Dissolving Silicides: Syntheses and Crystal Structures of New Ammoniates Containing Si_5^{2-} and Si_9^{4-} Polyanions and the Role of Ammonia of Crystallisation

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The dissolution of the ternary material $K_6Rb_6Si_{17}$ in liquid ammonia yields the solvate compound $Rb_4Si_9 \cdot 5NH_3$, which contains fourfold negatively charged nine atom silicon clusters Si_9^{4-}. Using additionally the [2.2.2] cryptand during the dissolution results in the solvate [K(2.2.2-crypt)]$_2Si_5 \cdot 4NH_3$, in which the Si_5^{2-} anion is present in the crystal structure. The Si_5^{2-} anion has the shape of a nearly ideal trigonal bipyramid. The starting material $K_6Rb_6Si_{17}$ contains both Si_4^{4-} and Si_9^{4-} Zintl anions. In ammoniate crystal structures, Si_9^{4-} anions are accessible independently of Si_4^{4-} anions, and ammonia of crystallisation plays a major role in the observed crystal symmetry. For the cryptate structures of Si_5^{2-} and Ge_5^{2-} anions ammonia of crystallisation is obligatory despite the loss of crystal symmetry compared to the crystal structures of the heavier homologues Pb_5^{2-} and Sn_5^{2-}.

Key words: Silicides, Zintl Anions, Liquid Ammonia, Crystal Structure Determination

Introduction

The most common bare electron-rich silicon clusters, so-called Zintl anions, are the mono-capped square antiprismatic Si_9^{4-} cage and the tetrahedral Si_4^{4-} cage, which are known as the anionic moieties in a variety of binary and ternary materials prepared by solid-state reactions [1, 2]. By contrast, the existence of silicide anions outside the solid state, especially in solution, was only recently established and is therefore not yet well understood [3 – 5].

For the heavier group 14 elements, especially the nine-atom species are of interest due to their versatile possibilities concerning chemical transformations: there is a new elemental Ge modification accessible *via* the thermal decomposition of a Ge_9^{4-}-containing starting material [6]; in solution E_9^{4-} anions act as nucleophiles as well as electrophiles towards different reactands [5, 7], and clathrate formation is possible by oxidising a binary Zintl phase in an ionic liquid [8]. Very recently, the successful preparation of new kinds of endohedral tetrel clusters containing inserted transition metal atoms spotlighted the Zintl compounds as very promising starting materials for a class of compounds which before could only be observed in the gas phase [9]. All these reaction options of bare tetrelide clusters have in common that the E_9^{4-} anions must be extractable from the solid state into solution without changing their electron count. A short time ago, we were able to show that this is also possible for the nonasilicide cluster Si_9^{4-} [10]. In the resulting solutions, a ligand exchange reaction leading to the first transition metal complex of a silicide could be performed [11].

Besides the nine atom cluster, the tetrahedral E_4^{4-} anions are well-known in solid-state materials [12], and evidence for their existence in solution was recently presented for E = Sn, Pb [13]. For E = Si, Ge, no congruent dissolution was observed yet. In contrast to that, trigonal bipyramidal E_5^{2-} cage anions are not known in solid-state compounds. They are only accessible *via* the solution route, and it is unknown how they are formed [3, 14]. The only solvent in which the dissolution of polysilicides was successful up to now is liquid ammonia [3 – 5, 10, 11].

Here we report about an ammoniate structure containing the rare Si_9^{4-} anion, which further consolidates the fact that this prototypical cluster may be

Table 1. Atomic distances (Å) in Si_9^{4-} cluster anions in the structure of $Rb_4Si_9 \cdot 5NH_3$ (**1**). For comparison, the distances in $Rb_4Si_9 \cdot 4.75NH_3$ (**3**) [10] and $[Rb(18\text{-crown-}6)]Rb_3Si_9 \cdot 4NH_3$ (**4**) [10] are given as well.

