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Cluster Compounds

$[(MesCu)_2(\eta^3\text{-}Si_4)]^{4-}$: A Mesitylcopper-Stabilized Tetrasilicide Tetraanion**

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Dedicated to Professor Hans H. Karsch on the occasion of his 65th birthday

In contrast to the rich chemistry of tetrasubstituted tetrahedranes,[1] the investigation of ligand-stabilized, small-cage compounds of the heavier Group 14 element silicon is a short story, even though the ligand-free tetrahedral tetraanions have been known for decades in binary alkali-metal (A) intermetallics A_4Si_4.[2,3] The first tetrahedral tetrasilane was prepared by Wiberg in 1993,[4] and the isolation of a tris-substituted tetrassilatetrahedranide followed 10 years later.[5] A synthesis from the easily accessible $[Si_4]^{4-}$ has not been reported to date. The field of silicon cluster compounds has recently gained a major step forward since discrete silicon clusters were observed in neat solids $A_{12}Si_{17}$ (A = K, Rb, Cs).[6,7] These phases contain $[Si_4]^{4-}$ and $[Si_9]^{4-}$ clusters in the ratio 2:1, but show very low solubility in ethylenediamine or dimethylformamide even at higher temperatures.[8] Related compounds with the nominal composition A_4E_9 (A = K–Cs, E = Ge–Pb) readily dissolve in these solvents, but corresponding silicon phases are not known. The application of liquid ammonia as a solvent recently led to the isolation of $[Si_9]^{n-}$ ($n = 2$–4),[8–10] and the formation of two Zintl ion complexes, $[Si_9ZnPh]^{3-}$ and $[(Ni(CO)_2)_2(\mu\text{-}Si_9)_2]^{8-}$, has also been achieved.[11,12] All attempts to obtain the other highly charged species $[Si_4]^{4-}$ from solutions of the precursor compounds $A_{12}Si_{17}$ (A = K, Rb, Cs) have not been successful to date.

Our investigations on the reactivity of Zintl ions $[E_9]^{4-}$ (E = Ge–Pb) towards low-valent Group 11 complexes led to the formation of the complexes $[(Ge_9)Cu(PR_3)]^{3-}$ (R = Cy, *i*Pr), $[(\eta^4\text{-}Ge_9)Cu(\eta^1\text{-}Ge_9)]^{7-}$, $[Ag(Sn_9\text{-}Sn_9)]^{5-}$, $[(Ge_9)Au_3(Ge_9)]^{5-}$, $[Au_3Ge_{45}]^{9-}$, and the endohedral clusters $[Cu@Sn_9]^{3-}$ and $[Cu@Pb_9]^{3-}$.[13–17] In continuation of these experiments, we investigated the reactions of R_3PCuCl (R = Cy, *i*Pr) and MesCu (Mes = 2,4,6-$Me_3C_6H_2$) with intermetallic phases $A_{12}Si_{17}$ (A = Rb or K/Rb). Herein, we present a highly charged $[Si_4]^{4-}$ unit obtained from solution, which is stabilized by two MesCu fragments and is the first structurally characterized silicon copper cluster, which has been anticipated only theoretically before.[18]

Phases of nominal composition $Rb_{12}Si_{17}$ (**1a**) and $K_6Rb_6Si_{17}$ (**1b**) were obtained by heating the elements in sealed tantalum containers to 900 °C.[8] Both phases have been characterized by means of X-ray powder diffraction. The data of **1a** fit the theoretical powder pattern of the structurally characterized phase (Supporting Information, Figure S1),[8] whilst **1b** can be identified as a mixture of the ternary phases $K_6Rb_6Si_{17}$ (**1b**) and $K_2Rb_2Si_4$ (**1c**) (Supporting Information, Figure S2, S3). ^{29}Si MAS NMR spectra of **1b** and **1c** showed the presence of tetrahedral $[Si_4]^{4-}$ units ($\delta = -309.7$ ppm) according to A_4Si_4 (A = Na–Cs), with chemical shifts ranging from $\delta = -280$ ppm to -360 ppm,[19] whereas no signals for $[Si_9]^{4-}$ could be detected.

