx 10-12$, $CsSi_{11-14}$), which subsequently decomposes to silicon (ca. 1050 K). The phases identified here are direct analogues of the germanides and stannides of the types $M_{12}E_{17}$, M_4E_9, M_6E_{25}, $M_8E_{44}\square_2$, and M_xE_{136}.[5]

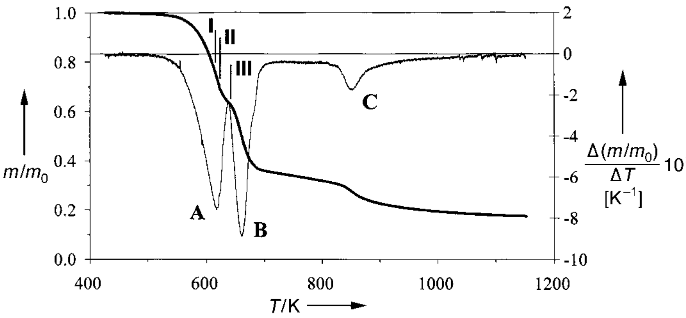

Figure 1. Thermal decomposition of Cs_4Si_4 in a Knudsen cell under dynamic vacuum (TG: bold lines; DTG: thin lines, m_0 = sample mass). See text for details of the analysis of the mass losses A–C and of products **I**–**III**.

We then tried to isolate individual phases during the decomposition. All attempts to characterize these phases by X-ray diffraction failed. Upon disappearance of the reflections of the M_4Si_4 phases, X-ray amorphous products were formed. After annealing for several weeks, these products gave sharp diagrams, but with many reflections of low intensity. We therefore applied Raman spectroscopy to the characterization of the phases close to $CsSi_2$.[10] We used three samples from region A (Figure 1), which were obtained by stopping the decomposition reaction.

The vibrations of the tetrahedranide anions E_4^{4-} (E = Si, Ge, Sn) have been described in detail by Kliche et al.[11] These

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anions are characterized by three intensive bands or groups of bands, which for Si_4^{4-} appear at 290, 355, and 480 cm^{-1}. The Raman spectra of the alkali metal compounds M_4E_9 and $M_{12}E_{17}$ showed that the cluster anions E_9^{4-} do also have simple characteristic vibrational patterns, the frequencies of which can be used for their identification.[5] In particular, the almost constant ratio of the breathing frequencies is important: $\kappa = \tilde{\nu}(E_9)/\tilde{\nu}(E_4) = 220:274 = 0.81$ (Ge) and $152:185 = 0.82$ (Sn). With $\tilde{\nu}(Si_4) = 475\ cm^{-1}$ for Cs_4Si_4 and $\kappa = 0.81$, we can thus expect $\tilde{\nu}(Si_9)$ at 385–390 cm^{-1}.

The product **I** at $m/m_0 = 0.76$ exhibits, besides the typical bands of the Si_4^{4-} anion at 282, 355, and 475 cm^{-1}, a new strong band at 387 cm^{-1} (Figure 2), which gains intensity at $m/m_0 = 0.69$ (**II**) and with a wavenumber of 386 cm^{-1} is the most intense band in the spectrum of **III** at $m/m_0 = 0.58$. Simultaneously, the intensity of the Si_4 bands decreases, and they are absent from the spectrum of **III**. Besides the band at 386 cm^{-1}, the weaker bands at 295 and 250 cm^{-1} can now be clearly seen. For the homologues Ge and Sn, several compounds exist in the region M:E ≈ 1:2. Among these, $M_{12}E_{17}$ ($ME_{1.42}$) and M_4E_9 ($ME_{2.25}$) are very well characterized.[5, 6] Both phases contain isolated cluster anions E_9^{4-}, which in $M_{12}E_{17}$ exist together with the anions E_4^{4-} in the ratio $E_9:E_4 = 1:2$. The spectra of the decomposition products **I**–**III** of Cs_4Si_4 indicate a similar situation in the system Cs–Si. The spectrum of **III** characterizes a substance which contains only the anions Si_9^{4-} (Cs_4Si_9). In principle, the anion Si_5^{2-} might have formed at the composition $CsSi_{2.5}$. However, in this case $\kappa = \tilde{\nu}(E_5)/\tilde{\nu}(E_4) = 0.98$ (E = Ge, Sn) would lead to an expected breathing frequency of $\tilde{\nu}(Si_5) = 465\ cm^{-1}$, which is clearly missing.

