Metalloid Clusters

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The Largest Metalloid Group 14 Cluster, $Ge_{18}[Si(SiMe_3)_3]_6$: An Intermediate on the Way to Elemental Germanium

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Dedicated to Professor Hansgeorg Schnöckel

Abstract: *The oxidation of* $[Ge_9(Hyp)_3]^-$ *(Hyp* = $Si(SiMe_3)_3$*) with an* Fe^{II} *salt leads to* $Ge_{18}(Hyp)_6$ *(**1**), the largest Group 14 metalloid cluster that has been structurally characterized to date. The arrangement of the 18 germanium atoms in **1** shows similarities to that found in the solid-state structure Ge(cF136). Furthermore, **1** can be described as a macropolyhedral cluster of two* Ge_9 *units. Quantum-chemical calculations further hint at a strained arrangement so that **1** can be considered as a first trapped intermediate on the way from* Ge_9 *units to elemental germanium with the clathrate-II structure (Ge(cF136)).*

Metalloid cluster compounds[1] of the general formula M_nR_m ($n > m$; M = metal, e.g., Al, Au, Sn; R = ligand, e.g., SC_6H_4COOH, $N(SiMe_3)_2$) are ideal model compounds to obtain direct insights into the gray area between molecular compounds and the solid state of metals or semi-metals.[2] In recent years, a variety of Group 14 metalloid clusters have been synthesized and structurally characterized.[3] The arrangement of the tetrel atoms in the cores of these clusters resembles arrangements found in normal- and high-pressure modifications of the corresponding elements. For example, the arrangement of the twelve germanium atoms in $Ge_{12}[FeCp(CO)_2]_8[FeCp(CO)]_2$[4] resembles the high-pressure modification Ge-II, and the fifteen tin atoms in $Sn_{15}[NDipp(SiMe_3)]_6$ (Dipp = 2,6-iPr$_2$C$_6$H$_3$) resemble a cutout of a body-centered cubic (bcc) structure,[5] which is stable for tin at a pressure of 45 ± 5 GPa.[6] Aside from structural similarities to known solid-state structures, completely novel structures have also been observed within metalloid clusters, for example, the empty polyhedral arrangement of 14 germanium atoms in $\{Li(thf)_2\}_3\{Ge_{14}[E(SiMe_3)_3]_5\}$ (E = Si, Ge),[7,8] or the arrangement of 17 tin atoms in $Sn_{17}[GaCl(ddp)]_4$ (ddp = $HC(CMeNDipp)_2$).[9] This structural variety shows that there is high complexity in the nanoscale regime, and the study of metalloid cluster compounds provides first insights into the seemingly simple process of the formation of a metal or semi-metal.

Recently, a novel solid-state structure of germanium, Ge(cF136), was obtained by the oxidation of the Zintl anion Ge_9^{4-} with an ionic liquid.[10] Within Ge(cF136), all germanium atoms are fourfold coordinated and arranged in the clathrate-II form with two different polyhedra, a pentagonal dodecahedron consisting of 20 atoms and a hexakaidecahedron with 28 atoms. Furthermore, the reaction of the Zintl phase Mg_2Ge with $GeCl_4$ yields mesostructured germanium with cubic pores,[11] whereas oxidation of the Zintl ion $(Ge_9^{2-})_n$ with ferrocenium hexafluorophosphate in the presence of a surfactant (cetyltriethylammonium bromide) leads to hexagonally mesoporous germanium.[12] Undoubtedly, the oxidation of the Zintl anion Ge_9^{4-} provides access to novel open solid-state structures of germanium, which are of interest for potential applications in optoelectronics and photovoltaics.[13,14] However, it is still unknown how these novel structures are formed, and herein, we describe a first compound to obtain information with regard to these processes.

