DOI: 10.1002/ejic.200900230

Si_9^{4-} Anions in Solution – Structures of the Solvates $Rb_4Si_9 \cdot 4.75NH_3$ and $[Rb(18\text{-crown-6})]Rb_3Si_9 \cdot 4NH_3$, and Chemical Bonding in Si_9^{4-}

Stefanie Joseph,[a] Christof Suchentrunk,[a] Florian Kraus,[b] and Nikolaus Korber*[a]

Keywords: Zintl anions / Silicon / Cluster compounds / Ab initio calculations / ELF (Electron Localisation Function)

Dissolving the ternary material $K_6Rb_6Si_{17}$ together with chelating ligands such as 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), dibenzo-18-crown-6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadecane) and [2.2.2]cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) in liquid ammonia yields the solvates $Rb_4Si_9 \cdot 4.75NH_3$ and $[Rb(18\text{-crown-6})]Rb_3Si_9 \cdot 4NH_3$. Single-crystal X-ray diffraction analysis reveals the presence of Si_9^{4-} anions, the existence of which in solution has been a matter of discussion until now. In both compounds, the Si_9^{4-} cages display slightly distorted monocapped square-antiprismatic shapes. Additionally, quantum chemical calculations, NBO analysis and ELF (electron localisation function) considerations have been made to gain a deeper insight into the chemical bonding of this Zintl anion. The ELF analysis shows that, whereas the Wade–Mingos–Williams rules obviously apply for the prediction of the molecular shape of the anions, no evidence for three-centre two-electron bonding can be found.

Introduction

Homoatomic Zintl anions of group 14 elements are a versatile and fascinating class of polyanions, the chemistry of which has experienced a renaissance in recent years.[1] They are especially interesting when they can be handled in solution where they undergo a variety of reactions with different kinds of reagents.[2] By far the most important homoatomic polyanions of group 14 elements are the nine-atom clusters. The highest reduced E_9^{4-} anions (E = Si to Pb) are known for all the heavier homologues of group 14 in the solid state phases A_4E_9 and $A_{12}E_{17}$ (A = Na to Cs).[3] The lower charged nonatetrelide anions E_9^{3-} are found in solvate structures of the same elements[4] whereas the highest oxidised E_9^{2-} anions have only been described for E = Si and Ge.[5] Solvate structures of the highest charged species E_9^{4-} have been reported for E = Ge, Sn and Pb.[6] A very versatile solvent for the extraction or generation of Zintl anions is liquid ammonia. Due to this fact, a multitude of ammoniate structures of Zintl anions have been described in the past.[7] Liquid ammonia was also crucial in preparing the first nonasilicide solvates a few years ago.[4a] If one compares the nonasilicide anions in compounds from solid-state reactions with the ones found in solution experiments, a discrepancy becomes evident. In the few solvate structures reported up to now, only Si_9^{2-} or Si_9^{3-} anions have been found (Table 1). No Si_9^{4-} cluster has so far been described outside of binary or ternary solids prepared by high-temperature routes. Therefore, it seems as if an extraction into solution implicates oxidation of the nonasilicide clusters Si_9^{4-} to yield the lower charged Si_9^{2-} and Si_9^{3-} anions.

Table 1. Hitherto known compounds prepared from solution, which contain bare nine-atom clusters of silicon.[4a,5a]

Si_9^{2-}	Si_9^{3-}
$[K(18\text{-crown-6})]_2Si_9 \cdot py$	$[K(crypt)]_3Si_9 \cdot 8NH_3$
	$[Rb(crypt)]_6Si_9Si_9 \cdot 6{,}3NH_3$
	$[K(crypt)]_3Si_9 \cdot 2{,}5py$

It was suggested by Sevov et al. that the highly charged Si_9^{4-} ion loses an electron during dissolution in liquid ammonia and that these species therefore form either in very small concentrations or not at all under such conditions.[4a] The chemical bonding situation in and the shape of E_9^{n-} clusters has been described by using the Wade–Mingos–Williams rules[8] due to the electron-deficient character of the bonds. In this context, it is interesting if quantum chemical calculations on Si_9^{n-} cages could reveal the existence of delocalised interactions, e.g. 2e3c bonds.

Here we report the successful extraction, without oxidation, of nonasilicide anions in liquid ammonia and two ammoniate crystal structures containing the as yet missing Si_9^{4-} anion, which completes the group 14 series of solvates of nonatetrelide tetraanions. Additionally, we carried out quantum chemical calculations, an NBO analysis, and ELF examinations to elucidate the bonding situation in Si_9^{4-} anions.

[a] Institut für Anorganische Chemie, Universität Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany
Fax: +49-941-943 1812
E-mail: nikolaus.korber@chemie.uni-regensburg.de
[b] Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

Results and Discussion

It has been known for a long time that the compounds $K_{12}Si_{17}$ and $Rb_{12}Si_{17}$ contain both Si_9^{4-} and Si_4^{4-} anions.[9,13] For our extraction experiments, we used a mixed cation material of the nominal composition $K_6Rb_6Si_{17}$. Only the Rb cations appear in the crystalline products characterised by X-ray crystallography.