Reactions of **1a** with R_3PCuCl (R = Cy, *i*Pr) in liquid ammonia and in the presence of [2.2.2]crypt (4,7,13,16,21,24-hexaoxa-1,10-diaza-bicyclo[8.8.8]hexacosane) led solely to the isolation of $Rb_4Si_9(NH_3)_5$ (**2**), which contains the fourfold negatively charged polysilicide anion $[Si_9]^{4-}$ (**2a**). The absence of copper was confirmed by semi-quantitative energy-dispersive X-ray (EDX) analysis. As shown in Figure 1, **2a** can be described as a monocapped square antiprism with slight distortion from C_{4v} symmetry ($d1$: Si1–Si3 = 3.373(2) Å; $d2$: Si2–Si4 = 3.539(1) Å; $d2/d1 = 1.05$). The structure of $[Si_9]^{4-}$ is comparable to that of the cluster anion first published by Korber et al. in the non-isotypic compound $Rb_4Si_9(NH_3)_{4.75}$.[10] However, the hexagonal arrangement of **2a** along a screw axis parallel to [001] (Supporting Informa-

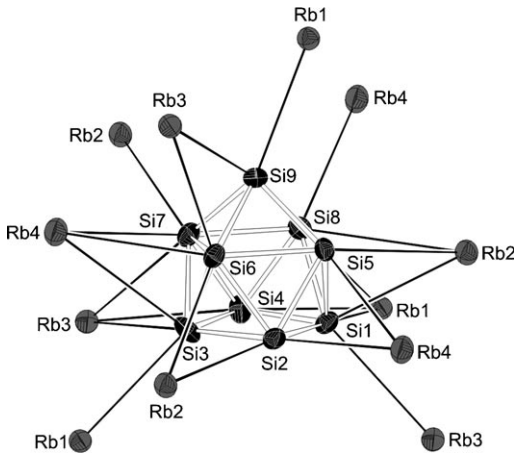

Figure 1. Structure of the polysilicide anion **2a**. Ellipsoids are set at 70% probability.

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tion, Figure S4) and its coordination environment, which consists of twelve rubidium atoms (Figure 1), are different to $Rb_4Si_9(NH_3)_{4.75}$.[10] Rb–Si distances range from 3.541(1) Å to 4.124(1) Å.

Cu–Si interactions could be accomplished by starting from $K_6Rb_6Si_{17}$ (**1b**), MesCu, and [18]crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) as a semi-sequestering agent. The reaction in liquid ammonia yielded red, plate-shaped crystals of $[Rb([18]crown\text{-}6)]_2Rb_{1.54}K_{0.46}[(MesCu)_2Si_4](NH_3)_{12}$ (**3**) after seven weeks of storage at −70 °C. EDX analysis of the crystals confirmed the approximate ratio of Cu, Si, Rb, and K. Compound **3** contains the first tetrahedral tetrasilicide(4−) anion obtained from liquid ammonia solution. It is stabilized by two MesCu units, $[(MesCu)_2Si_4]^{4-}$ (**3a**), and is the first transition metal complex of a tetrahedral polyanion $[E_4]^{4-}$ (E = Si–Pb). Corresponding experiments with $K_2Rb_2Si_4$ (**1c**), which contains solely $[Si_4]^{4-}$ anions, did not lead to colored solutions, thereby reconfirming the insolubility of pure alkali monosilicides A_4Si_4 (A = Na–Cs) in liquid ammonia.[8]

The asymmetric unit of crystals of **3** contains two [18]crown-6-sequestered cations (Rb2, Rb4), two ligand-free alkali metal atoms (Rb3, A1) (occupation ratio Rb/K = 0.54:0.46), and 12 NH_3 molecules per cluster unit, leading to a fourfold negative charge for the polyanion **3a**.

