Alkali Metal Tetrelide–Tetrelates: "Double Salts" With $[E_4]^{4-}$ Zintl Anions (E = Si, Ge) and the First Dimeric Cyclotrisilicate Ions $[Si_6O_{17}]^{10-}$**

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The inclusion of neutral or charged element clusters in the channels and cavities of zeolite frameworks is a well established method for the preparation of nanostructured materials. Compounds with metal and semiconductor clusters of defined sizes show quantum size effects and can display catalytic properties that are modified by the particle size.[1–4] In general such composites are prepared by the incorporation of the metal or semiconductor unit into an existing zeolite framework by chemical or physical methods. The most common methods are the insertion of molecules and cationic exchange, with subsequent decomposition of the molecules or reduction of the ions within the zeolite framework.[5–8] However, this method is not suitable for the incorporation of the interesting semiconducting elements of Groups 13–15 as the conditions required for the introduction of such ions lead to the degradation of the zeolite structure.[5, 6] The introduction of anions and their subsequent oxidation is, in general, not possible. Herein we describe reactions in which silicate anions with skeleton building potential and semiconductor clusters are simultaneously formed and coexist in the crystal lattice in an "intergrowth" structure.[9, 10]

The extremely air-sensitive black platelike crystals of the title compound were prepared by the reaction of stoichiometric amounts of Si and SiO_2 with the elemental alkali metals (see Experimental Section).

In the crystal structure of $Cs_{10}Si_7O_9$ (**1**),[11a] and corresponding to the ionic formula $Cs_{10}[Si_4][Si_3O_9]$, the Zintl anion $[Si_4]^{4-}$, which is known from the binary Zintl phase A^IE^{IV}[12], and is isosteric and isostructual with white phosphorus (Figure 1a) coexists with the cyclotrisilicate ion $[Si_3O_9]$, known from silicates of the form $A_6[Si_3O_9]$[13]. The two isotypic rubidium compounds $Rb_{14}Si_{10}O_{17}$ (**2a**) and $Rb_{14}Ge_4Si_6O_{17}$ (**2b**)[11b] can also be formally separated into ions in the same way, which, in addition to the silicide known from **1**, and the germanide ion $[E_4]^{4-}$ in the mixed compound, gives the anion $[Si_6O_{17}]^{10-}$, previously unknown for the silicates and composed of two condensed cyclotrisilicate rings (Figure 1b).[14]

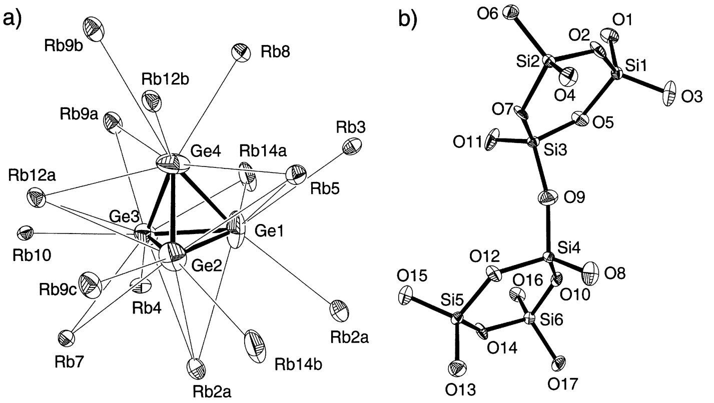

Figure 1. ORTEP plot[18] of the anions in $Rb_{14}Ge_4Si_6O_{17}$: a) germanide ion $[Ge_4]^{4-}$ with the coordination through the Rb centers ($d_{Ge\text{-}Ge} = 234-240$ (**1**), 236–240 (**2a**), 252–258 (**2b**) pm); b) silicate ion $[Si_6O_{17}]^{10-}$ (range of $d_{Si\text{-}O}$ for **1**, **2a**, and **2b**: $d_{Si\text{-}O_t} = 155-161$ pm, $d_{Si\text{-}O_b} = 163-166$ pm).