Crystal Structure of $Rb_4Si_9 \cdot 4.75NH_3$

The asymmetric unit of the crystal structure of $Rb_4Si_9 \cdot 4.75NH_3$ (**1**) contains four crystallographically independent nonasilicide clusters, 16 rubidium cations and 19 ammonia molecules. The rubidium cations occupy 20 positions of which 14 positions have a site symmetry of one. Six rubidium cations occupy the special Wykoff positions 2*a* and 2*b* and thus, according to the site symmetry of 3, each contributes a positive charge of 1/3. Altogether there are 16 positive charges, which have to be compensated for in the structure by four Si_9 cage molecules of which all silicon atoms are situated on general positions possessing a site symmetry of 1. As there is no indication that any of the ammonia molecules are deprotonated and in fact exist as amide anions, the nonasilicide clusters are assigned a fourfold negative charge, one of them is shown in Figure 1. All distances within the clusters of **1** are given in Table 2. The occurrence of four crystallographically independent clusters with similar dimensions is also known for the solid-state phase $Rb_{12}Si_{17}$.[9,13]

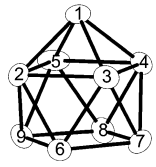

Figure 1. One of the four crystallographically independent Si_9^{4-} anions in **1**. The numbering scheme refers to the assignment in Table 2.

Each silicide cluster in **1** is coordinated by 10 to 13 rubidium cations at distances between 3.480 and 3.990 Å which span edges or reside on triangular or quadrangular faces. The nonasilicide anions are connected by means of common rubidium cations to form a rubidium–Si_9 network. Each rubidium cation is additionally coordinated by 3 to 4 ammonia molecules within a distance between 2.980 and 3.380 Å. A differentiation due to the Wykoff positions occupied by the rubidium cations can be made: along the threefold rotation axis, a strand consisting of ammonia molecules, rubidium cations and Si_9^{4-} anions is built from rubidium cations occupying the Wykoff position 2*b*. A second kind of strand of the same manner can be found along the 6_3 screw axis with rubidium ions on position 2*a* acting as bridging cations (Figure 2). According to the special positions of the rubidium cations the strand along the 6_3 screw axis is found only once, whereas the strand along the threefold rotation axis is observed twice per unit cell. The remaining ammonia molecules and rubidium cations on general positions 6*c* generate aggregates (Figure 3) and are situated between these strands. Overall a dense 3D rubidium–Si_9–ammonia network is generated.

Table 2. Atom distances in the Si_9^{4-} anions of **1** and **2**. For numbering scheme see Figure 1.

	Cluster 1 in **1** [Å]	Cluster 2 in **1** [Å]	Cluster 3 in **1** [Å]	Cluster 4 in **1** [Å]	Cluster in **2** [Å]
Si1–Si2	2.451(4)	2.464(3)	2.444(3)	2.459(3)	2.473(3)
Si3	2.455(3)	2.442(3)	2.451(4)	2.445(3)	2.468(3)
Si4	2.423(4)	2.439(3)	2.443(4)	2.452(3)	2.451(3)
Si5	2.446(4)	2.455(3)	2.470(4)	2.436(3)	2.450(3)
Si2–Si3	2.541(3)	2.587(3)	2.557(3)	2.615(3)	2.660(3)
Si5	2.881(4)	2.729(3)	2.798(3)	2.761(4)	2.650(4)
Si6	2.444(4)	2.481(3)	2.437(3)	2.446(3)	2.439(3)
Si9	2.465(5)	2.457(3)	2.441(3)	2.467(4)	2.462(3)
Si3–Si4	2.748(3)	2.781(3)	2.757(4)	2.679(3)	2.646(3)
Si6	2.519(3)	2.438(4)	2.444(3)	2.471(3)	2.475(3)
Si7	2.479(3)	2.444(4)	2.470(3)	2.467(4)	2.453(3)
Si4–Si5	2.633(4)	2.619(3)	2.586(4)	2.650(4)	2.710(3)
Si7	2.441(4)	2.449(4)	2.466(4)	2.464(4)	2.456(3)
Si8	2.481(4)	2.450(3)	2.462(3)	2.468(3)	2.458(3)
Si5–Si8	2.460(4)	2.478(3)	2.435(3)	2.418(4)	2.467(3)
Si9	2.416(4)	2.454(3)	2.462(4)	2.444(4)	2.460(3)
Si6–Si7	2.429(4)	2.480(4)	2.433(4)	2.454(4)	2.451(3)
Si9	2.429(4)	2.482(4)	2.452(3)	2.471(3)	2.454(3)
Si7–Si8	2.448(4)	2.464(4)	2.453(3)	2.477(4)	2.496(3)
Si8–Si9	2.431(5)	2.471(3)	2.476(3)	2.469(4)	2.451(3)
Si6–Si8 = *d*1	3.105(5)	3.304(3)	3.303(3)	3.435(4)	3.504(3)
Si7–Si9 = *d*2	3.732(4)	3.676(3)	3.623(3)	3.544(4)	3.473(3)
*d*2/*d*1	1.20	1.11	1.10	1.03	1.01