Atom1–Atom2	Cluster in **1**	Cluster 1 in **3**	Cluster 2 in **3**	Cluster 3 in **3**	Cluster 4 in **3**	Cluster in **4**
Si1–Si2	2.430(4)	2.451(4)	2.464(3)	2.444(3)	2.459(3)	2.473(3)
Si3	2.419(5)	2.455(3)	2.442(3)	2.451(4)	2.445(3)	2.468(3)
Si4	2.425(5)	2.423(4)	2.439(3)	2.443(4)	2.452(3)	2.451(3)
Si5	2.414(4)	2.446(4)	2.455(3)	2.470(4)	2.436(3)	2.450(3)
Si2–Si3	2.598(4)	2.541(3)	2.587(3)	2.557(3)	2.615(3)	2.660(3)
Si5	2.668(4)	2.881(4)	2.729(3)	2.798(3)	2.761(4)	2.650(4)
Si6	2.437(4)	2.444(4)	2.481(3)	2.437(3)	2.446(3)	2.439(3)
Si9	2.438(4)	2.465(5)	2.457(3)	2.441(3)	2.467(4)	2.462(3)
Si3–Si4	2.681(4)	2.748(3)	2.781(3)	2.757(4)	2.679(3)	2.646(3)
Si6	2.444(4)	2.519(3)	2.438(4)	2.444(3)	2.471(3)	2.475(3)
Si7	2.446(5)	2.479(3)	2.444(4)	2.470(3)	2.467(4)	2.453(3)
Si4–Si5	2.620(4)	2.633(4)	2.619(3)	2.586(4)	2.650(4)	2.710(3)
Si7	2.416(4)	2.441(4)	2.449(4)	2.466(4)	2.464(4)	2.456(3)
Si8	2.433(4)	2.481(4)	2.450(3)	2.462(3)	2.468(3)	2.458(3)
Si5–Si8	2.433(4)	2.460(4)	2.478(3)	2.435(3)	2.418(4)	2.467(3)
Si9	2.426(4)	2.416(4)	2.454(3)	2.462(4)	2.444(4)	2.460(3)
Si6–Si7	2.451(5)	2.429(4)	2.480(4)	2.433(4)	2.454(4)	2.451(3)
Si9	2.429(4)	2.429(4)	2.482(4)	2.452(3)	2.471(3)	2.454(3)
Si7–Si8	2.463(5)	2.448(4)	2.464(4)	2.453(3)	2.477(4)	2.496(3)
Si8–Si9	2.444(5)	2.431(5)	2.471(3)	2.476(3)	2.469(4)	2.451(3)
Si6–Si8 = $d1$	3.386(4)	3.105(5)	3.304(3)	3.303(3)	3.435(4)	3.504(3)
Si7–Si9 = $d2$	3.532(5)	3.732(4)	3.676(3)	3.623(3)	3.544(4)	3.473(3)
$d2/d1$	1.04	1.20	1.11	1.10	1.03	1.01

dissolved and recrystallised from solutions. Additionally, the crystal structure of the new compound $[K@crypt]_2Si_5 \cdot 4NH_3$ is presented, and the Si_5^{2-} cluster in this structure is compared to that of the known E_5^{2-} anions.

