$\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$: A $Ge_{10}Si$ framework reveals a structural transition onto elemental germanium†

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The reaction of the metastable high temperature molecule GeCl synthesized *via* a co-condensation technique with $LiSi(SiMe_3)_3$ leads to a metalloid $Ge_{10}Si$ cluster compound, in which the arrangement of the germanium atoms can be seen as a cutout from the structure of elemental germanium.

The progress in miniaturization, especially in the computer industry is leading to the fact, that the borderland between the solid and the molecular state gets more and more into the focus of scientific as well as technical interest. For germanium, it was shown that germanium nanoparticles with diameters in the range of 2–4 nm exhibit a molecular character instead of nanocrystalline germanium with a diamond lattice.[1] Therefore no structural information is available about germanium nanoparticles with diameters <1–2 nm, which are better described as molecular cluster compounds of germanium. During the last years a bottom-up approach to this borderland was established through the synthesis of metalloid cluster compounds of the general formulae Ge_nR_m ($n > m$).[2] These clusters comprise of ligand bound germanium atoms and also naked germanium atoms, that exclusively form Ge–Ge bonds.[3] As germanium nanoparticles exhibit the same molecular formulae, the metalloid cluster compounds are good model compounds[3] to get an insight into the structural behaviour of these nanoparticles.

The molecular structure of the metalloid cluster compounds is well established by crystal structure analyses. However, no structural transition onto the diamond lattice of the solid state has been described to date, thus the arrangement of the germanium atoms cannot be described as a cutout of the solid state structure of α-germanium (Fig. 1).

In the case of the smallest metalloid cluster compound Ge_5R_4 ($R = CH(SiMe_3)_2$) **3**,[4] a capped butterfly arrangement of five germanium atoms is observed in the cluster core. The Ge_6Ar_2 compound **5** ($Ar = C_6H_3$-2,6-$Dipp_2$; Dipp = C_6H_3-2,6-$i Pr_2$)[5] exhibits a distorted octahedral arrangement of six germanium atoms and in the case of the Ge_8R_6 compound **4** [$R = N(SiMe_3)_2$; $(OtBu)_2C_6H_3$][6] a more or less distorted cubic arrangement is observed. The arrangement of the germanium atoms inside the anionic metalloid cluster compound $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **6** is best described as a tricapped trigonal prismatic arrangement of nine germanium atoms inside the cluster core.[7] Only the arrangement in the cationic species $[Ge_{10}(SitBu_3)_6I]^+$ **2** might be seen as a topological approach to the solid state structure of germanium, a fact that has not been recognized before (see below).[8]

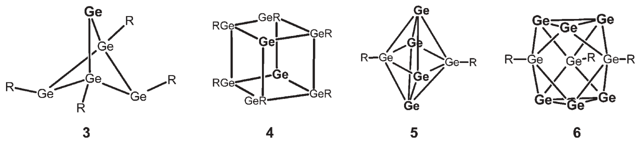

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Fig. 1 Structural formulae of metalloid cluster compounds of germanium (R = ligand); the naked germanium atoms are highlighted in bold.

Here we describe the first mixed Ge–Si metalloid cluster compound $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$ **1** (Fig. 2), in which 10 germanium and one silicon atom are present in the cluster core and in which the arrangement of the 10 germanium atoms can be