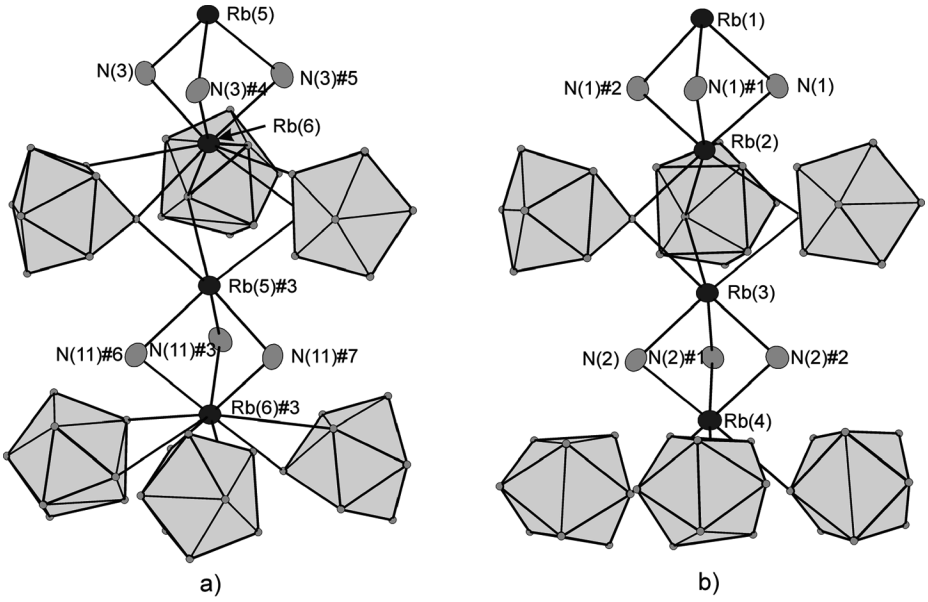

Figure 2. Rb–NH_3–Si_9 strands along the *c* axis in **1**. (a) Strand along the 6_3 screw axis. (b) Strand along the threefold rotation axis. Symmetry operations to generate equivalent atoms: #1: 1 – *y*, 1 + *x* – *y*, *z*; #2: –*x* + *y*, 1 – *x*, *z*; #3: 1 + *x* – *y*, *x*, 0.5 + *z*; #4: 1 – *x* + *y*, 2 – *x*, *z*; #5: 2 – *y*, 1 + *x* – *y*, *z*; #6: *y*, 1 – *x* + *y*, *z*; #7: 2 – *x*, 2 – *y*, 0.5 + *z*. H atoms of the ammonia molecules are omitted for clarity.

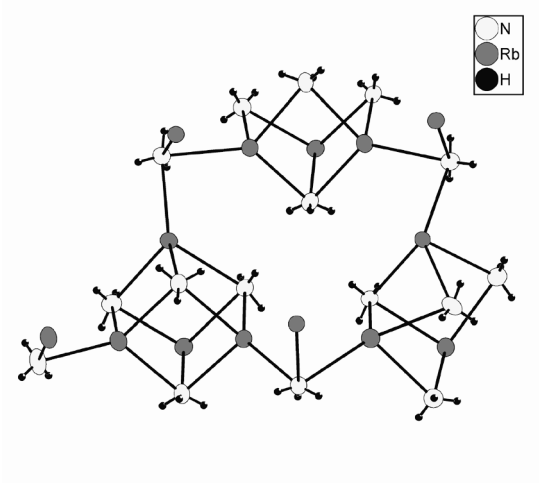

Figure 3. Rb–NH_3 aggregates which are situated between the strands.

Crystal Structure of [Rb(18-crown-6)]Rb_3Si_9·4NH_3

The asymmetric unit of [Rb(18-crown-6)]Rb_3Si_9·4NH_3 (**2**) contains one Si_9^{4-} anion, four crystallographically independent rubidium cations and four ammonia molecules as well as the crown ether molecule. One of the four ammonia molecules shows disorder, which could be resolved during the refinement by applying a split model (ratio 0.5:0.5). The anion is coordinated by seven rubidium cations with distances between 3.460 and 3.980 Å. Six of these cations are additionally coordinated by ammonia molecules at distances of 2.920 and 3.240 Å. One of the rubidium cations lies in the cavity of an 18-crown-6 molecule and is not further coordinated by ammonia. In contrast to the 3D network of Rb_4Si_9·4.75NH_3, 2D extended double layers are formed in the current system due to the network-breaking character of 18-crown-6 (Figure 4).