Results

Crystal structure of $Rb_4Si_9 \cdot 5NH_3$

Dissolving $K_6Rb_6Si_{17}$ in the absence of any chelating substances yields the compound $Rb_4Si_9 \cdot 5NH_3$, which contains Si_9^{4-} anions, Rb^+ cations and ammonia molecules coordinating to the alkali metal cations. In contrast to the recently published crystal structure of $Rb_4Si_9 \cdot 4.75$ NH_3 [10], where, similar to the solid-state structure of $Rb_{12}Si_{17}$, four crystallographically independent Si_9^{4-} anions are present in the asymmetric unit, the compound discussed here only contains one crystallographically independent nonasilicide anion (Fig. 1). By only slightly changing the amount of ammonia of crystallisation, the space group changes from $P6_3$ ($Rb_4Si_9 \cdot 4.75NH_3$) to the enantiomeric space group pair $P6_1/P6_5$. $P6_3$ and $P6_1/P6_5$ are connected by a non-isomorphic group-subgroup relationship ($P6_3$ is a subgroup of $P6_1/P6_5$ by tripling of the c axis of the enantiomeric space group pair $P6_1/P6_5$). However, in the case presented
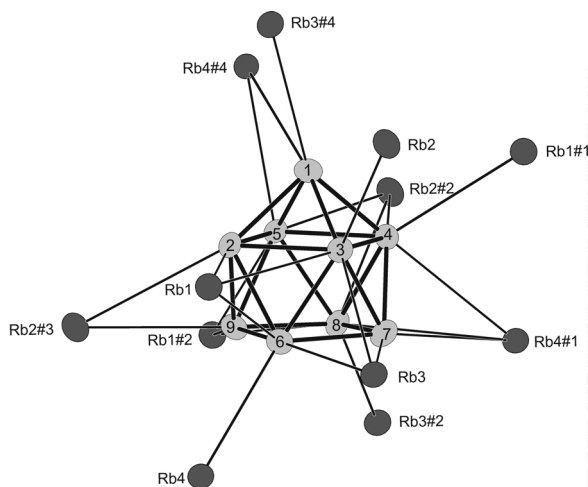

Fig. 1. Si_9^{4-} anion in $Rb_4Si_9 \cdot 5NH_3$. Shortest Rb–Si distance: Rb1#2–Si9 3.539(3) Å, longest Rb–Si distance: Rb4#4–Si1 4.099(4) Å. Displacement ellipsoids at the 50 % probability level. Symmetry operations for generating equivalent atoms: #1: 1+x, y, z; #2: 1+x, 1+y, z; #3: x, 1+y, z; #4: 1+x, 1−x+y, 1/6+z.

here, no symmetry reduction pathway leading from $Rb_4Si_9 \cdot 4.75NH_3$ to $Rb_4Si_9 \cdot 5NH_3$ may be formulated due to the much larger unit cell of the compound containing less ammonia. The emplacement of little more ammonia leads to a smaller unit cell yielding
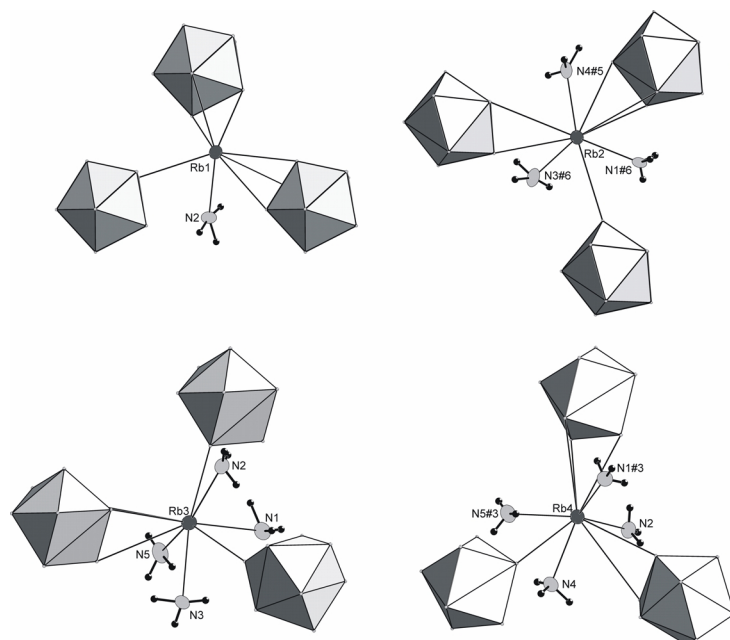
Fig. 2. Coordination spheres of the four crystallographically independent rubidium cations in $Rb_4Si_9 \cdot 5NH_3$. Rb–N distances (Å): Rb1–N2 3.210(1), Rb2–N3#6 3.131(0), Rb2–N1#6 3.436(0), Rb2–N4#5 3.295(0), Rb3–N1 3.14(0), Rb3–N2 3.215(0), Rb3–N3 3.087(0), Rb3–N5 3.01(0), Rb4–N1#3 3.20(0), Rb4–N2 3.20(0), Rb4–N4 3.19(0), Rb4–N5#3 3.081(0). Displacement ellipsoids of Rb and N atoms at the 50 % probability level. Symmetry operations for generating equivalent atoms: #3: x, $1+y$, z; #5: y, $1-x+y$, $1/6+z$; #6: $1+y$, $1-x+y$, $1/6+z$.