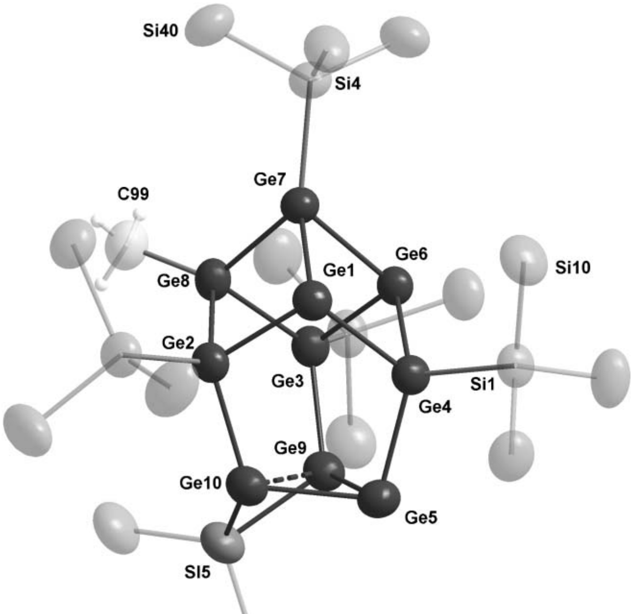

Fig. 2 Molecular structure of $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$ **1** (methyl groups of the $SiMe_3$ units are omitted for clarity), vibrational ellipsoids with 50% probability. Selected bond lengths [pm] and angles [°]: Ge1–Ge4: 246.35(14); Ge4–Ge5: 250.85(15); Ge4–Ge6: 248.90(13); Ge6–Ge7: 250.97(14); Ge7–Ge8: 248.85(12); Ge3–Ge9: 244.88(14); Ge9–Si5: 238.2(3); Ge10–Si5: 241.4(3); Ge7–Si4: 243.1(3); Ge4–Si1: 239.7(2); Ge8–C99: 200.5(10); Ge9–Ge10: 274.23; Ge1–Ge6: 296.2(1); Ge5–Ge10–Si5: 96.82(9); Ge7–Ge1–Ge4: 107.44(4); Ge7–Ge8–Ge2: 90.28; Ge8–Ge2–Ge10: 122.05(5).‡

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described as a distorted part of the solid state structure of α-germanium. **1** is formed beside the metalloid cluster species $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **6** during the reaction of metastable GeCl[9] with $LiSi(SiMe_3)_3$ and is isolated with $[Li(THF)_4]^+$ as counter ion in the from of dark red crystals. For the synthesis of **1**, the reaction mixture must be heated to 40 °C, where **1** is formed from a to date unknown precursor through rearrangement of a $Si(SiMe_3)_3$ ligand. During the rearrangement, the $Si(SiMe_3)_3$ ligand is decomposed in that way, that the central silicon atom is integrated into the cluster core. Additionally, a methyl group of the ligand is directly bound to a germanium atom of the cluster core (Ge8 in Fig. 2).[10] A similar reaction behaviour of cluster enlargement *via* the dismantling of a ligand was observed during gas phase reactions[11] of the anionic cluster compound $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **6** and additionally during the synthesis of the cluster compounds $[E_4Si[Si(SiMe_3)_3]_3(SiMe_3)_2]^-$ (E = Ga, Al).[12] As in all cases the same ligand is present, such reaction behaviour seems to be quite common for the $Si(SiMe_3)_3$ ligand.

The Ge–Ge distances in the cluster core of **1** vary between 245 pm and 253 pm, being in the expected range of a Ge–Ge single bond.[13] Only the Ge–Ge distance in the Ge_2Si triangle (Ge9, Ge10, Si5) is, with 275 pm, significantly longer (dashed line in Fig. 2). Structurally **1** can be described as a distorted cubic arrangement of seven germanium atoms (Ge1, Ge2, Ge3, Ge4, Ge6, Ge7, Ge8), where the eighth corner of the hypothetical cube is occupied by a Ge_3 triangle (Ge5, Ge9, Ge10). This description is similar to the one used by Sekiguchi *et al.* for the arrangement of the ten germanium atoms inside the cationic cluster species $[Ge_{10}(Si\textit{t}Bu_3)_6I]^+$, **2**.[8] This structural similarity is hereby very unusual as there are significant differences between both compounds:

(a) The average oxidation state of the germanium atoms inside the cluster core is strongly different being 0.8 in the case of **2** and 0.6 or 0.4 in the case of **1**, depending on whether the germanium atoms inside the Ge_2Si triangle are assigned a formal oxidation state of 1 or 0.