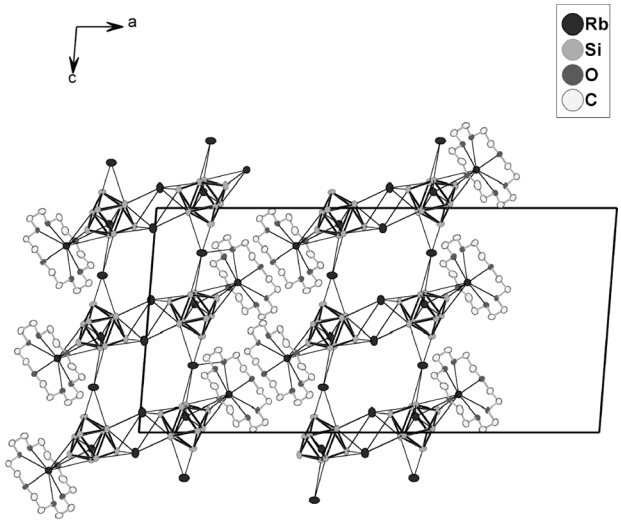

Figure 4. Rb^+–Si_9^{4-} double layers in **2**, which are separated by 18-crown-6 molecules.

The dimensions of the anion are also given in Table 2. Taking a closer look at the double layer along the *c* axis, tubes inside the structure generated by the ionic interactions between rubidium cations and Si_9^{4-} anions can be observed. The diameter of the tubes is 6.9 Å (Figure 5). Inside these tubes, disordered molecules of ammonia are situated. The nonasilicide anions in **1** and **2** are both distorted from the ideal monocapped square-antiprismatic shape, which one would expect for a fourfold negatively charged nine-atom cluster of a group 14 element. A good first indication of

Table 3. Two average values and standard deviations of the two distance groups found for the cluster in **2**.

	Bond lengths of the capped square of the cluster in **2**	Remaining bond lengths of the cluster in **2**
d(Si–Si)$_{average}$ [Å][a]	2.667	2.460
σ(Si–Si) [Å][b]	0.029	0.013
σ(Si–Si) [%]	1.1	0.6

[a] $d(Si-Si)_{Average} = \bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$. [b] $\sigma(Si-Si) = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}$.

this distortion is the ratio of the diagonals of the uncapped quadrangular face, which is ideally one for a monocapped square antiprism. For a more detailed consideration, the tilt angles of the triangular faces can be taken into account. For an ideal cluster with C_{4v} symmetry the tilt angles α1 to α4 should have the same value, whereas α5 ought to be 0 ° (Table 4). It can be easily seen from Tables 2 and 4 that the nonasilicide cages in **1** are considerably more distorted than the cages observed in **2**, which probably results from the much closer packing in **1**. Due to the rather symmetric appearance of the cage in **2**, an error analysis was carried out, which considered all the bond lengths and the angles of the cage. For a monocapped tetragonal antiprism one expects two significantly differing bond lengths: on the one hand the distances of the capped square (Si2–Si5) and on the other hand the remaining distances.[13] Table 3 shows the average values and the corresponding standard deviations of these two groups of distances.

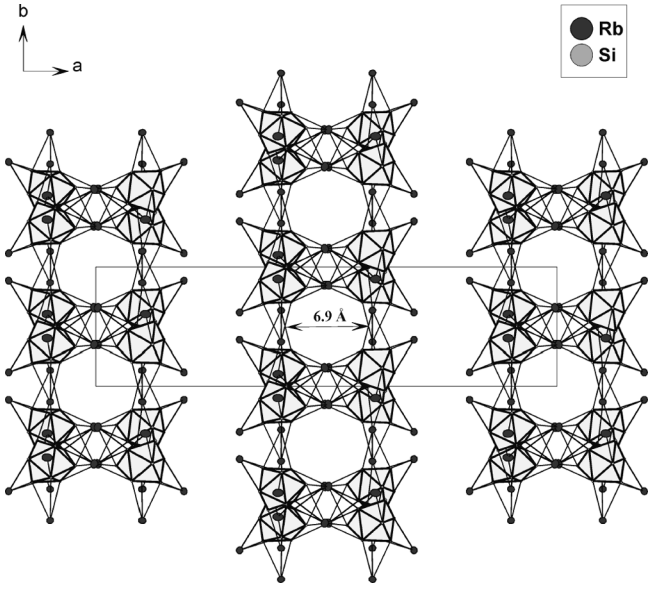

Figure 5. Tubes inside the double layers built from Rb^+ cations and Si_9^{4-} anions. Ammonia molecules inside the tubes and 18-crown-6 molecules are omitted for clarity.