only one crystallographically independent nonasilicide cluster. The interatomic distances of this nonasilicide anion are very similar to those found for the anions in the solvate $Rb_4Si_9 \cdot 4.75NH_3$ and in the binary compound $Rb_{12}Si_{17}$. For these known anions, an approximated point group of C_{4v} was assumed. Based on this observation and after comparing all relevant bond lengths and angles, the Si_9^{4-} anion in the new compound $Rb_4Si_9 \cdot 5NH_3$ can also be assigned approximately C_{4v} symmetry. Table 1 shows Si–Si distances of the Si_9^{4-} anions in the known ammoniate crystal structures of $Rb_4Si_9 \cdot 4.75NH_3$ [10], [Rb(18-crown-6)]$Rb_3Si_9 \cdot 4NH_3$ [10], and $Rb_4Si_9 \cdot 5NH_3$ presented here. The ratio of the diagonals of the non-capped quadrangular face, which ideally is one for a monocapped square antiprism, gives an indication of the degree of distortion. The crystallographic symmetry of all clusters is of course C_1. Because the anion happens to be situated on the threefold screw axis but obviously has C_{4v} rather than D_{3h} symmetry, the c axis of the unit cell becomes unusually long. The anion is coordinated by all four crystallographically independent Rb^+ cations. Because of their "special" position in the unit cell, the complete first coordination sphere of the Si_9^{4-} anions sums up to 12 Rb ions (Fig. 1). The cations span edges or reside on triangular faces of the nonasilicide anion at distances between 3.435 and 4.099 Å. The coordination sphere of

the Rb cations is completed by one to four ammonia molecules (Fig. 2). The Rb–N distances are within the known range for ammonia-rubidium cation interactions. For a detailed listing of all Rb–N distances see the caption of Fig. 2. Considering only the Rb–NH_3 interactions, one-dimensional chains can be observed (Fig. 3a). This rubidium ammonia arrangement is remarkably different compared to the isolated aggregates found in the compound $Rb_4Si_9 \cdot 4.75NH_3$ containing less ammonia. The chains found in the crystal structure presented here proceed along the crystallographic axes a and b, and layers of parallel chains are arranged orthogonally in AAB sequences (Fig. 3b). The Si_9^{4-} anions are situated between these chains. Taking into account both the ionic interactions between the rubidium cations and the Si_9^{4-} clusters and the ion-dipole interactions between the cations and the ammonia molecules of solvation, a close network results, which is different from that of the already known compound with a very similar sum formula. Although the ion-dipole interactions between Rb^+ and ammonia are strong, the crystals of $Rb_4Si_9 \cdot 5NH_3$ are very sensitive to temperatures above -20 °C.