The structure of the anions and their coordination by the alkali metal cations strongly resembles that of the respective parent compound classes the Zintl phases on the one hand and the oxosilicates on the other: the E–E bonds in the almost perfectly tetrahedral Zintl anions $[E_4]^{4-}$ (Figure 1a) are only slightly shorter than those in the binary Zintl phases RbSi, CsSi, and RbGe.[12] The coordination of the tetrel atoms by the alkali metal cations is also similarly related.[*]

Comparison of the two crystallographically independent trisilicate ions in **1** and the anion $[Si_6O_{17}]^{10-}$ in **2a**/**2b** with the silicate ion in $Cs_6[Si_3O_9]$[13] also shows a good agreement of the bonding parameters: the Si–O bonds to the terminal O atoms (O_t) in each case are significantly shorter than those to the bridging O ligands O_b, the Si–O bonds to the O atoms linking the two rings in **2a**/**2b** are 160(1) and 165(1) pm in **2a**, both bonds are 163(1) pm in **2b**, the bridging angles at the oxygen atoms are 168(1) and 165.8(7)°, respectively.

In both structure types the anions are arranged in alternate layers of silicide/germanide (A) and silicate anions (B) in the pattern …ABA′B′… that lie perpendicular to the *ab* plane (Figure 2a). By bisecting the double tetrahedral three ring, the stacking pattern of the Rb compound can alternatively be described as…AB1B2A′B1′B2′…, where the layers indicated with primes are given by inversion, in accord with the concept of "chemical twinning"[9, 10] (Figure 2b). Thus the unit cells of the two types of structure are also closely metric related: the lattice constants perpendicular to the stacking direction (*a* and *b* axis) are similar in each case.

An alternative description of the two structure types can be based on the stacking of layers in the plane of the trisilicate

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[*] The coordination of the E_4 cluster by 11 of the 14 independent Rb atoms is in very good agreement with the coordination in the cluster in RbGe. In **2a** and **2b** 15 Rb atoms, and in RbSi and RbGe 16 Rb atoms are in direct contact with the four E atoms of the cluster. In **2a** and **2b** there are three μ_3 as well as three μ_2 bonds and in RbGe there are four μ_3 bonds, so that the coordination number for the E_4 cluster in each case is 24.

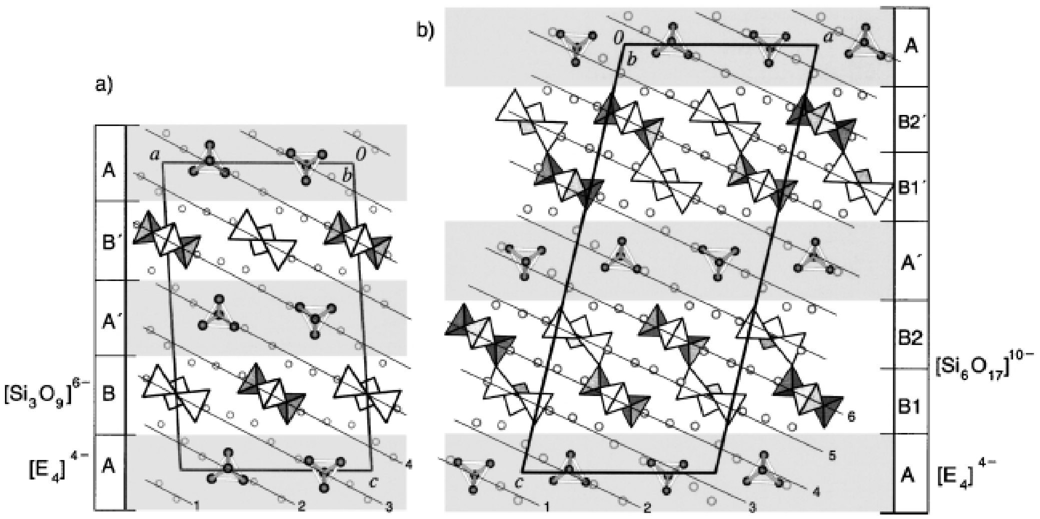

Figure 2. Crystal structures of $Cs_{10}Si_7O_9$ (a) and $Rb_{14}E_{10}O_{17}$ (E = Si, Ge) (b) in the perpendicular projection [010] (Polyhedra: SiO_4-tetrahedra; dark spheres: E; light spheres: Rb, Cs; A: silicide/germanide layers, B: silicate layers).[19]