It can be easily seen that they only differ within small tolerances. A larger deviation can be observed for the tilt angles according to Table 4, which altogether leads approximately to a point group C_{4v} within a tolerance of 3.7%. The crystallographic point group of the cage in **2** is of course C_1. The fact that all silicon atoms are situated on general positions results in all the clusters having unique shapes. These are not enforced by crystallographic symmetry but, rather, reflect the real nature of the clusters. For nonastannide clusters Sn_9^{4-}, fluxional behaviour not only in solution but also in the solid state was detected by NMR spectroscopy.[10] For nonasilicide clusters no such observations have been made so far, and it can be safely assumed that they are much more rigid than the heavier homologues.

Table 4. Tilt angels of the Si_9^{4-} anions in **1** and **2**.

	Angle	Tilted triangular faces		Value [°]
Cluster 1 in **1**	α_1	Si(1)–Si(2)–Si(3)	Si(2)–Si(3)–Si(6)	37.0(3)
	α_2	Si(1)–Si(4)–Si(5)	Si(4)–Si(5)–Si(8)	40.6(4)
	α_3	Si(3)–Si(4)–Si(7)	Si(1)–Si(3)–Si(4)	25.6(7)
	α_4	Si(1)–Si(2)–Si(5)	Si(2)–Si(5)–Si(9)	21.9(2)
	α_5	Si(6)–Si(7)–Si(8)	Si(6)–Si(8)–Si(9)	11.2(4)
Cluster 2 in **1**	α_1	Si(1)–Si(2)–Si(3)	Si(2)–Si(3)–Si(6)	33.9(3)
	α_2	Si(1)–Si(4)–Si(5)	Si(4)–Si(5)–Si(8)	34.1(2)
	α_3	Si(3)–Si(4)–Si(7)	Si(1)–Si(3)–Si(4)	23.1(4)
	α_4	Si(1)–Si(2)–Si(5)	Si(2)–Si(5)–Si(9)	26.1(6)
	α_5	Si(6)–Si(7)–Si(8)	Si(6)–Si(8)–Si(9)	7.1(7)
Cluster 3 in **1**	α_1	Si(1)–Si(2)–Si(3)	Si(2)–Si(3)–Si(6)	34.4(7)
	α_2	Si(1)–Si(4)–Si(5)	Si(4)–Si(5)–Si(8)	34.3(0)
	α_3	Si(3)–Si(4)–Si(7)	Si(1)–Si(3)–Si(4)	25.4(5)
	α_4	Si(1)–Si(2)–Si(5)	Si(2)–Si(5)–Si(9)	23.(5)
	α_5	Si(6)–Si(7)–Si(8)	Si(6)–Si(8)–Si(9)	6.3(1)
Cluster 4 in **1**	α_1	Si(1)–Si(2)–Si(3)	Si(2)–Si(3)–Si(6)	32.1(7)
	α_2	Si(1)–Si(4)–Si(5)	Si(4)–Si(5)–Si(8)	30.3(8)
	α_3	Si(3)–Si(4)–Si(7)	Si(1)–Si(3)–Si(4)	29.0(0)
	α_4	Si(1)–Si(2)–Si(5)	Si(2)–Si(5)–Si(9)	25.9(5)
	α_5	Si(6)–Si(7)–Si(8)	Si(6)–Si(8)–Si(9)	2.4(0)
Cluster in **2**	α_1	Si(1)–Si(2)–Si(3)	Si(2)–Si(3)–Si(6)	28.8(1)
	α_2	Si(1)–Si(4)–Si(5)	Si(4)–Si(5)–Si(8)	27.1(1)
	α_3	Si(3)–Si(4)–Si(7)	Si(1)–Si(3)–Si(4)	29.12(8)
	α_4	Si(1)–Si(2)–Si(5)	Si(2)–Si(5)–Si(9)	29.6(1)
	α_5	Si(6)–Si(7)–Si(8)	Si(6)–Si(8)–Si(9)	1.1(2)

Chemical Bonding in Si_9^{4-}

Despite the distortions of the nonasilicide cages in **1** and **2**, all of them are much closer to the shape of a monocapped square antiprism than to the competing nine-atom cage structure, i.e. the threefold capped trigonal prism. This is in accordance with the Wade–Mingos–Williams rules,[8] which predict monocapped square-antiprismatic geometries for a fourfold negatively charged nine-atom species with 22 cluster-bonding electrons. With the aid of the electron localisation function (ELF)[11] and the NBO analysis, we have tried to gain deeper insights into the chemical bonding of Si_9^{4-}. Since one can apply the Wade–Mingos–Williams rules and the 3c−2e bond to silicides like Si_9^{4-}, we were especially interested in the comparison of the ELF of Si_9^{4-} with that