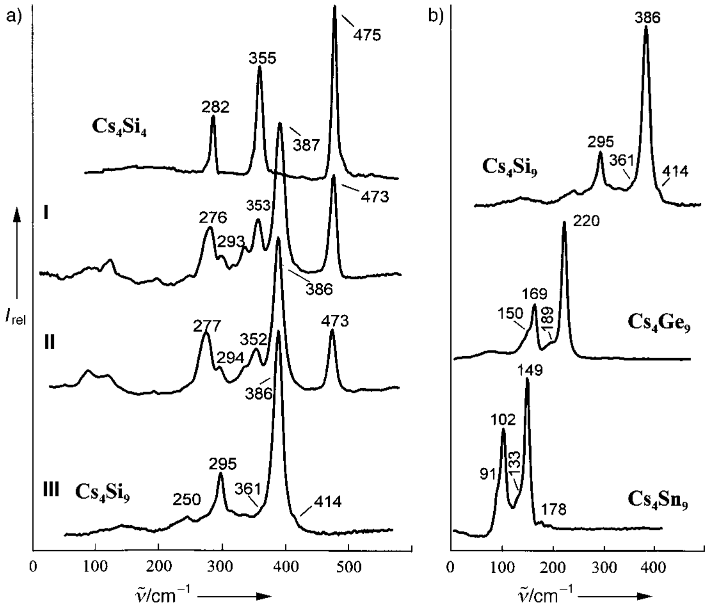

Figure 2. a) Raman spectra of Cs_4Si_4 and of the reaction products **I**–**III**. b) Comparison of the Raman spectrum of the decomposition product Cs_4Si_9 with those of Cs_4Ge_9 and Cs_4Sn_9.[5]

As in the case of the homologues Ge_9^{4-} and Sn_9^{4-}, the structure and the Raman spectrum of the anion Si_9^{4-} were calculated by quantum chemical methods.[12] The optimization of the bare anion Si_9^{4-} indicated, as for Pb_9^{4-},[14] that the configuration with the symmetry 4*mm* (C_{4v}) is a minimum on the potential energy surface, but with very small energy differences to other arrangements. For example, a configuration with $\bar{6}m2$ (D_{3h}) symmetry is only 2.5 $kJ\,mol^{-1}$ less stable. It is a degenerate transition state with an imaginary vibrational mode of E' symmetry. Figure 3a shows the optimized structure with 4*mm* (C_{4v}) symmetry. No experimental comparison was available for this structure (see below). However, an indirect comparison is possible by means of the ratios of the corresponding bond lengths d_i(E–E) in the known clusters Ge_9 and Sn_9. These ratios agree well with those of the E14 diamond structures (d(Si–Si)/d(Ge–Ge) = 0.960, d(Si–Si)/d(Sn–Sn) = 0.837).

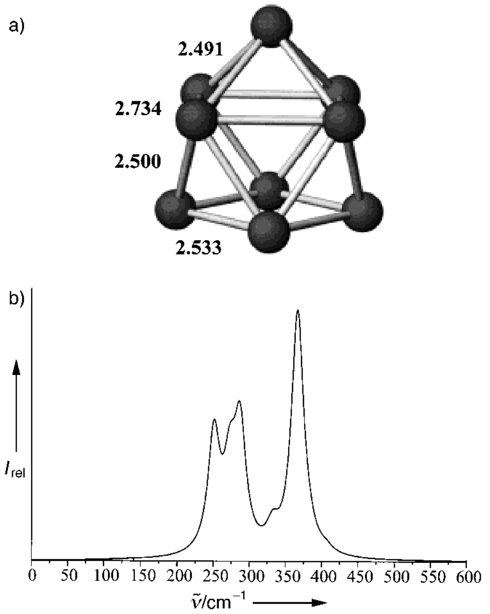

Figure 3. a) Quantum chemically optimized structure of the Si_9^{4-} anion (point symmetry 4*mm*) with bond lengths [Å]. b) Calculated Raman spectrum of the Si_9^{4-} anion (see also Figure 2b).

The calculated Raman frequencies and intensities agree well with the experimental data (Figures 2b and 3b). For the breathing mode, $\tilde{\nu}(Si_9) = 367\ cm^{-1}$ (experimental: 386 cm^{-1}). Discrepancies in the intensities may be caused by systematic errors in the calculation on the isolated anion (large negative charge of the relatively small cluster anion; deviations from 4*mm* (C_{4v}) symmetry due to the influence of the surrounding cations or of packing effects in the crystal).

Together with the thermogravimetric measurements, the spectroscopic and quantum chemical results leave no doubt that binary compounds of the anion Si_9^{4-} are formed during the controlled thermal decomposition of cesium monosilicide.