(b) **2** is a cationic metalloid cluster compound, while **1** is an anionic one.

(c) The substitution pattern is different, this means that the ligands are bound to different germanium sites of the cluster core, *e.g.* Ge4 is bound to a ligand and Ge5 is naked in the case of **1**, while Ge4 is naked and Ge5 binds a ligand in the case of **2** (see Fig. 3).

As now despite all these differences a similar arrangement of the 10 germanium atoms inside both clusters is realized, this arrangement is favourable for a metalloid cluster compound with 10 germanium atoms. The reason for this similarity might be the fact, that this arrangement can be seen as a structural approach to elemental germanium as shown in Fig. 3, where the characteristic arrangement of the diamond lattice, six-membered rings in chair conformation are emphasized.

Consequently, here exists for the first time a topological transition onto the solid state structure of α-germanium, which is more pronounced in the case of **1**, as here the oxidation state is closer to the value (0) of the solid state.[14] Hence **1** and **2** may be termed elementoid clusters. An adamantine arrangement of tetrel atoms in a molecular compound was recently reported by Marschner *et al.* in the silicon cluster compound $Si_{10}(SiMe_3)_4Me_{12}$ too.[15] However, in the case of the silicon compound, no naked silicon atoms are present, thus a classical bonding situation is present, where every silicon atom forms four 2c2e bonds. Despite this, the bonding situation in **1** is more complicated, as here naked germanium atoms with a coordination number of three are present, that are not tetrahedrally coordinated. To get a first insight into the bonding situation of **1** quantum chemical calculations on the model compound $Ge_{10}SiH_7^-$ **1′** have been performed, for which a similar arrangement of the $Ge_{10}Si$ core was calculated.[16] With the aid of an Ahlrichs–Heinzmann population analysis, shared electron numbers (SEN's)[17] for the two centre bonding components are calculated, that reproduce the trend in the bond lengths well. Thus the tetrahedrally coordinated germanium atoms (Ge2, Ge3, Ge7, Ge8) feature a classical bonding situation having four 2c2e bonds. In contrast, the three naked germanium atoms (Ge1, Ge5, Ge6) as well as the "invert tetrahedral" coordinated germanium atoms (Ge9, Ge10) form only three 2c2e bonds. The bond between the invert tetrahedral coordinated germanium atoms is weakened, with respect to a classical 2c2e bond as the two centre SEN is only 0.76.

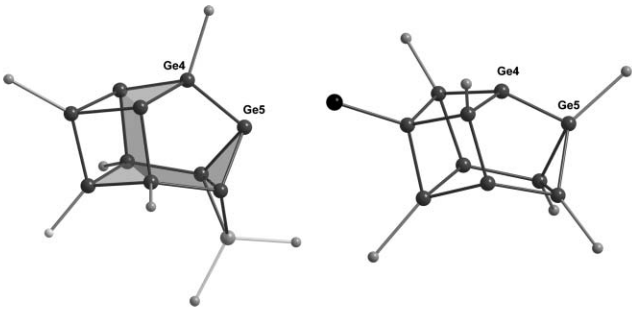

Fig. 3 Arrangement of the germanium atoms in the cluster cores of $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$ **1** (left) and $[Ge_{10}(Si\textit{t}Bu_3)_6I]^+$ **2** (right). From the ligands only the directly bound ligand atom is shown. The six membered rings in chair conformation are emphasized in the case of **1** by a polyhedral presentation.