To trap and stabilize reactive intermediates on the way to bulk phases, bulky ligands are necessary. Therefore, the metalloid germanium cluster $[Ge_9(Hyp)_3]^-$ (**2**; Hyp = $Si(SiMe_3)_3$) is an ideally suited starting material owing to its relative stability, high-yielding synthesis, and good solubility. **2** was first synthesized by a disproportionation reaction of the subvalent monohalide GeBr,[15] and can also be obtained by the reaction of the Zintl anion Ge_9^{4-} with $ClSi(SiMe_3)_3$.[16] Furthermore, it has recently been shown that **2** is useful for "build-up reactions" to obtain metalloid cluster compounds with the composition $[(Hyp)_3Ge_9{-}M{-}Ge_9(Hyp)_3]^X$ ($X = -1$: M = Cu, Ag, Au; $X = 0$: M = Zn, Cd, Hg)[17] or even larger clusters, such as $[Ge_9(Hyp)_3]{-}Cu{-}[Ge_9(Hyp)_3]{-}Cu{-}PPh_3$.[18] To further investigate the reactivity of **2** towards other transition metals, we reacted a THF solution of **2** with $FeCl_2$ in the presence of 1,2-bis(diphenylphosphino)ethane (dppe), which led to an instant color change. After work-up of the reaction mixture, black crystals of the neutral metalloid cluster $Ge_{18}(Hyp)_6$ (**1**) were obtained from a pentane extract. Compound **1** is the largest Group 14 metalloid cluster that has been structurally characterized to date (Figure 1). During the formation of **1**, a salt metathesis reaction and a redox process occur, as the anionic compound **2** is oxidatively coupled to give the neutral compound **1**. The oxidant is the iron(II) salt, which is reduced to iron(I) and crystallizes as dark green $[Fe(dppe)_2][Ge_9(Hyp)_3]$ crystals.[19] The redox process can be described by the following equation:

$$4\,K[Ge_9(Hyp)_3] + 2\,FeCl_2 + 4\,dppe \rightarrow$$
$$Ge_{18}(Hyp)_6 + 2\,[Fe(dppe)_2][Ge_9(Hyp)_3] + 4\,KCl$$

However, the yield of crystalline **1** from the pentane extract is very low (ca. 5%), and after prolonged reaction

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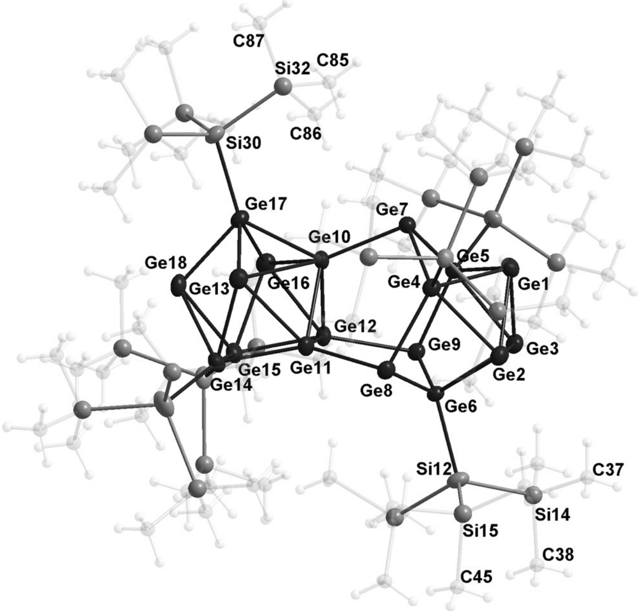

Figure 1. Molecular structure of Ge$_{18}$[Si(SiMe$_3$)$_3$]$_6$ (**1**). CH$_3$ groups shown in light gray, thermal ellipsoids set at 25% probability only for the germanium atoms and the directly bound silicon atoms for the sake of clarity. Selected bond lengths [pm] and angles [°]: Ge1–Ge2 258.47(15), Ge2–Ge3 255.65(15), Ge2–Ge6 264.28(14), Ge4–Ge8 254.61(14), Ge6–Ge8 258.01(14), Ge6–Ge9 258.67(13), Ge7–Ge10 257.60(12), Ge8–Ge11 259.94(13), Ge9–Ge12 261.72(13), Ge10–Ge17 249.18(13), Ge11–Ge12 256.08(14), Ge13–Ge17 254.05(14), Ge14–Ge18 266.02(15), Ge17–Ge18 249.87(15), Ge6–Si12 241.6(3), Ge17–Si30 238.8(3), Si12–Si14 236.2(4), Si12–Si15 234.6(5), Si30–Si32 235.0(5), Si14–C37 185.1(15), Si14–C38 191.1(13), Si15–C45 205(2), Si32–C85 188.2(17), Si32–C86 189.3(15), Si32–C87 188.3(13); Ge3-Ge1-Ge2 59.34(4), Ge8-Ge6-Si12 113.86(8), Ge4-Ge7-Ge10 98.25(4), Ge6-Ge8-Ge11 95.38(4), Ge15-Ge14-Ge18: 61.14(4).