Crystal structure of (K@[2.2.2]crypt)$_2$Si$_5 \cdot 4NH_3$

If $K_6Rb_6Si_{17}$ is dissolved in the presence of the [2.2.2]-cryptand and additional substances like choline
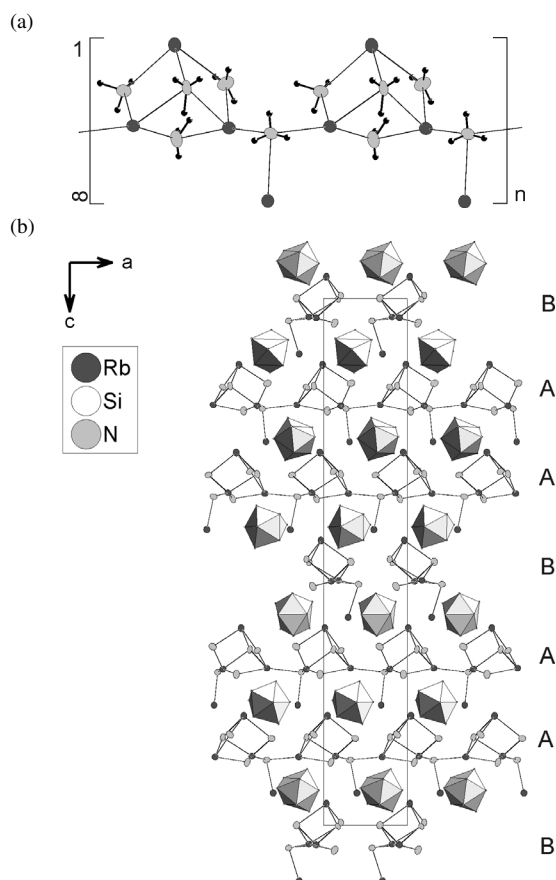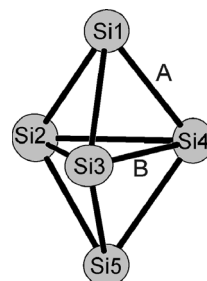
(a)

(b)

Fig. 3. Rb–NH$_3$ interactions in Rb$_4$Si$_9$ · 5NH$_3$. a) One-dimensional chains of Rb cations and ammonia molecules. b) The position of the chains in the unit cell shows that layers of parallel strands are arranged orthogonally in AAB sequences. In between these layers the Si$_9^{4-}$ anions are situated. Displacement ellipsoids of Rb and N atoms at the 50 % probability level.

chloride, triphenylphosphine or Pt(PPh$_3$)$_4$, the compound (K@[2.2.2]crypt)$_2$Si$_5$ · 4NH$_3$ crystallises from the resulting ammonia solutions. The asymmetric unit of (K@[2.2.2]crypt)$_2$Si$_5$ · 4NH$_3$ contains two potassium cations, which are enclosed in [2.2.2]-cryptand molecules, one Si$_5^{2-}$ anion and four molecules of ammonia. For two ammonia molecules no H atoms could be located, due to disordering, which leads to comprehensible discrepancies between the reported sum formula and the formula resulting from the atom sites. The compound crystallises isostructurally to the known (Rb@[2.2.2]crypt)$_2$Si$_5$ · 4NH$_3$ [3, 4]. Fig. 4 shows the Si$_5^{2-}$ anion. Its Si–Si distances are within the expected range and are given in the caption of Fig. 4. To make the group 14 pentatetrelide cages com-

(M@[2.2.2]crypt)$_2E_5$	Si$_5^{2-}$	Ge$_5^{2-}$	Sn$_5^{2-}$	Pb$_5^{2-}$
A, Å	2.38	2.48	2.87	3.00
B, Å	2.56	2.67	3.06	3.23
A/B	0.93	0.93	0.94	0.93
	Solvent participation in crystal structure		No solvent molecules participate in crystal structure	

Fig. 4. Si$_5^{2-}$ anion in (K@[2.2.2]crypt)$_2$Si$_5$ · 4NH$_3$, Si–Si distances (Å): Si1–Si2 2.385(2), Si1–Si3 2.395(2), Si1–Si4 2.383(2), Si2–Si3 2.552(2), Si2–Si4 2.571(2), Si3–Si4 2.551(2), Si2–Si5 2.383(2), Si3–Si5 2.3756(19), Si4–Si5 2.384(2). The table gives the average values of the equatorial bond lengths (B) and distances to the apical atom (A) in E_5^{2-} anions of group 14. For comparison of the anions the ratio A/B can be taken into account.

