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$Ge_{14}[Ge(SiMe_3)_3]_5Li_3(THF)_6$: the largest metalloid cluster compound of germanium: on the way to fullerene-like compounds?†

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The reaction of GeBr with $LiGe(SiMe_3)_3$ yields the largest metalloid cluster compound of germanium $Ge_{14}[Ge(SiMe_3)_3]_5Li_3(THF)_6$, in which 14 germanium atoms are arranged as a hollow sphere in the cluster core, showing that in the case of germanium also fullerene-like compounds might be present in the borderland between the molecular and solid states.

Metalloid cluster compounds, in which more metal–metal than metal–ligand bonds are present[1] are ideal compounds to get a deeper insight into the borderland between the molecular and the solid state and therefore research in the area of metalloid cluster compounds opens the possibility to build up an understanding of the process of formation as well as dissolution of a metal or semi-metal on the molecular scale.[2] In the case of germanium great progress was made in the field of metalloid compounds recently.[3] So, during the last years a couple of metalloid cluster compounds of germanium were synthesized comprising six (Ge_6Ar_2 **1**; Ar = $C_6H_3Dipp_2$; Dipp = C_6H_3-2,6-iPr$_2$),[4] eight ($Ge_8[N(SiMe_3)_2]_6$ **2**,[5] $Ge_8(OiPr_2C_6H_3)_6$ **3**[6]), nine ($\{Ge_9[Si(SiMe_3)_3]_3\}^-$ **4**)[7] and ten ($[Ge_{10}(SitBu_3)_6I]^+$ **5**;[8] $\{Ge_{10}Si[Si(SiMe_3)_3]_4(SiMe_3)_2Me\}^-$ **6**;[9] $(THF)_{18}Na_6Ge_{10}[Fe(CO)_4]_8$ **7**[10]) germanium atoms inside the cluster core.

Taking a look into the structural and electronic properties of these metalloid cluster compounds **1–7** reveals, that a dynamic system is present in the borderland between the molecular and solid states; *e.g.* the arrangement of the 10 germanium atoms in **5** and **6** can be seen as a structural approach to the solid state structure of α-germanium.[9] In contrast to this, the arrangement of the 10 germanium atoms in **7** hints to novel polyhedrons in the field of germanium chemistry, and the delocalized bonding electrons inside all compounds open the way to a metallic modification of germanium.[11] Thus, so far no trend can be observed and consequently, the most fascinating question to be answered in this area is: what happens in the case of larger cluster compounds on the way to elemental germanium; will there be a closer approach to the solid state structure of elemental germanium or are other polyhedral arrangements possible, or can a metal-like arrangement (coordination number 12) be realized?

To answer this question first of all it is necessary to synthesize and characterize larger compounds so that trends might be made observable. Here we present the so far largest structurally characterized metalloid cluster compound of germanium $(THF)_6Li_3Ge_{14}[Ge(SiMe_3)_3]_5$ **8**, whose structure is shown in Fig. 1 and which is synthesized by a reaction of GeBr with $LiGe(SiMe_3)_3$.‡

Compound **8** co-crystallizes with $Ge(SiMe_3)_4$ in the form of dark red crystals in the hexagonal crystal system in the space group $P6_3/m$, whereby a disorder of the molecule is present, which is described by a statistic model.§ Due to the disorder the refinement of the crystal structure of **8** as well as the collection of sufficient data were quite difficult. Since a statistical description of the disorder needs more parameters, as two different positions have to be refined, reflections up to a 2θ value of 60° are collected. The measurement was performed at the synchrotron light source ANKA at the research centre of Karlsruhe.[12] With the aid of the intensive synchrotron