times, **1** could not be identified in the reaction mixture by NMR spectroscopy at all. These results indicate that **1** is not stable under the reaction conditions; however, it can be extracted from the crude reaction mixture with pentane and crystallized from this extract.

In **1**, six of the 18 germanium atoms are bound to a ligand so that the cluster core is nearly completely shielded. Only one three-membered ring of naked germanium atoms is partially open, as can be seen from the space-filling model (see the Supporting Information, Figure S3). In contrast to starting material **2**, where the ligand-bound germanium atoms do not form a direct bond, two ligand-bound germanium atoms in **1** (Ge14, Ge15) form a Ge–Ge bond with a bond length of 254.7 pm, indicating that a severe rearrangement of the core has taken place during the reaction. The Ge–Si bonds in **1** are in the normal range for Si(SiMe$_3$)$_3$ ligated germanium clusters.[7,15,23] Within the cluster, the Ge–Ge bonds vary from 249 to 268 pm, and also fall in the normal range for metalloid germanium clusters.[3] In **1**, two Ge$_9$(Hyp)$_3$ units are still recognizable; however, they are strongly distorted with respect to the tricapped trigonal-prismatic arrangement of the nine germanium atoms in the starting material (Figure 2).

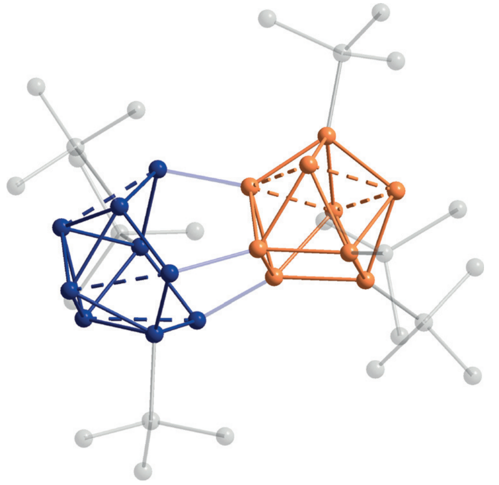

Figure 2. Molecular structure of Ge$_{18}$(Hyp)$_6$ (**1**) without the SiMe$_3$ groups. The different subunits are emphasized by different colors; the *hypho-* and *nido*-type fragments are shown in blue and orange, respectively. The connecting Ge–Ge bonds and the silicon atoms of the ligands are shown in light gray (dashed Ge–Ge bonds in the *nido* fragment: 284–295 pm, in the *hypho* fragment: 304–309 pm).

Therefore, one Ge$_9$(Hyp)$_3$ unit can be described as a distorted monocapped square-antiprismatic *nido* cluster containing the germanium atoms Ge10–Ge18 (orange in Figure 2). The other subunit (Ge1–Ge9) can be described as a *hypho* Ge$_9$(Hyp)$_3$ fragment (blue in Figure 2), which can be obtained from **2** by expanding one three-membered ring of naked germanium atoms so that they are now closer to the naked germanium atoms of the other three-membered ring (dashed blue lines in Figure 2) than to each other. As one subunit might be described as a *nido* and the other one as a *hypho* subunit, **1** fulfills the $m+n+o$ rule for fused polyhedra.[20] Thereby, every ligand-bound germanium atom provides three electrons for cluster bonding (6×3), every naked germanium that bears a lone pair provides two electrons (9×2), and the three connecting germanium atoms provide four electrons for cluster bonding (3×4), leading to a total of 48 electrons for cluster bonding. As the cluster contains 18 atoms ($m=18$) and consists of two fused polyhedra ($n=2$), with one *nido*- and one *hypho*-type cluster ($o=1+3$), 24 orbitals are available for cluster bonding. As 48 electrons are available, **1** can be described as a macropolyhedral cluster. However, the *nido* and *hypho* Ge$_9$ subunits are strongly distorted, leading to some very long Ge–Ge distances of more than 300 pm (dashed lines in Figure 2), which are much longer than the other Ge–Ge distances within the cluster core.