parable to each other, the two main distances A and B and their ratio are given in the Table of Fig. 4. It is obvious that all pentatetrelide cages are very similar in shape. Despite of this fact, their respective cryptate compounds adopt different space groups. Due to solvent participation for E = Si, Ge, the low-symmetry triclinic crystal system is observed, and a reasonable structure refinement was only possible in the non-centrosymmetric space group $P1$. This has already been reported for the Rb$^+$-containing compound [3]. The compounds of the heavier homologues Sn and Pb display high-symmetry structures in the trigonal space group $P\bar{3}c1$. Apart from the space group, the relationship between all E_5^{2-}-containing compounds is evident (Fig. 5).

Conclusion

For the heavier group 14 elements, nonatetrelide cage anions E_9^{4-} (E = Ge–Pb) and tetrahedral anions E_4^{4-} (E = Sn, Pb) are accessible by dissolution of the corresponding binary Zintl precursor phases A_4E_4 or A_4E_9 (A = alkali metal). The dissolution of A_4E_9 and A_4E_4 phases in the absence of any chelating substances yields a variety of solvate structures, which all still contain E_9^{n-} (E = Ge, n = 3, 4; E = Sn, n = 3, 4; E =
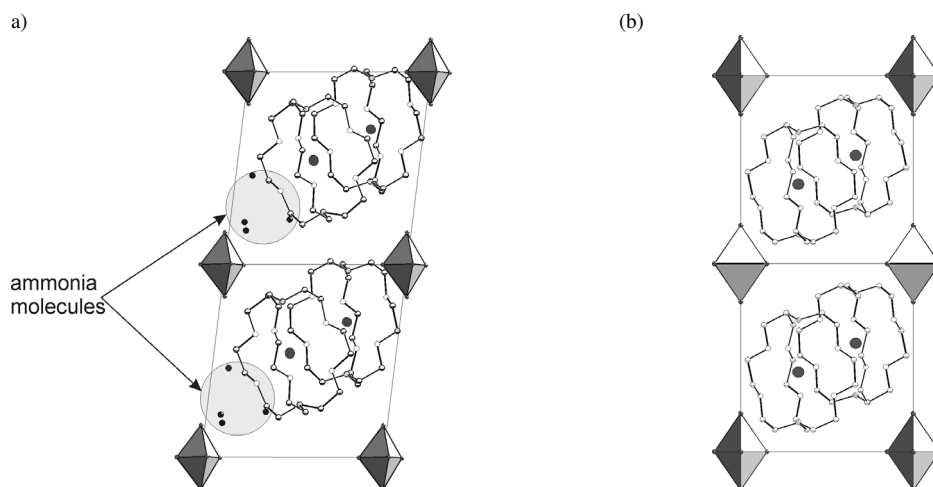
a)

(b)

Fig. 5. Structural relationship of a) $(M@[2.2.2]crypt)_2 E_5 \cdot 4NH_3$ (E = Si, Ge) and b) $(M@[2.2.2]crypt)_2 E_5$ (E = Sn, Pb).

Pb, n = 4), respectively E_4^{4-} anions (E = Sn, Pb). In the presence of ligands chelating alkali metal cations, ligands like 18-crown-6 and [2.2.2]-cryptand, the dissolution of A_4E_9 phases retains the nonatetrelide cages, only their electron number per cage differs, and several examples for all heavier homologues of group 14 can be found in solvate crystal structures. In contrast to that, the dissolution of A_4E_4 materials in the presence of [2.2.2]crypt does not yield tetrahedral anions, and only E_5^{2-} anions (E = Ge–Pb) can be obtained.