rings (lines in Figure 2), which are composed of Zintl anions and trisilicate building blocks in the ratio corresponding to the overall composition, that is, 1:1 (**1**) or 1:2 (**2a**/**2b**) and run perpendicular [101] (**1**) and [$10\bar{1}$] (**2a**/**2b**) (identity after four and six layers, respectively).

For the mixed-valent compound **2b** the presence of the very different valence states Ge^- and Si^{4+} can be explained by the somewhat higher electronegativity of Ge compared to Si, the corresponding investigation of the Si system shows that the Zintl anion $[Si_4]^{4-}$ can exist even next to the oxosilicate ions (i.e. Si^{4+}). Thus, mixed-valent compounds can be prepared which contain Si centers in oxidation states that differ by *five* units. The very narrow temperature range for the synthesis and the extreme reactivity of the phases show that a comproportion reaction (for example to "SiO", see Experimental Section) is thermodynamically favorable. Some time ago we prepared the first tetrelide–tetrelate compounds by the reduction of SnO_2 with elemental rubidium, these compounds contain adjacent Zintl anions $[Sn_4]^{4-}$ and stannate(II) ions $[Sn^{II}O_3]^{4-}$ [15] and thus a difference in the oxidation states of three. Recently, with the preparation of the alkali metal auride-aurates,[16] similar "intergrowth" structures have been reported for the first time for transition metals.

Experimental Section

$Cs_{10}Si_7O_9$ **1**: Cs (1592.0 mg, 11.978 mmol; Alkalimetall-Handelsgesellschaft Bonn), Si (84.1 mg, 2.995 mmol; Aldrich, 99.95%), and SiO_2 (323.9 mg, 5.390 mmol; Strem, 99.8%) were heated under argon in corundum crucibles in steel autoclaves to 973 K in 2 h, cooled at 100 Kh^{-1} to 953 K and subsequently at 2 Kh^{-1} to 933 K. After turning off the tube furnace the cooled sample was an almost pure phase of **1**. The X-ray powder diffraction pattern revealed only the weak intensities of elemental silicon. Under the stereomagnifier a small amount of the yellow-ocher X-ray amorphous component of the as yet not fully characterized „SiO" phase could be seen.

$Rb_{14}Si_{10}O_{17}$ **2a**: Stoichiometric amounts of the element/oxide Rb (1026.0 mg, 12.01 mmol; Alkalimetall-Handelsgesellschaft Bonn); Si (36.1 mg, 1.286 mmol; Aldrich, 99.95%); SiO_2 (437.9 mg, 7.288 mmol; Strem, 99.8%) were employed as above and heated at 350 Kh^{-1} and annealed for 2 h at 973 K, cooled with 20 Kh^{-1} to 773 K and finally rapidly cooled to room temperature. The X-ray powder diffraction pattern of the samples showed, as a small second phase, reflections assigned to the disilicate $Rb_6Si_2O_7$.[13]

$Rb_{14}Ge_4Si_6O_{17}$ **2b**: SiO_2 (35.4 mg; Merck, p.a.), Ge (28.7 mg; ChemPur, 99.99%), and Rb (116 mg; ChemPur, 99.5%) in the ratio 6:4:14 were heated in a welded Nb ampoule over 24 h to 773 K (both heating and cooling with 90 Kh^{-1}). As well as reflections corresponding to the title compound the X-ray powder diffraction pattern showed lines resulting from RbGe.[12] In air the crystals decomposed to an orange product. A very small number of single crystals were isolated from a sample containing mostly RbGe, which was obtained when Rb (307 mg; Alpha, 99.8%), Ge (194 mg; Fluka, 99.999%), and Si (35 mg; Alpha, 99.9%) in molar ratio 12:9:4 were employed in a corresponding reaction at 1173 K (heating with 150 Kh^{-1}, cooling with 10 Kh^{-1}). Small amounts of oxygen are possible as a result of impurities in the starting materials or in the inert gas. In the single crystal the presence of Ge was confirmed by EDX and LA-ICP-MS measurements on a gold coated crystal (EDX = energy dispersive X-ray analysis; LA = laser ablation; ICP = inductive coupled plasma).