of boranes, i.e. are there three-centre bonds in Si_9^{4-}, or can it be described by a classical Lewis formula? We have carried out ab initio calculations on the Si_9^{4-} anion with Gaussian03[12] at the HF/6-311+G(3df) level of theory in D_{3h} and C_{4v} symmetry and performed single-point calculations using the crystallographic structures of Si_9^{4-} and $Rb_{12}Si_9^{8+}$. Since all calculations with various methods on the D_{3h} symmetric structure of Si_9^{4-} led to transition states of the second order they will not be discussed further. Figure 6 shows the ELF of the structure-optimised Si_9^{4-} anion in C_{4v} symmetry which is found to be a ground state in the calculations in accordance with results of earlier calculations.[13] From the ELF calculations it is evident that in the basal four-membered plane of Si_9^{4-} only four disynaptic valence basins are found connecting the Si atoms. There is no tetrasynaptic valence basin. The connection of the basal square to the upper square is also only made by disynaptic valence basins, no trisynaptic valence basins were found. The same holds true for the connection of the upper square of silicon atoms to the apical silicon atom. It is interesting to note that no disynaptic valence basins were found between the silicon atoms of the upper square. The same result was obtained from the NBO analysis − no three- or four-centre bonds were found (Figure 6).

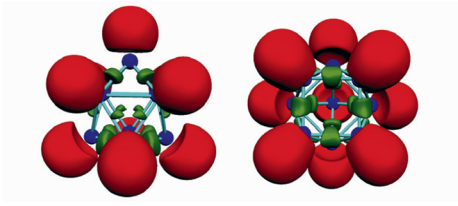

Figure 6. ELF of Si_9^{4-} in C_{4v} symmetry with $\eta(r) = 0.76$. Core basins are colour-coded blue, monosynaptic valence basins V(Si) are red and disynaptic valence basins V(Si, Si) are green.

A population analysis of the ELF basins shows all Si-core basins C(Si) to be populated with 10.01 e with a low variance of 0.37. Such values are regularly obtained for third-row elements.[14] The population of the four monosynaptic valence basins V(Si) of the silicon atoms of the basal plane is 2.29 e with a variance of 1.03, the apical Si atom has a population of 2.24 e with a variance of 0.98. The four formally negatively charged Si atoms show a population of 2.16 e with a variance of 0.99. The disynaptic valence basins V(Si, Si) (Si–Si bonds) of the basal plane are occupied by 1.43 e with a variance 0.93, and the disynaptic valence basins between the Si atoms of the basal plane and the formally negatively charged Si atoms show a population of 1.08 e with a variance 0.80, and the disynaptic valence basins between the latter and the apical Si atoms are populated with 1.36 e with a variance 0.92. The population analysis for Si_9^{4-} and $Rb_{12}Si_9^{8+}$, with shapes obtained from the X-ray structure analysis, essentially show the same results. It is easily understood that in $Rb_{12}Si_9^{8+}$, the V(Si) are a little less populated and the V(Si, Si) a little more, but the values are close to those of the naked Si_9^{4-} anion. Summing up, these results are in stark contrast to those obtained from calculations on hydro-*closo*-borates like $B_6H_6^{2-}$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ where trisynaptic valence basins, i.e. 3c–2e-like bonds are found.[15] Thus, the Wade–Williams–Mingos rules can be applied to such silicides and predict the correct type of cluster, here a *nido* cluster. However, the applicability of the Wade–Williams–Mingos rules seems not to be a conditio sine qua non for three-center two-electron bonding in these silicide cages.

Conclusions

We have been able to show that it is possible to extract Si_9^{4-} anions into liquid ammonia without accompanying oxidation. By dissolving the nominal ternary phase $K_6Rb_6Si_{17}$ in liquid ammonia, the ammoniates **1** and **2** could be crystallised, and their X-ray structures show the involvement of Si_9^{4-} anions. Quantum chemical calculations, NBO analysis and the ELF considerations showed the absence of more-centre bonds for such silicides. Nevertheless, the Wade–Mingos–Williams rules can be applied for prediction of the shape of the cluster. NMR investigations on the stability of nonasilicide anions in solution are in progress.

Experimental Section

Synthesis of $K_6Rb_6Si_{17}$: A phase with the nominal composition $K_6Rb_6Si_{17}$ was synthesised by solid-state reaction. K (0.49 g, 12.5 mmol), Rb (1.08 g, 12.5 mmol) and Si (1 g, 35.5 mmol) were placed in a Duran glass ampoule, which had been dried in vacuo before, and sealed under argon. The ampoule was placed in a second quartz glass ampoule for safety and heated to 470 °C at a rate of 10 °C h^{-1}. The temperature was maintained for 72 h. Afterwards, the product was cooled at a rate of 20 °C h^{-1}. The blue-black precursor phase was stored in a glove box under argon.

Synthesis of 1: $K_6Rb_6Si_{17}$ (0.25 g, 0.2 mmol) and dibenzo-18-crown-6 (0.074 g, 0.2 mmol) were weighed into two baked out reaction vessels which were separated by a frit. Liquid ammonia (30 mL) was condensed into each vessel, upon which the silicide immediately turned yellow. The reaction mixture was kept at a temperature of 233 K. After 7 months, [2.2.2]cryptand (0.05 g, 0.1 mmol) was added. After 12 months, yellow prism-shaped crystals could be obtained.