In addition to the two centre bonding components, three centre bonding components are found inside the cluster core with SEN's from 0.23 to 0.25 in the three membered rings Ge7–Ge1–Ge6 (0.23), Ge1–Ge6–Ge4 (0.24), Ge5–Ge9–Ge10 (0.25) and Ge9–Ge10–Si5 (0.23). Therefore the additional bonding electrons that are available through the presence of the naked atoms are delocalized over the cluster core as it is the case for all other metalloid cluster compounds and no multiple bonds are formed.[2]

The appearance of a three centre bonding component in the three-membered ring build of two germanium and one silicon atom shows, that the silicon atom belongs to the cluster core. Hence, **1** is the first mixed metalloid Ge–Si cluster. Hereby the bonding situation inside the four-membered ring built up of three germanium atoms Ge5, Ge9 and Ge10 and the silicon atom Si5 (Fig. 2), where the germanium atoms Ge9 and Ge10 are inverse tetrahedrally bound, is most interesting.

Such an unusual bonding situation, with inverse tetahedrally bound tetrel atoms was recently found in the cluster compound $Si_8(Si\textit{t}Bu_3)_6$,[18] where the inverse tetrahedrally bound silicon atoms form an extremely short Si–Si bond. In comparison to this, the Ge–Ge bond in **1** is elongated with respect to the other Ge–Ge bonds. This elongation is not due to steric reasons as it is also calculated in $Ge_{10}SiH_7^-$ **1′**. Also, ring strain seems not to be responsible as many three membered ring systems are known with shorter Ge–Ge or Ge–Si bonds.[19] Otherwise the elongation could be the outcome of a structural approach to α-germanium, in which a nonbonding distance of 397.6 pm is found at this place. The elongation additionally shows, that **1** might also be a member of the growing class of singlet biradicaloid compounds[20] as the bonding situation is equivalent to that in the Sn_5R_6 propellanes,[21] where the bridgehead bond is also elongated.

More theoretical calculations will be necessary to understand the complex bonding situation inside **1**, especially the bonding between the inverse tetrahedrally coordinated germanium atoms Ge9 and Ge10. Additionally the theoretical studies might help to understand the substitution pattern. These theoretical investigations can be nicely supported by gas phase experiments, during which the bonding situation can be examined experimentally using ion impact dissociation experiments (SORI-CAD).

Additionally, the isolation of two metalloid cluster compounds $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$ **1** and $\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **6** out of the same reaction mixture shows, that more and maybe larger metalloid cluster compounds can be isolated by varying the reaction conditions.

The isolation and structural characterization of larger cluster compounds is hereby of special interest, as thus the question could be answered if larger metalloid cluster compounds would also show a structural resemblance to the structure of elemental germanium. Thereby, an approach on the normal pressure phase must not necessarily occur as, for example, the largest metalloid cluster compound of group 14, the Sn_{15} compound $Sn_{15}R_6$ (R = $NAr(SiMe_3)$; Ar = C_6H_3-2,6-*i*-Pr_2), shows a structural resemblance to a high pressure modification (45 ± 5 bar) of elemental tin.[22]

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Notes and references

‡ Crystallographic data for **1**, $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}Li(THF)_4\cdot C_5H_{12}$: M_r = 2273.59 g mol^{-1}, monoclinic, space group *C*2/*c*, a = 25.1875(10), b = 19.9932(5), c = 47.964(2) Å, β = 103.885(3), V = 23448(2) $Å^3$, Z = 8, $\rho_{ber.}$= 1.281 g cm^{-3}, μ_{Mo} = 2.752 mm^{-1}, $2\theta_{max}$ = 44.40°, 38491 measured reflections, 14003 independent (R(int.) = 0.0742), absorption correction: numeric (min/max transmission 0.9580/0.3147). Stoe IPDS II - diffractometer ($Mo_{K\alpha}$-radiation, (λ = 0.71073 Å), 200 K). The structure was solved by using SHELX-97 programms and refined by full-matrix least square methods. The refinement converged to final R_1 = 0.0556 for 9159 observed reflections ($I > 2\sigma$), wR_2 = 0.1481 for all 14003 independent reflections. CCDC 611634. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611165c

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