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[11] a) Crystal data for $Cs_{10}Si_7O_9$ (**1**) at $T = 200(4)$ K: monoclinic, space group $P2/c$ (No. 13), $a = 1487.7(9)$, $b = 819.3(5)$, $c = 2361.6(15)$ pm, $\beta = 93.53(1)^\circ$; $V = 2873(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.86$ gcm^3; diffractometer: Bruker AXS CCD (Mo$_{K\alpha}$ radiation, graphite monochromator); $\mu(Mo_{K\alpha}) = 12.85$ mm^{-1}; $2\theta_{max} = 45^\circ$; 16877 measured reflections; 3689 unique reflections; Lorentz, polarization, and multi-scan absorption correction;[11d] structure solution was by direct methods;[11e] least-squares refinement (all Cs atoms anisotropic) with SHELXL-97;[11f] 156 free parameters; GOF = 1.063, R-value ($I \geq 2\sigma(I)$): $R1 = 0.096$, $wR2 = 0.2943$; max./min. residual electron density: $5.4/-3.1 \times 10^{-6}$ e$^-$pm^{-3}.[11c] b) Crystal data for $Rb_{14}Si_{10}O_{17}$ (**2a**)[17]/$Rb_{14}Ge_4Si_6O_{17}$ (**2b**) at 295 K: monoclinic, space group $P2_1/c$ (No. 14), $a = 1455.6(7)$/1455.4(3), $b = 789.2(3)$/792.3(2), $c = 3276.8(9)$/3287.3(7) pm, $\beta = 103.50(1)$/103.50(3)°; $V = 3660(2)$/3686(1) Å^3, $Z = 4$, $\rho_{calcd} = 3.27$/3.47 gcm^{-3}; diffractometer: Bruker AXS CCD/Siemens SMART (Mo$_{K\alpha}$ radiation, graphite monochromator); $\mu(Mo_{K\alpha}) = 18.72$/21.85 mm^{-1}; $2\theta_{max} = 50$/42.1°; 22913/11926 measured reflections; 6509/3855 unique reflections; Lorentz, polarization, and multi-scan absorption correction;[11d] structure solution was by direct methods;[11e] least-squares refinement (all atoms anisotropic) with

SHELXL-97;[11f] 371/370 free parameters; GOF = 0.785/1.074, *R*-value ($I \geq 2\sigma(I)$): $R1 = 0.0723/0.043$, $wR2 = 0.179/0.114$; max./min. residual electron density: $+1.9/+0.9$ and $-1.5/-1.0 \times 10^{-6}$ e$^-$pm^{-3}, respectively.[11c] c) Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411970 ($Cs_{10}Si_7O_9$), -411971 ($Rb_{14}Si_{10}O_{17}$), and -411972 ($Cs_{14}Ge_4Si_6O_9$).d) Bruker AXS, SAINT, and SADABS, **1983**; e) G. Sheldrick, SHELXS-97, Universität Göttingen, **1997**; f) G. Sheldrick, SHELXL-97, Universität Göttingen, **1997**.

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[14] Dimeric cyclotrisilicate anions were recently found in single crystals of $Rb_{10}Si_6O_{17}$ (space group *Pbca*, $a = 1283{,}7(3)$, $b = 1367{,}1(3)$, $c = 1384{,}6(3)$ pm). S. Hoffmann, T. Fässler, unpublished results.