Synthesis of 2: $K_6Rb_6Si_{17}$ (0.2 g, 0.16 mmol) and 18-crown-6 (0.02 g, 0.076 mmol, dried for 48 h at 60 °C in vacuo) were placed in a reaction vessel which was dried previously in vacuo. Dry ammonia (ca. 15 mL) was then condensed onto the mixture. The reaction vessel was kept at 233 K for 2 months. A yellow, acicular crystal suitable for X-ray structure analysis was obtained.

X-ray Diffraction Studies: Thermally unstable, air- and moisture-sensitive crystals of **1** and **2** suitable for X-ray structure analysis were isolated and directly transferred from the mother liquor into a perfluorether oil at 213 K. The crystals were mounted onto a STOE-IPDS I diffractometer by using the crystal-cap system. Data collection was carried out at 123 K by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data reductions were performed with the STOE IPDS I program package. The structures of **1** and **2** were determined with the SHELXS-97[16] package by using direct methods and were refined anisotropically with SHELXL-97[17] against $|F^2|$ for all non-hydrogen atoms. All hydro-

Table 5. Crystal data for compounds **1** and **2**.

	1	**2**
Empirical formula	$Rb_4Si_9{\cdot}4.75NH_3$	$[Rb(C_{12}H_{24}O_6)]Rb_3Si_9{\cdot}4NH_3$
Formula mass	630.88	927.2
Colour, habit	yellow, prism	yellow, needle
Space group	$P6_3$ (no. 173)	$C2/c$ (no. 15)
a [Å]	30.540(2)	38.670(8)
b [Å]		9.920(2)
c [Å]	16.858(1)	18.980(4)
β [°]		94.51(3)
V [Å^3]	13617	7258
Z	24	8
$\rho_{calcd.}$ [g cm^{-3}]	1.997	1.691
μ [mm^{-1}]	9.05	5.690
2θ range [°]	4.62–56.24	4.64–56.14
Reflections collected	211708	8737
Independent reflections (R_{int})	22060 (0.1371)	5020 (0.1378)
Final R indices [$I > 2\sigma(I)$]: R_1, wR_2	0.0421, 0.0802	0.0776, 0.1919
Final R indices (all data): R_1, wR_2	0.0725, 0.0895	0.1122, 0.2070
Goodness-of-fit on F^2	0.832	0.887
Data/restraints/parameters	22060/1/725	5020/0/350
Largest difference peak/hole [e Å^{-3}]	0.129/–0.867	1.80/–1.57

gen atoms of 18-crown-6 and the ammonia molecules were placed in calculated positions by using a riding model (HFIX). The data sets were corrected for absorption by using the empirical methods of the PLATON[18] program package. All thermal ellipsoids of the atoms in the figures are shown at the 50% probability level. Crystallographic data of **1** and **2** are given in Table 5. CSD-417956 (**1**) and CCDC-723374 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained from http://www.fiz-karlsruhe.de/request_for_deposited_data.html (**1**) and www.ccdc.cam.ac.uk/data_request/cif (**2**).

[1] T. F. Fässler, *Coord. Chem. Rev.* **2001**, *215*, 347–377.

[2] a) S. C. Sevov, J. M. Goicoechea, *Organometallics* **2006**, *25*, 5678–5692; b) L. Yong, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1149–1153; c) L. Yong, S. D. Hoffmann, T. F. Fässler, *Eur. J. Inorg. Chem.* **2005**, *18*, 3663–3669.

[3] a) C. Hoch, M. Wendorff, C. Rohr, *J. Alloys Compd.* **2003**, *361*, 206–221; b) C. Hoch, M. Wendorff, C. Roehr, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2002**, *58*, i45–i46; c) S. Ponou, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2007**, *633*, 393–397; d) V. Queneau, S. Sevov, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1754–1756.

[4] a) J. M. Goicoechea, S. C. Sevov, *J. Am. Chem. Soc.* **2004**, *126*, 6860–6861; b) C. Suchentrunk, N. Korber, *Inorg. Chim. Acta* **2006**, *359*, 267–272; c) S. C. Critchlow, J. D. Corbett, *J. Am. Chem. Soc.* **1983**, *105*, 5715–5716; d) T. F. Fässler, M. Hunziker, *Inorg. Chem.* **1994**, *33*, 5380–5381.

[5] a) J. M. Goicoechea, S. C. Sevov, *Inorg. Chem.* **2005**, *44*, 2654–2658; b) C. H. E. Belin, J. D. Corbett, A. Cisar, *J. Am. Chem. Soc.* **1977**, *99*, 7163–7169.