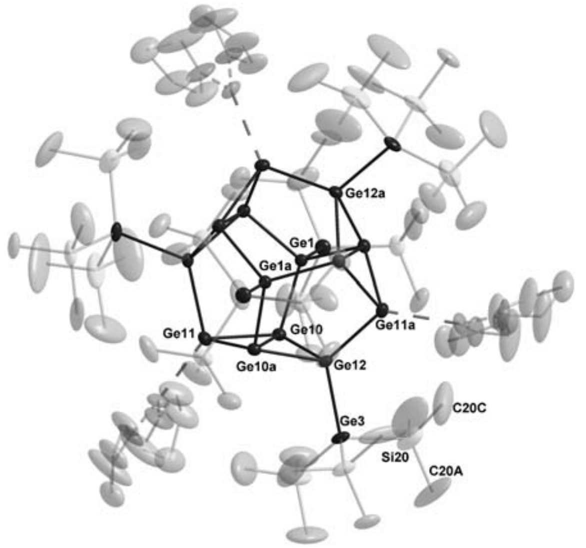

Fig. 1 Molecular structure of $(THF)_6Li_3Ge_{14}[Ge(SiMe_3)_3]_5$ **8** (without hydrogen atoms); vibrational ellipsoids with 50% probability. Selected bond lengths [Å] and angles [°]: Ge1–Ge10: 2.4566(6); Ge1–Ge1a: 4.114; Ge11–Ge12a: 6.597; Ge10–Ge11: 2.5022(10); Ge10–Ge12: 2.4865(12); Ge10–Ge10a: 2.8563(13); Ge12–Ge11a: 2.5641(17); Ge12–Ge3: 2.511(7); Ge3–Si20: 2.388(8); Si20–C20a: 1.86(2); Si20–C20C: 1.94(3); Ge11–Ge10–Ge12: 108.75(3); Ge10–Ge12–Ge10a: 70.11(5); Ge1–Ge10–Ge11: 109.06(4).

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radiation ($\lambda = 0.8$ Å) sufficient data were collected to refine the structure of **8** by a split model (60 : 40) to a very good R_1 value of 4.57% with an excellent reflection/parameter value of 12.4. The arrangement of the germanium atoms in both parts of the split model is identical within standard deviations and in Fig. 1 the part with 60% occupancy is shown, on which the following structural discussion is based.

The realized arrangement of the 14 germanium atoms in the cluster core of **8** is unique in the field of metalloid cluster compounds and it presents a new arrangement in germanium chemistry. Most important is the fact that here a "hollow" arrangement is realized, thus the 14 germanium atoms build up an empty polyhedron which is not spherical but discus-like, as the shortest Ge–Ge distance between two germanium atoms on opposite sides (Ge1–Ge1a) is 4.11 Å, while the longest (Ge11–Ge12a) amounts to 6.60 Å. The polyhedron is built up of six five-membered rings and three four-membered rings in a butterfly arrangement, where a Ge–Ge distance of 2.856 Å is formed along the diagonal of the four-membered ring (Ge10–Ge10a). A comparable polyhedron [Sn_{14}] was found lately inside the Zintl-phase $Na_{29}Zn_{24}Sn_{32}$ by Fässler *et al.*[13] However, the Sn_{14} polyhedron is more spherical, filled (a sodium cation is present inside the Sn_{14} polyhedron) and is a cut-out of a solid state structure and not a molecular compound. Therefore significant differences in the bonding situation are to be expected. Nevertheless, as in both cases a closed arrangement of 14 atoms is present, such a structural feature seems to be energetically favourable for the heavier elements of group 14. Additionally, the similarity of the E_{14} polyhedra (E = Ge, Sn) in the Zintl-phase $Na_{29}Zn_{24}Sn_{32}$ and the molecular metalloid cluster compound $(THF)_6Na_3Ga_{14}[Ge(SiMe_3)_3]_5$ **8** raise the question whether it might be possible to get access to anionic polyhedral Sn_{14} compounds by dissolution of the Zintl-phase $Na_{29}Zn_{24}Sn_{32}$, *e.g.* in ethylenediamine (EN). A similar approach was established for the Zintl anion Ge_9^{4-} by dissolution of the Zintl-phase K_4Ge_9 in EN.[14]

A completely different Sn_{14} polyhedron was described by Power *et al.* in the metalloid cluster compound $Sn_{15}Dipp_6$ (Dipp = $NArSiMe_3$; Ar = C_6H_3,2,6-*i*Pr_2). Here eight tin atoms are arranged cubically around a central tin atom and the four-membered rings of the cube are capped by a Sn–Dipp unit, leading to a Sn_{14} polyhedron around the central tin atom.[15] However, in the case of the Sn_{14} polyhedron in $Sn_{15}Dipp_6$ the central tin atom plays an important role, leading to the observed spherical Sn_{14} polyhedron. As no central atom is present inside **8**, a completely different discus-like polyhedron is formed.