The central structural motif of **3a** consists of a slightly distorted silicon tetrahedron capped by two MesCu fragments (Figure 2). All Si–Si bonds within the tetrahedron, except for

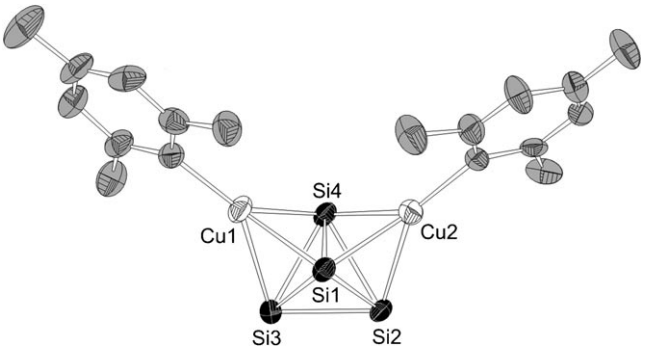

Figure 2. Structure of the functionalized tetrahedral polysilicide anion **3a**. Carbon atoms are shown in gray; ellipsoids are set at 70% probability. Selected bond lengths [Å]: Si1–Si2 2.457(2), Si1–Si3 2.428(2), Si1–Si4 2.607(2), Si2–Si3 2.391(2), Si2–Si4 2.440(2), Si3–Si4 2.443(2), Cu1–Si1 2.397(2), Cu1–Si3 2.548(2), Cu1–Si4 2.351(2), Cu2–Si1 2.416(2), Cu2–Si2 2.468(2), Cu2–Si4 2.358(2).

Si1–Si4 (2.607(2) Å), range from 2.391(2) to 2.457(2) Å and compare well with the bond lengths of the $[Si_4]^{4-}$ tetrahedron in Rb_4Si_4 (2.432 Å),[20] whereas uncharged tetrasilanes $(R_3Si)_4Si_4$ (R = *t*Bu) have on average slightly shorter Si–Si bonds in the range from 2.32 to 2.36 Å.[4,5] The number of known tetrahedral tetrasilanes is rather limited. The only known anion $[Si_4(SiMeDis_2)_3]^-$ (Dis = $CH(SiMe_3)_2$) consists of a distorted Si_4 tetrahedron with three $SiMeDis_2$ substituents in which five Si–Si bonds are in the range from 2.30 to 2.35 Å, and one bond including the unsubstituted silicon atom is substantially elongated (2.73 Å).[5] NMR experiments indicate a migration of the three substituents along the Si_4 skeleton.

The longer Si1–Si4 distance in **3a** is a consequence of the two interactions of copper atoms with these silicon atoms, which are in the range 2.351(2)–2.416(2) Å. The Cu–Si distances to Si2 and Si3 are slightly longer and lie between 2.468(2) and 2.548(2) Å. These interactions are longer than those observed in molecular copper complexes with linear, σ-bonded Si-Cu-Si units ($d_{Cu\text{-}Si} \approx 2.334(3)$ Å).[21–23] A rather similar asymmetric coordination of copper above silicon triangles is mentioned in theoretical calculations of neutral species with the general composition $CuSi_x$ ($x = 4, 5$).[18] The Cu–C and the C–C bonds of the MesCu fragments in **3a** are not affected by the coordination to the silicon tetrahedron.[24]

Apart from the two copper atoms, five alkali metal atoms coordinate to the Si_4 cluster in **3a** with distances in the range from 3.572(2) to 3.801(2) Å. Thus, the coordination number of the $[Si_4]^{4-}$ unit is decreased compared to that in binary silicides A_4Si_4 with 16 alkali metals surrounding the tetrahedron. In crystals of **3**, clusters **3a** form dimeric units around the crystallographic center of inversion that are connected by bridging Rb3 atoms (Figure 3). The atoms of the silicon