Another possible explanation for the arrangement of the 18 germanium atoms in the cluster core is the structural similarity of **1** with different solid-state structures of elemental germanium (Figure 3). An adamantine arrangement of nine germanium atoms is obvious in the center of **1**,[21] which is similar to that observed within α-germanium and the metalloid germanium clusters [Ge$_{10}$(Si*t*Bu$_3$)$_6$I]$^+$ and [Ge$_{10}$Si(Hyp)$_4$(SiMe$_3$)$_2$(Me)]$^-$.[22,23] Furthermore, the fusion of the two Ge$_9$(Hyp)$_3$ units leads to the formation of edge-sharing,

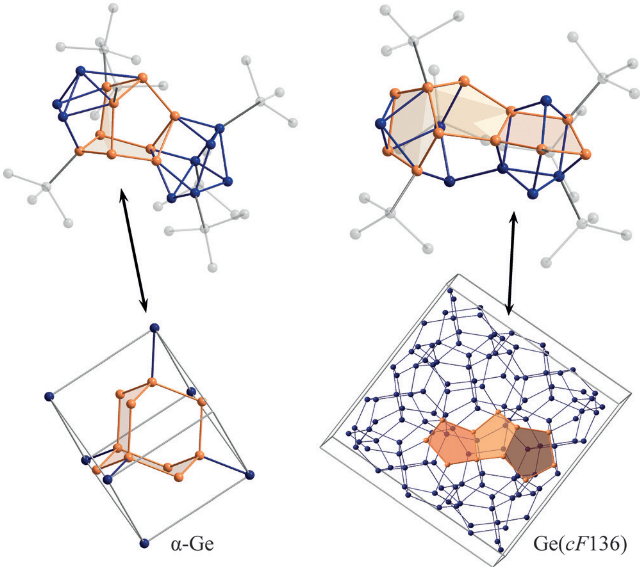

Figure 3. Top: Molecular structure of $Ge_{18}[Si(SiMe_3)_3]_6$ (**1**) without the Me groups. Left: The adamantine arrangement of the germanium atoms inside the cluster core is emphasized by polyhedral representation. Right: The structure of the edge-sharing, nearly planar five-membered rings is emphasized by polyhedral representation. Both structural motifs are similar to those found in α-Ge as well as Ge(cF136) (bottom), which are also shown in polyhedral representation.

nearly planar five-membered Ge_5 rings, a central feature of the solid-state structure of Ge(cF136). As both **1** and Ge(cF136) are obtained by the oxidation of a precursor with Ge_9 units, the arrangement of the germanium atoms in **1** can be seen as a first step of going from Ge_9 clusters to the solid-state structure Ge(cF136) with further conversion being prevented by the six bulky ligands. However, the fact that these ligands do not completely shield the cluster core might lead to high reactivity. Indeed, **1** is not stable in THF solution and decomposes even at room temperature as confirmed by ^{1}H NMR analysis of a [D_8]THF solution of dissolved crystals of **1** (see Figure S4).