Due to the high symmetry of the Ge_{14} polyhedron ($3/m$) in **8**, only four different kinds of germanium atoms are present inside the cluster core. The Ge–Ge distances inside the cluster core vary in a narrow range between 2.457 and 2.502 Å. Only the Ge–Ge distance of the diagonal contact (Ge10–Ge10a) of the butterfly arrangement is at 2.856 Å significantly different. A first insight into the bonding situation of **8** was performed with quantum chemical calculations on **8**, for which similar Ge–Ge distances are calculated as found by crystal structure analysis.[16] The result of an examination of the bonding situation within **8** with the aid of an Ahlrichs–Heinzmann population analysis is shown in Fig. 2. Thus for the ligand bound germanium atom Ge1 a classical bonding situation with 4 tetrahedrally arranged 2c2e bonds is present. The Ge–Ge distances of 2.457 Å are thereby comparable to those found in elemental α-germanium (2.445 Å[17]).

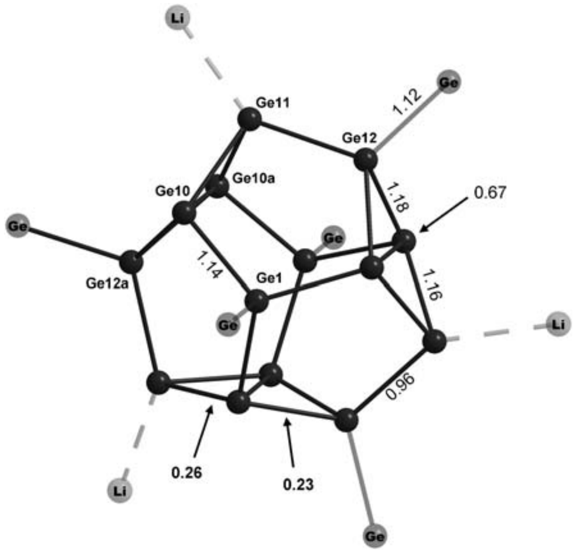

Fig. 2 Calculated molecular structure of **8** (the $SiMe_3$ and THF groups are omitted for clarity): calculated SENs[17] for the two- and three-centre bonding components are shown where the 3Z-SENs are bold. Selected bond distances [Å]: Ge1–Ge10: 2.5189; Ge10–Ge10a: 2.9140; Ge10–Ge11: 2.5309; Ge11–Ge12: 2.6189; Ge10–Ge12a: 2.5313.

In the case of Ge12 (ligand bound) as well as Ge11 (lithium coordinated), four nearly tetrahedrally arranged binding partners are present, too. Consequently, a nearly classical bonding situation is also expected for these germanium atoms. This assumption is supported by the shared electron numbers (SENs)[18] of the two centre bonding components that are all nearly 1 (0.96–1.18). In the case of the naked germanium atom (Ge10), a non-classical bonding situation is present, as first of all, only three Ge–Ge distances in the range of a single bond are formed (2.457–2.502 Å). The fourth Ge–Ge distance is at 2.856 Å significantly longer. Additionally the four binding partners are not arranged tetrahedrally but "inverse tetrahedrally", a description used by Wiberg *et al.* for the bonding pattern of the two central silicon atoms in $Si_8(Si\mathit{t}Bu_3)_6$.[19] Such a bonding motif is also present in the metalloid cluster compound **6**. Due to the non-classical bonding situation three centre bonding components inside the butterfly-like four-membered ring with SENs up to 0.26 are formed. Hence, inside **8** two different kinds of rings are present (four- and five-membered rings) in which also different bonding situations are present, representing a similar bonding situation as observed in the metalloid Ge_{10} cluster compound with transition metal ligands $(THF)_{18}Na_6Ge_{10}[Fe(CO)_4]_8$ **7**.[10]