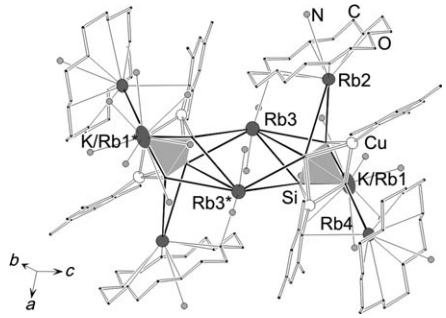

Figure 3. Section of the crystal structure of **3** around a center of inversion showing two central structural motifs **3a** interconnected by two Rb3 atoms. Crown ethers, MesCu fragments, Si tetrahedra, and ammonia molecules are shown schematically for clarity; ellipsoids for K/Rb, Rb, and Cu are set at 70% probability. Selected bond lengths [Å]: K/Rb1–Si2 3.664(2), K/Rb1–Si3 3.572(2), K/Rb1–Si4 3.740(2), Rb2–Si3 3.682(2), Rb3–Si1 3.668(2), Rb3–Si2 3.518(2), Rb3–Si3 3.641(2), Rb3–Si1* 3.701(2), Rb3–Si2* 3.740(2), Rb4–Si4 3.801(2).

cluster coordinate in η^2 and η^3 fashions to the Rb3 atoms. The coordination spheres of the Rb3 atoms are completed by NH_3 molecules. Further, the cluster binds in η^1 and η^2 fashions to the Rb2 and Rb4 cations which additionally coordinate to crown ether molecules. The coordination sphere of the mixed K/Rb1 site is completed by seven NH_3 molecules; two of them build a bridge to K/Rb1* (Supporting Information, Figure S5). Owining to the loss of ammonia, compound **3** decomposes immediately after warming up. Therefore, further spectroscopic investigations were not possible.

Single-point quantum-chemical calculations using a polar continuum solvent model were performed with Gaussian09[25a] on the fourfold negatively charged ions $[(MesCu)_2Si_4]^{4-}$ and $[(MeCu)_2Si_4]^{4-}$, the twofold negatively charged ion $[Cu_2Si_4]^{2-}$ (here MesCu has been considered as Cu^I) as well as for the $[Si_4]^{4-}$ anion with parameters taken from the

crystal structure determination of Rb_4Si_4.[20] These calculations revealed that the anions are stable, as indicated by large HOMO–LUMO gaps of 5.59, 5.57, 6.26, and 6.80 eV for $[(MesCu)_2Si_4]^{4-}$, $[(MeCu)_2Si_4]^{4-}$, $[Cu_2Si_4]^{2-}$, and $[Si_4]^{4-}$, respectively.

Chemical bonding of isolated $[Si_4]^{4-}$ tetrahedra as the subunits in the neat solid Na_4Si_4 had been discussed qualitatively before[26,27] by means of the electron localization function (ELF).[26,28] We analyzed the ELF of $[(MeCu)_2Si_4]^{4-}$, $[Cu_2Si_4]^{2-}$, and $[Si_4]^{4-}$. As the MeCu and Cu^+ complexes of $[Si_4]^{4-}$ gave similar results, for the sake of clarity we show the ELF of $[Cu_2Si_4]^{2-}$. The analysis of $[(MeCu)_2Si_4]^{4-}$ is given in the Supporting Information. The three-dimensional representations of the ELF isovalue surfaces for $[Si_4]^{4-}$ and $[Cu_2Si_4]^{2-}$ are shown in Figure 4.[25b] $[Si_4]^{4-}$ shows one monosynaptic valence basin ① per Si atom populated with 2.71 electrons. Six disynaptic valence basins ②, populated with 1.50 electrons, occur outside the tetrahedral edges above each Si–Si bond vector (Figure 4a). The displacement of bonding vectors can be illustrated by the angle α defined by the two core attractors of silicon atoms and the disynaptic attractor under consideration (Figure 4b). The deviation of α from zero reflects the bond strain. In $[Si_4]^{4-}$, α ranges from 26.2° to 26.6°.[29]