For silicon the case is different, there is no precursor material which contains Si_9^{4-} anions independent of Si_4^{4-} anions. Silicides A_4Si_9 were only observed spectroscopically as intermediates in the decomposition of monosilicides, but could not be prepared as crystalline phases [2]. Therefore Si_9^{4-} anions are only available in the more highly reduced binary compound $A_{12}Si_{17}$ which contains the tetrahedral anions as well. $A_{12}Si_{17}$ phases can be dissolved only in very dry liquid ammonia, because the silicides are very sensitive towards traces of humidity. On our way to elucidate the solvation behaviour of silicide Zintl phase materials we were able to crystallise compounds with both Si_9^{4-} and Si_5^{2-} anions *via* dissolving the nominally ternary material $K_6Rb_6Si_{17}$, which contains Si_9^{4-} and Si_4^{4-} anions. In the absence of any chelating substances the nonasilicide-containing compound $Rb_4Si_9 \cdot 5NH_3$ crystallises. A further example for a pentasilicide dianion was found upon dissolving the same precursor phase $K_6Rb_6Si_{17}$ in the presence of the [2.2.2]-cryptand and additionally choline chloride ([(CH$_3$)$_3$NC$_2$H$_4$OH]Cl), triphenylphosphine

or Pt(PPh$_3$)$_4$. The role of these additional substances, which do not appear in any cage compound crystal structures, is not clear so far, but it is assumed that the solvation process is very sensitive towards additional proton accepting or donating compounds, which influence the autoprotolysis of liquid ammonia. Anyway, their use seems to be obligatory for the crystallization of pentasilicides.

The trigonal bipyramidally shaped silicides only crystallise together with four molecules of ammonia, which seem to be essential for the smaller group 14 pentatetrelide cages Si_5^{2-} and Ge_5^{2-}, despite the loss of crystal symmetry compared to the structures with the heavier homologues, Pb_5^{2-} and Sn_5^{2-}. For ammoniates of nonasilicide anions crystallisation is possible with different amounts of ammonia of crystallisation, which is reflected in space group symmetry and the constitution of the cation-ammonia network of the obtained compounds.

Experimental Section

All manipulations described below were performed in a purified Ar atmosphere (glove box, O$_2$ and H$_2$O levels below 1 ppm) by using reaction vessels dried at least four times *in vacuo*. The [2.2.2]-cryptand, choline chloride, PPh$_3$ and Pt(PPh$_3$)$_4$ were dried *in vacuo* before use. $K_6Rb_6Si_{17}$ was prepared in glass ampoules according to the known procedure [10, 11].

$Rb_4Si_9 \cdot 5NH_3$ (**1**)

0.12 g (0,098 mmol) $K_6Rb_6Si_{17}$ was placed into a baked-out reaction vessel. Approximately 20 mL of liquid ammonia

Table 2. Crystal structure data for **1** and **2**.

	1	**2**
Formula	$H_{15}N_5Rb_4Si_9$	$C_{36}H_{84}K_2N_8O_{12}Si_5$
M_r	679.86	1039.8
Crystal size, mm^3	$0.15 \times 0.15 \times 0.1$	$0.5 \times 0.3 \times 0.2$
Crystal system	hexagonal	triclinic
Space group	$P6_5$	$P1$
a, Å	8.880(1)	11.379(2)
b, Å	a	11.962(2)
c, Å	48.55(1)	12.023(2)
α, deg	90	118.08(3)
β, deg	90	98.67(3)
γ, deg	120	91.95(3)
V, $Å^3$	3315	1417.0(5)
Z	6	1
D_{calcd}, $g\,cm^{-3}$	2.38	1.20
$\mu(MoK_\alpha)$, cm^{-1}	9.3	0.3
$F(000)$, e	2268	548
hkl range	$\pm10, \pm10, -59{\rightarrow}58$	$\pm14, \pm15, \pm15$
Refl. measured / unique /	18320 / 4226 /	24663 / 12495 /
R_{int}	0.0755	0.0599
Param. refined	167	605
$R(F) / wR(F^2)^a$ (all refl.)	0.0546 / 0.0617	0.0847 / 0.1430
q_1 / q_2 (weighting scheme)^a	0.0035 / 0.0	0.0782 / 0.0
x(Flack)	0.003(15)	0.00
GoF $(F^2)^b$	0.822	0.89
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	0.62 / −0.73	0.48 / −0.41