We attempted to prepare silicides of the types $M_{12}E_{17}$ und M_4E_9 directly from the elements, in analogy to the corresponding germanides and stannides[5, 6] (e.g., Cs:Si = 4:9; sealed Nb ampoules, reaction at 1000 K for 1 h; annealing at 675 K for several days). The X-ray powder diagrams of products with the compositions $Cs_{12}Si_{17}$ and Cs_4Si_9 showed, in addition to reflections for Cs_4Si_4 and Si, numerous weak and diffuse reflections, which could not be indexed. Variations of temperature (575–875 K) and annealing times did not give significant improvements. However, the diffraction pattern is in all cases reproducible. The Raman spectra are very similar to those of the decomposition products. The band at 386 cm^{-1} (Si$_9^{4-}$) is distinctly recognizable. The other bands found at 475 and/or 480 cm^{-1}, and at 353, 334, and 278 cm^{-1} and/or 519 cm^{-1}, may be assigned to the anion Si$_4^{4-}$ and to elemental silicon. Even though no new products that exhibit only the spectrum of the anion Si$_9^{4-}$ were obtained by this route, the synthesis from the elements Cs and Si does clearly produce compounds with this anion.

Meanwhile, our results have been confirmed by the investigations of Quéneau et. al.[16] who isolated the compound Rb$_{12}$Si$_{17}$ and elucidated its crystal structure. In full accordance with our predictions,[5] this structure contains the clusters Si$_4^{4-}$ and Si$_9^{4-}$. The bond lengths obtained from the structural analysis (d(Si–Si) = 2.40, 2.64, 2.37, 2.38 Å) largely agree with our values (Figure 3a), but are generally somewhat smaller. This might be due to the quality of the experimental data ($R_F = 0.176$; $I > 2\sigma(I)$). In any case, it is clear that a combination of structural analyses, quantum chemical methods, and quantitative analyses of the vibrational spectra can prove,[5] and allow more than to suggest,[17] the existence of new cluster compounds.

Received: April 6, 1997 [Z11687IE]
German version: *Angew. Chem.* **1998**, *110*, 2507–2509

Keywords: ab initio calculations · clusters · Raman spectroscopy · silicon · thermogravimetry

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[10] Spectroscopic investigations have also been carried out in the systems with sodium, potassium, and rubidium. Only in the system Rb–Si could characteristic bands of the Si$_9^{4-}$ anion be observed.

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[12] The structure of Si$_9^{4-}$ was optimized at the HF/6-31G(D) level in point symmetry 4*mm* (C_{4v}) with the Gaussian 94 program.[13] The harmonic vibrational frequencies and Raman intensities were calculated analytically. It is not expected that Si$_9^{4-}$ as a free anion in the gas phase will be stable with respect to electron loss. Nevertheless, sufficiently accurate structures and vibrational spectroscopic data should be obtainable with the medium-sized 6-31G(D) basis set employed. It is known that a limited basis set disfavors the removal of electrons and thus approximately simulates a confining positive potential in the condensed phase (cf. P. Pyykkö, Y. Zhao, *J. Phys. Chem.* **1990**, *94*, 7753). The Hartree–Fock method was preferred to the currently very popular density functional methods for two reasons: a) The usual density functionals in our experience give bonds that are too long and stretching frequencies that are too low for heavy p-block main group elements. This holds for the heavier E$_9^{4-}$ ions and also for neutral molecules (M. Kaupp, *Chem. Ber.* **1996**, *129*, 535). b) For technical reasons, the calculation of Raman intensities with density functional methods is presently not possible in the Gaussian 94 program.

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Self-Organization of a Heteroditopic Molecule to Linear Polymolecular Arrays in Solution**

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Nature displays a variety of supramolecular structures within a scale of 1 to 100 nm, beautifully put together with relatively simple building blocks by means of self-organization.[1] Over the last few decades chemists have elegantly adopted a variety of noncovalent bonding interactions to construct supramolecular architectures in the way that Nature does it.[2] The versatility and efficiency of utilizing such noncovalent forces[3] inspired us to design and to prepare a heteroditopic molecule to create linear oligo- and polymolecular arrays self-organized in solution by host–guest complexation.[4]

The synthetic methodology employed for **3** from **1a**[5] is depicted in Scheme 1. According to CPK models, the

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[**] This work was supported by the National Science Foundation (USA) through Individual Investigator Award CHE-95–21738. The authors thank Dr. Philip Mason for valuable discussions on the interpretation of the ^{1}H NMR data.