In $[Cu_2Si_4]^{2-}$ (Figure 4c–e) four rather similar monosynaptic valence basins (①, lone pairs) V(Si1), V(Si2), V(Si3), and V(Si4) can be identified, as shown for $\eta(r) = 0.7635$ in Figure 4d. V(Si2) and V(Si3) are filled with 2.90 electrons, whilst V(Si1) and V(Si4), located at the atoms involved in the elongated Si1–Si4 bond in **3a**, are populated with 3.84 electrons. The Si1–Si4 bond elongation is also displayed by the disynaptic valence basins ②. V(Si1,Si4), shown for $\eta(r) = 0.625$ in Figure 4c, is populated with 0.67 electrons whereas V(Si1,Si2), V(Si1,Si3), V(Si2,Si4), and V(Si3,Si4) at $\eta(r) = 0.7635$ exhibit a higher degree of localized bonding electrons with a population of 1.16 electrons (Figure 4d). V(Si2,Si3), shown for $\eta(r) = 0.815$ in Figure 4e, is occupied with 1.37 electrons and represents the shortest bond length in **3a**. The population of the disynaptic attractors also correlates nicely with the Si–Si bond length under consideration.

The mean angle α in $[Cu_2Si_4]^{2-}$ for the disynaptic attractors ranges from 21.7° to 23.8° and is thus generally smaller than in $[Si_4]^{4-}$, indicating less bond strain in the former. Angle β represents the orientation of a lone pair with respect to an adjacent Si–Si bond vector and reflects the repulsion of a lone pair and neighboring basins according to the VSEPR model.[26,27] For $[Si_4]^{4-}$, the mean β angle is 144.8° allowing for the small Si-Si-Si angles of the ψ-tetrahedral coordination of the silicon atoms. In **3a**, the two angles β with values of 148.5° and 152.0° for V(Si1) and V(Si4) with respect to Si1–Si4, respectively, are larger than the two angles for V(Si2) and V(Si3) with respect to the Si2–Si3 bond vector (141.3° and 139.8°, respectively). This accommodates the increased repulsion of the lone pairs at Si1 and Si4 with the two copper core basins owing to shorter Cu–Si distances if compared to Si2 and Si3. No disynaptic V(Cu,Si) bond attractors are present, and thus the Cu–Si bond is considered as an electrostatic interaction. Consequently the MesCu fragments in **3a** can be regarded as uncharged ligands that coordinate to a fourfold negatively charged $[Si_4]^{4-}$ cluster.