The steric demand of the ligands in **1** plays a vital role: Quantum-chemical calculations[24] show that the arrangement of the germanium atoms inside the cluster core changes when the $Si(SiMe_3)_3$ moieties are substituted by the less bulky ligands H and SiH_3. Hence, only calculations with the complete $Si(SiMe_3)_3$ ligand lead to an arrangement that is similar to the experimental one, directly showing the strained structure in **1**.[25] An analysis of the bonding in **1** further shows that the variation in the shared electron numbers (SENs)[26] for the two-center bonding components follows the trend in the bond lengths within the cluster core. Thereby, the weakest bonds are the Ge–Ge bonds connecting the Ge_9 units, namely Ge10–Ge7, Ge11–Ge8, and Ge12–Ge9, with SENs of only 0.73–0.78 for the two-center bonding components. This result further corroborates the hypothesis that in **1**, the further fusion of the Ge_9 units is prevented by the six bulky Hyp ligands. Aside from the two-center bonding components in **1**, there are also three-center bonding components with a maximum SEN of 0.32 within the three-membered ring consisting of the germanium atoms Ge1, Ge2, and Ge3.

In conclusion, we have presented the synthesis and structural characterization of the largest metalloid Group 14 cluster compound, $Ge_{18}(Hyp)_6$ (**1**), where the arrangement of the germanium atoms in the cluster core is structurally similar to different solid-state structures of elemental germanium. Cluster compound **1** was obtained by the oxidation of the anionic precursor $[Ge_9(Hyp)_3]^-$ (**2**), in close analogy to the synthesis of Ge(cF136) from Ge_9^{4-}. Consequently, **1** resembles Ge(cF136) both structurally and chemically, providing first insights into the process of the formation of this germanium clathrate.

Experimental Section

All reactions were performed under nitrogen atmosphere by using Schlenk techniques or in an argon-filled glove box. Solvents (THF, pentane) were dried over sodium/benzophenone and distilled prior to use. K_4Ge_9, HypCl, and $K[Ge_9(Hyp)_3]$ were prepared according to known procedures ($Hyp = Si(SiMe_3)_3$).[16,27]

Synthesis of $Ge_{18}[Si(SiMe_3)_3]_6$ (**1**): $FeCl_2$ (18 mg, 0.14 mmol) and dppe (54 mg, 0.14 mmol) were stirred in THF (3 mL) until fully dissolved. $K[Ge_9(Hyp)_3]$ (400 mg, 0.28 mmol) dissolved in THF (5 mL) was added to this solution, and the reaction mixture was stirred for 18 hours. The color of the solution changed from red to black, indicating that the reaction proceeded. The solvent was then removed under reduced pressure. The black residue was first extracted with pentane and then with Et_2O, where the amounts of dissolved material were 100 mg and 320 mg, respectively. Slow crystallization from concentrated pentane extract at +6 °C led to the formation of large, black, plate-like crystals of **1** growing outside the mother solution (ca. 10 mg). From the ether extract, 40 mg of dark green crystals of $[Fe(dppe)_2][Ge_9(Hyp)_3]$[19] were obtained. ^{1}H NMR of **1** ([D_8]-THF): $\delta = 0.40$ ppm.

Crystal structure data for $Ge_{18}[Si(SiMe_3)_3]_6$ (**1**): $Ge_{18}Si_{24}C_{54}H_{162}$: $M_r = 2792.6\ \mathrm{g\,mol^{-1}}$, crystal dimensions $0.1 \times 0.1 \times 0.05\ \mathrm{mm^3}$, monoclinic, space group $P2_1/c$, $a = 32.858(3)$ Å, $b = 26.969(3)$ Å, $c = 32.808(3)$ Å, $\beta = 119.875(4)°$, $V = 25209(4)$ Å^3, $Z = 8$, $\rho_{calc.} = 1.472\ \mathrm{g\,cm^{-3}}$, $\mu_{Mo} = 4.475\ \mathrm{mm^{-1}}$, $2\theta_{max} = 52.788°$, 435376 reflections measured, 51559 independent reflections ($R_{int} = 0.0923$), absorptions correction: semi-empirical (min./max. transmission 0.5639/0.7454), $R1 = 0.0543$, $wR2 = 0.1341$, Bruker APEX II diffractometer ($Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), 280 K).[28] The structure was solved by direct methods and refined against F^2 for all observed reflections. Programs used: SHELXS and SHELXL.[29] CCDC 1437886 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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