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2)+(q_1 P)^2+q_2 P]^{-1}$, where $P = (Max(F_o^2, 0)+2F_c^2)/3$; refinement of F^2 against all reflections; the weighted R factor wR and goodness of fit GoF are based on F^2, conventional R factors R are based on F, with F set to zero for negative F^2.

was condensed onto it, upon which the solution immediately turned yellow. The reaction mixture was kept at a temperature of 233 K. After at least 2 months orange, prism-shaped crystals were obtained. The number of crystals increased when more concentrated silicide solutions were used.

[(K@crypt)$_2$Si$_5$]·4NH$_3$ (2)

0.12 g (0.098 mmol) $K_6Rb_6Si_{17}$, 0.075 g [2.2.2]-cryptand and one additional substance (choline chloride, triphenylphosphine or Pt(PPh$_3$)$_4$, in stoichiometric amounts) were placed into a baked out reaction vessel, and 15 mL of dry liquid ammonia was condensed onto the mixture. After at least 2 months storage at 233 K yellow-orange, irregularly shaped crystals of [(K@crypt)$_2$Si$_5$]·4NH$_3$ were obtained.

X-Ray crystallography

The air- and moisture-sensitive crystals were transferred directly from the mother liquor into a perfluoroether to isolate and to transfer them onto a Stoe-IPDS I diffractometer, using the crystal-cap system. Data collection was carried out at 123 K using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The data reductions were performed with the Stoe IPDS I program package. The structure solutions of **1** and **2** were found with the Shelxs-97 [15] package by using Direct Methods and refined with anisotropic displacement parameters for all non-hydrogen atoms using Shelxl-97 [16]. All hydrogen atoms of the cryptand were placed at calculated positions using a riding model (HFIX).The positions of the remaining H atoms were taken from difference Fourier analyses. An empirical absorption correction was applied with DELrefABS as incorporated in Platon [17].

The reflections of the crystal of $Rb_4Si_9 \cdot 5NH_3$ have been indexed using a hexagonal primitive lattice within the Laue groups 6/*m* or 6/*mmm*. Thereby, only space groups of the Laue class 6/*m* yielded reasonable models for further refinements. Refinement was possible in space group $P6_5$ according to the observed absolute structure (Flack $x = 0.003(15)$). Additionally, merohedral twinning (matrix $\bar{1}$ 0 0 1 1 0 0 0 $\bar{1}$) with a BASF parameter of 0.426(1) for the second domain was considered.

Crystals of (K@[2.2.2]crypt)$_2$Si$_5 \cdot 4NH_3$ show twinning by inversion, and a second domain could be refined using the TWIN instruction with a BASF parameter of 0.13(4).

Crystallographic data of $Rb_4Si_9 \cdot 5NH_3$ and (K@[2.2.2] crypt)$_2$Si$_5 \cdot 4NH_3$ is given in Table 2.

CSD-380407 ($Rb_4Si_9 \cdot 5NH_3$, **1**) and CCDC-747558 ((K@[2.2.2]crypt)$_2$Si$_5 \cdot 4NH_3$, **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http: //www.fiz-informationsdienste.de/en/DB/icsd/depot_anforde rung.html) *via* http://www.fiz-kasrlsruhe.de/request_for_de posited_data.html ($Rb_4Si_9 \cdot 5NH_3$), or from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/ data_request/cif ((K@crypt)$_2$Si$_5 \cdot 4NH_3$).

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