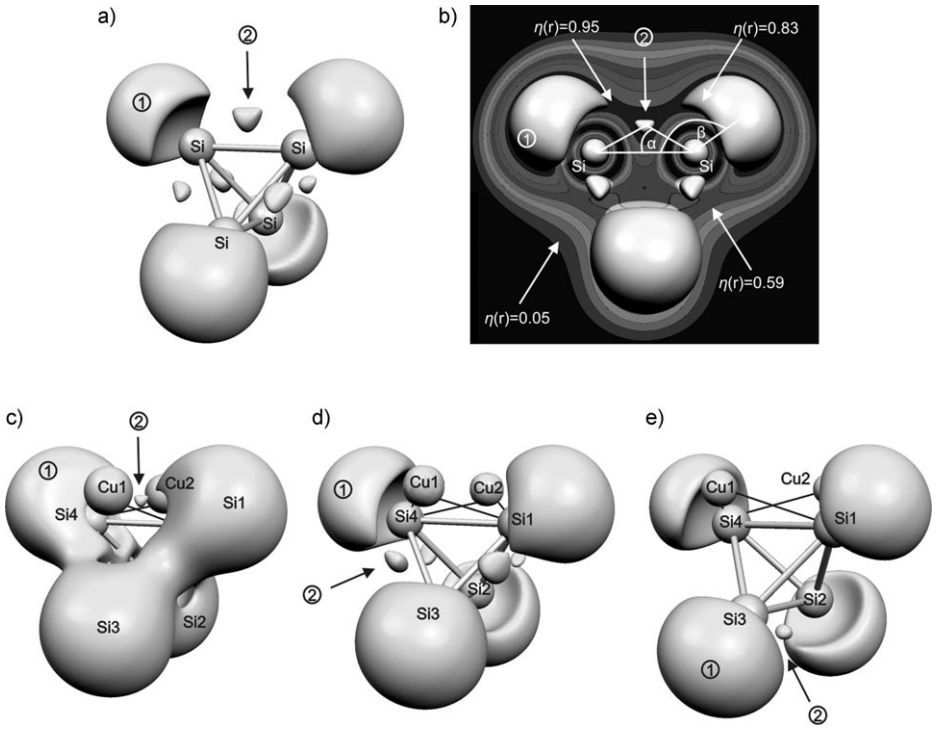

Figure 4. a) 3D ELF isosurface for $[Si_4]^{4-}$ with $\eta(r) = 0.83$, and b) 2D ELF and 3D isosurface for $[Si_4]^{4-}$ plotted on a plane bisecting two Si atoms. Monosynaptic and disynaptic valence basins are shown as gray surfaces with $\eta(r) = 0.83$. Contour lines are shown with $\eta(r)$ ranging from 0.05 to 0.95 in steps of 0.10. Angles α and β are discussed in the text. c–e) 3D-ELF isosurfaces for $[Cu_2Si_4]^{2-}$ with c) $\eta(r) = 0.625$, d) $\eta(r) = 0.7635$, and e) $\eta(r) = 0.815$. Core basins, monosynaptic valence basins V(Si) and disynaptic valence basins V(Si/Si) are shown as gray surfaces. A color picture is shown in the Supporting Information, Figure S8.

In summary, the formation of $[(MesCu)_2Si_4]^{4-}$ (**3a**) shows that highly charged silicon clusters can be obtained and handled in solution. The title anion fills the gap between alkylated Si_4R_4 cage molecules and the $[Si_4]^{4-}$ clusters in binary Zintl phases. The coordination of the MesCu fragment is comparable to the coordination of copper(I) to tetrahedral P_4 as it has been reported in $[Cu(P_4)_2]^+$. The copper atom bridges two P_4 molecules which coordinate in a η^2 fashion. The coordinated P–P bond is also elongated by approximately 0.2 Å compared to the other P–P distances.[30] The

$[Cu(P_4)_2]^+$ ion has been obtained only in the presence of weakly coordinating counter anions. Our results show that related ions can be obtained even in the presence of strongly coordinating solvent molecules such as NH_3.

Experimental Section

All manipulations were carried out under a purified argon atmosphere using standard Schlenk and glovebox techniques. $Rb_{12}Si_{17}$ (**1a**) and $K_6Rb_6Si_{17}$ (**1b**) were prepared from stoichiometric amounts of the elements in sealed tantalum containers. These containers were encapsulated in evacuated fused silica tubes, heated to 900 °C for 1 h, and slowly cooled down to room temperature at a rate of 0.1 °C min^{-1}. ^{29}Si MAS NMR (**1b**): $\delta = -309.7$ ppm.[19] $K_2Rb_2Si_4$ (**1c**) was similarly synthesized from stoichiometric amounts of the elements which were heated to 600 °C and cooled down to room temperature at a rate of 0.2 °C min^{-1}. ^{29}Si MAS NMR (**1c**): $\delta = -309.7$ ppm.[19] R_3PCuCl (R = Cy, *i*Pr) and MesCu were prepared according to literature procedures.[31–33] [2.2.2]Crypt was dried in vacuo. [18]Crown-6 was sublimed under dynamic vacuum at 80 °C. Liquid ammonia was dried and stored over sodium metal. Dimethylformamide (DMF) was stored over CaH_2 and freshly distilled before use.