[6] a) D. Kummer, L. Diehl, *Angew. Chem.* **1970**, *82*, 881; L. Diehl, K. Khodadadeh, D. Kummer, J. Strähle, *Z. Naturforsch., B: Chem. Sci.* **1976**, *31*, 522; b) A. Joannis, *C R. Hebd. Seances Acad. Sci.* **1891**, *113*, 795; E. Zintl, A. Harder, *Z. Phys. Chem.* **1931**, *154*, 47; J. D. Corbett, P. A. Edwards, *J. Am. Chem. Soc.* **1977**, *99*, 3313; C. H. E. Belin, J. D. Corbett, A. Cisar, *J. Am. Chem. Soc.* **1977**, *99*, 7163; c) J. Campbell, D. A. Dixon, H. P. A. Mercier, G. Schrobilgen, *Inorg. Chem.* **1995**, *34*, 5798.

[7] a) N. Korber, F. Richter, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1512–1514; b) N. Korber, F. Richter, *Chem. Commun.* **1996**, *17*, 2023–2024; c) E. Zintl, J. Goubeau, W. Dullenkopf, *Z. Phys. Chem., A* **1931**, *154*, 1–46; d) C. Suchentrunk, J. Daniels, M. Somer, W. Carrillo-Cabrera, N. Korber, *Z. Naturforsch., B: Chem. Sci.* **2005**, *60*, 277–283; e) N. Korber, A. Fleischmann, *J. Chem. Soc., Dalton Trans.* **2001**, *4*, 383–385.

[8] a) K. Wade, *Adv. Inorg. Chem.* **1976**, *18*, 1–66; b) D. M. P. Mingos, *Acc. Chem. Res.* **1984**, *17*, 311–319; c) R. E. Williams, *Adv. Inorg. Chem.* **1976**, *18*, 67–142.

[9] V. Queneau, E. Todorov, S. V. Sevov, *J. Am. Chem. Soc.* **1998**, *120*, 3263–3264.

[10] J. Rosdahl, T. F. Fässler, L. Kloo, *Eur. J. Inorg. Chem.* **2005**, *14*, 2888.

[11] a) A. D. Becke, K. E. J. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397–5403; b) A. Savin, A. D. Becke, J. Flad, R. Nesper, H. Preuss, H. G. von Schnering, *Angew. Chem.* **1991**, *103*, 421–424; c) A. Savin, A. D. Becke, J. Flad, R. Nesper, H. Preuss, H. G. von Schnering, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 409–412; d) B. Silvi, A. Savin, *Nature* **1994**, *371*, 683–686; e) A. Savin, R. Nesper, S. Wengert, T. F. Fässler, *Angew. Chem.* **1997**, *109*, 1892–1918; f) T. F. Fässler, A. Savin, *Chem. Unserer Zeit* **1997**, *31*, 110–120; g) A. Savin, R. Nesper, S. Wengert, T. F. Fässler, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1808–1832; h) S. Noury, X. Krokidis, F. Fuster, B. Silvi, *Comput. Chem.* **1999**, *23*, 597–604.

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Menucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, *Revision C.02*, Gaussian, Inc., Wallingford, CT, **2004**.

[13] H. G. von Schnering, M. Somer, M. Kaupp, W. Carrillo-Cabrera, M. Baitinger, A. Schmeding, Y. Grin, *Angew. Chem. Int. Ed.* **1998**, *37*, 2359–2361.

[14] a) M. Kohout, A. Savin, *Int. J. Quantum Chem.* **1996**, *60*, 875; b) F. Kraus, N. Korber, *Chem. Eur. J.* **2005**, *11*, 5945–5959; c) F. Kraus, T. Hanauer, N. Korber, *Angew. Chem.* **2005**, *117*, 7366–7370; d) F. Kraus, T. Hanauer, N. Korber, *Angew. Chem. Int. Ed.* **2005**, *44*, 7200–7204; e) F. Kraus, T. Hanauer, N. Korber, *Inorg. Chem.* **2006**, *45*, 1117–1123.

[15] a) A. Burkhardt, U. Wedig, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **1992**, *619*, 437; b) W. Hönle, Y. Grin, A. Burkhardt, U. Wedig, M. Schultheiss, H. G. von Schnering, R. Kellner, H. Binder, *J. Solid State Chem.* **1997**, *133*, 59; c) R. Kellner, N. Stöckle, R. Vaas, S. Soylemez, A. Pfitzner, H Binder, W. Hönle, Y. Grin, A. Burkhardt, M. Schultheiss, U. Wedig, J. Nuss, H.-G. von Schnering, H. Borrmann, A. Simon, *Advances in Boron Chemistry*, The Royal Society of Chemistry, London, **1997**, p. 38–45; d) H. Binder, R. Kellner, K. Vaas, M. Hein, F. Baumann, M. Wanner, R. Winter, W. Kaim, W. Hönle, Y. Grin, U. Wedig, M. Schultheiss, R. K. Kremer, H. G. von Schnering, O. Groeger, G. Engelhardt, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1059; e) F. Kraus, Dissertation, University of Regensburg, Germany **2005**.

[16] *SHELXS-97*: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[17] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**.

[18] A. L. Spek, *PLATON*, Utrecht University, The Netherlands, **2001**.

Received: March 11, 2009
Published Online: August 4, 2009