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The First Biscarbene Complex of a Group 4 Metal: $[Zr\{C(Me_2P{=}NSiMe_3)_2\}_2]$**

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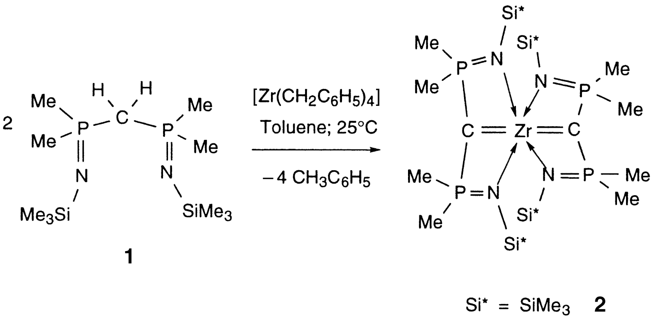
Robert McDonald, and Ronald G. Cavell*

The wealth of chemistry demonstrated by metal – carbene species, summarized in a recent set of reviews,[1] illustrates the great versatility that can be expected from these compounds. Carbenes stimulate much interest because of the many applications to catalysis and organic syntheses.[2] We have recently reported on an extensive series of "pincer" and bridged dimer complexes derived from complete deprotonation of the methylene center in bis(iminophosphanyl)-methanes.[3–7] These complexes, which provide an alternative approach to the generation of this reactive metal – carbon center, were assembled in all cases with a metal/carbon combining ratio of 1:1 with only one phosphinimine ligand per metal atom. These complexes possess "carbene" character in that the metal is multiply bound to the carbon center.

These complexes provided a number of Group 4 examples which have been relatively rare[8] in contrast to the extensive examples of conventional Group 5, 6, and 7 metal carbenes.[2, 9–11] The reactivity patterns of these "pincer" carbenes with metals of Group 4 parallel the behavior of alkylidenes.[3, 6] We now report on a novel zirconium biscarbene complex of this ligand system that contains a linear assembly of two of these metal – carbon multiple bond units and is the first example of such a structure. The compound was obtained by a spontaneous double deprotonation of the methylene backbone of two ligands by a tetraalkylzirconium compound in the same fashion as that used previously to make some of the singly derivatized complexes. Biscarbene complexes of early transition metals are exceptionally rare there being only a few structurally characterized examples of biscarbene complexes of Group 5 metals.[12–15]

The reaction of $CH_2(Me_2P{=}NSiMe_3)_2$[16] (**1**) with $[Zr(CH_2C_6H_5)_4]$[17] in a 2:1 ratio in toluene gave the biscarbene complex $[Zr\{C(Me_2P{=}NSiMe_3)_2\text{-}\kappa^3C,N,N'\}_2]$ (**2**) in 30 – 40 % yield as a result of complete deprotonation of the acidic methylene groups of the ligands [Eq. (1)]. Surprisingly, under similar reaction conditions, analogous reactions carried out with the ligands $CH_2(R_2P{=}NSiMe_3)_2$ (R = Ph or Cy) containing Ph or Cy instead of Me groups on the phosphorus center did not yield the desired biscarbene product. This demonstrates the uniqueness of the behavior of this methyl-substituted ligand and suggests that steric factors play a key role in the formation of this biscarbene complex.



(1)

The high symmetry of complex **2** is illustrated by the observation of a single sharp resonance signal in the $^{31}P\{^1H\}$ NMR spectrum. The absence of methylene backbone proton signals for the ligand in the ^1H NMR spectrum and the appearance of a positive triplet for the backbone (P-C-P) carbon atoms in the $^{13}C\{^1H\}$ APT spectrum (APT = attached proton test) confirms the double deprotonation of the methylene groups of the ligand. Both in the $^{31}C\{^1H\}$ and the ^1H NMR spectra, the signals of the P-methyl groups appear as "deceptively simple" triplets due to coupling with phosphorus centers that are chemically but not magnetically equivalent, commensurate with the high symmetry of the system.[18]

The molecular structure of **2** (Figure 1) is highly symmetric.[19] The core structure consists of two mutually perpendicular six-membered bicyclic planes, each containing the

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