Crystal structure determination: The thermally very unstable, air- and moisture-sensitive crystals of **2** and **3** were transferred from the mother liquor into perfluoropolyalkylether oil at 213 K under a cold N_2 stream. They decompose immediately upon leaving the cold N_2 stream due to the loss of ammonia. For data collection, the single crystals were fixed on a glass capillary and positioned in a 120 K cold N_2 stream using the crystal cap system. Data collection: Stoe IPDS 2T diffractometer equipped with a rotating anode ($Mo_{K\alpha}$ radiation) for compound **2**; Oxford-Diffraction Xcalibur3 diffractometer ($Mo_{K\alpha}$ radiation) for compound **3**. Structures were solved by Direct Methods (SHELXS-97)[34] and refined by full-matrix least-squares calculations against F^2 (SHELXL-97).[35] CCDC 769515 (**2**) and CCDC 769514 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2: Compound **1a** (225 mg, 0.15 mmol), [2.2.2]crypt (100 mg, 0.27 mmol), and Cy_3PCuCl (57 mg, 0.15 mmol) or iPr_3PCuCl (39 mg, 0.15 mmol) were weighed into a Schlenk tube and dissolved in approximately 2 mL liquid ammonia at −78 °C. The resulting red suspension, still containing an insoluble residue, was kept at −70 °C. Compound **2** crystallized as orange cube-shaped crystals after several weeks in approximately 20% yield. Crystal size: $0.12 \times 0.12 \times 0.07$ mm^3; unit cell parameters: $a = 8.8725(2)$, $b = 8.8725(2)$, $c = 48.7883(18)$ Å, $V = 3326.12(16)$ Å^3; hexagonal, space group $P6_5$ (No. 170), $Z = 6$, $\rho_{calcd} = 2.04$ g cm^{-3}, $\mu = 9.3$ mm^{-1}, $\theta_{max} = 25.10°$, 7468 measured reflections, 3467 independent reflections, Flack $x = 0.002(5)$, $R_{int} = 0.032$, $R_1 = 0.022$, and $wR_2 = 0.056$ for reflections with $I \geq 2\sigma(I)$, $R_1 = 0.022$, and $wR_2 = 0.056$ for all data. EDX analysis confirmed the absence of copper in compound **2**. Observed ratio for Rb/Si: 36(7)/64(11) atom%.

3: Compound **1b** (92 mg; 0.075 mmol), [18]crown-6 (36 mg; 0.135 mmol) and MesCu (14 mg; 0.075 mmol) were weighted into a Schlenk tube and dissolved in approximately 1 mL liquid ammonia at −78 °C. The resulting red suspension, still containing an insoluble residue, was kept at −70 °C. Compound **3** crystallized as red plate-shaped crystals after seven weeks. Crystal size: $0.4 \times 0.2 \times 0.1$ mm^3; unit cell parameters: $a = 14.7747(4)$, $b = 15.6008(3)$, $c = 16.3727(4)$ Å, $\alpha = 84.728(2)°$, $\beta = 81.188(2)°$, $\gamma = 71.771(2)°$, $V = 3538.27(15)$ Å^3; triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$, $\rho_{calcd} = 1.44$ g cm^{-3}, $\mu = 3.2$ mm^{-1}, $\theta_{max} = 27.57°$, 43623 measured reflections, 16193 independent reflections, $R_{int} = 0.046$, $R_1 = 0.046$, and $wR_2 = 0.109$ for reflections with $I \geq 2\sigma(I)$, $R_1 = 0.095$, and $wR_2 = 0.118$ for all data. Positions and ADPs of K1 and Rb1 were set to be equal. EDX analysis confirmed the nominal composition for Cu/Si/Rb/K in compound **3**: Calculated: 20/40/35/5 atom%; observed: 17(4)/40(6)/36(5)/7(2) atom%.

Evaporation of ammonia from the red reaction mixture of **1b**, MesCu, and [18]crown-6 led to a brown residue with suitable crystallinity for Xray powder diffraction. Electrospray ionization (ESI) mass spectra of a DMF solution of this residue showed the presence of *m*/*z* 303.120 $[([18]crown\text{-}6)K]^+$ and 349.068 $[([18]crown\text{-}6)Rb]^+$ in the positive mode, whereas no unambiguous correlations could be found in the negative mode.

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