Additionally, the presence of an "empty" polyhedron of 14 germanium atoms shows, that closed three-dimensional arrangements are possible for the heavier congeners of carbon without a stabilizing atom in the centre.[20] Thus, an approach to fullerene-like molecules seems possible also for germanium, where **8** can be seen as the first member of this class of compounds. The structural and electronic properties of the largest metalloid cluster compound $(THF)_6Li_3Ge_{14}[Ge(SiMe_3)_3]_5$ **8** presented here reveal that the borderland between the molecular and the solid state is even more complicated as now also fullerene-like structures might be realized and therefore in the future further surprises might be expected in this fascinating area.

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Notes and references

‡ Synthesis of $Ge_{14}[Ge(SiMe_3)_3]_5Li_3(THF)_6$: liquid germanium was treated with HBr under high vacuum at 1550 °C, and the resulting gaseous products (*ca.* 20 mmol GeBr) were co-condensed with a mixture of toluene–N*n*Pr$_3$ (5 : 1; 100 ml) at a surface at −196 °C. After the co-condensate was allowed to warm to −78 °C an emulsion consisting of a dark-red oil in a pale yellow solution was obtained. This emulsion was subsequently treated with $(THF)_3Li[Ge(SiMe_3)_3]$ (10.3 g, 20 mmol) dissolved in toluene (100 ml) at −78 °C. The reaction mixture was then slowly allowed to warm to room temperature to yield a nearly black solution. Removal of the solvent *in vacuo* yielded a black oil, which upon extraction with toluene gave a black toluene solution. The toluene extract was heated for 2 days to 70 °C, leading to a black precipitate. Afterwards the solvent was changed to ether and after filtration and storage at −28 °C dark red crystals of $Ge_{14}[Ge(SiMe_3)_3]_5Li_3(THF)_6$ were obtained. NMR: ^{1}H and ^{13}C NMR spectra in C_6D_6 do not show any resolved signals due to hindered rotation (see space filling model, Fig. S1 in the ESI†) of the $SiMe_3$ as well as the THF groups. The only sharp signals to be observed are those of the co-crystallized $Ge(SiMe_3)_4$: ^{1}H NMR(250 MHz): $\delta = 0.31$ (s, $SiMe_3$); ^{13}C NMR (100 MHz: $\delta = 4.23$ (CH_3); $^{29}Si\{^1H\}$ NMR (79 MHz): $\delta = -5.15$ ($SiMe_3$).

§ Crystal structure data for $\{Ge_{14}[Ge(SiMe_3)_3]_5\}Li_3(THF)_6\cdot Ge(SiMe_3)_4\cdot Et_2O$: $C_{85}H_{229}Ge_{20}Li_3O_7Si_{19}$: $M_r = 3370.01$ g mol^{-1}, crystal size 0.5 × 0.2 × 0.1 mm, hexagonal, space group: $P6_3/m$, $a = 20.3002(10)$, $c = 22.100(2)$ Å, $V = 7887.0(9)$ Å^3, $Z = 2$, $\rho_{\text{calc.}} = 1.419$ g cm^{-3}, $\mu_{0.8\text{Å}} = 3.927$ mm^{-1}, $2\theta_{\max} = 63.18°$, 13 986 collected reflections, 5778 independent reflections ($R_{\text{int}} = 0.0289$), absorption correction: numerical (min/max-transmission 0.2423/0.6931), R_1 $[I > 2\sigma(I)] = 0.0457$, wR_2 (all data) = 0.1161. ANKA-synchrotron light source ($\lambda = 0.8$ Å), Bruker SMART-Apex—Diffractometer (149 K). The structure was solved by direct methods and refined against F^2 for all observed reflections. Programs used: SHELXS and SHELXL (G. M. Sheldrick, University of Göttingen; G. M. Sheldrick, *SHELXTL*, Version 5.1, Bruker AXS, 1998). CCDC-680514 contains the supplementary crystallographic data for this paper.

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