Cluster Compounds

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$[AuGe_{18}\{Si(SiMe_3)_3\}_6]^-$: A Soluble Au–Ge Cluster on the Way to a Molecular Cable?**

*Christian Schenk and Andreas Schnepf**

Metalloid clusters of Group 14 have been established as a discrete group of cluster compounds[1,2] during the last years.[3,4] The metalloid clusters of the general formula $[M_nR_m]$ ($n > m$; M = Si, Ge, Sn, Pb) contain ligand-bound metal atoms as well as "naked" metal atoms. Since the "naked" metal atoms inside these clusters exhibit an oxidation state of 0, the average oxidation state of the metal atoms within metalloid Group 14 cluster compounds is between 0 and 1. Therefore, these cluster compounds can be seen as intermediates on the way to the elemental state, and structural approaches toward the solid-state phase have been reported recently.[2,5]

Another interesting class of Group 14 cluster compounds that has been known for a long time is the Zintl anions.[6] In the case of the Zintl anions, characterization of the anionic species could be accomplished and subsequent reactions could be established during the last few years. Most results were obtained with the Zintl anion $[Ge_9]^{4-}$, which was linked to a dimer,[7] an oligomer,[8] or a polymer.[9] Additionally, $[Ge_9]^{4-}$ was treated with several transition-metal compounds; for example, the reaction with $[Ni(cod)_2]$ leads to the cluster species $[Ni_3Ge_{18}]^{4-}$, in which two $\{Ge_9\}$ units are connected through a $\{Ni_3\}$ bridge.[10] Furthermore, Au-bound Zintl anions such as $[Au_3Ge_{18}]^{5-}$ (**1**)[11] and $[Au_3Ge_{45}]^{9-}$ (**2**)[12] could be synthesized.

In the case of metalloid Group 14 cluster compounds no subsequent reaction has been reported, and thus we wondered if such reactions might also be possible. A promising candidate for such reactions seemed to be the metalloid cluster compound $[Ge_9R_3]^-$ (**3**, R = $Si(SiMe_3)_3$),[13] in which six naked germanium atoms are readily available for subsequent reactions. First results prove the case for our assumption, and we present herein the first subsequent reaction of a metalloid cluster compound, leading to the cluster compound $[AuGe_{18}R_6]^-$ (**4**, R = $Si(SiMe_3)_3$). For the synthesis of **4**, we treated a solution of **3** in THF with $[AuCl(PPh_3)]$. The reaction solution changed color from orange to red, and a white precipitate of LiCl was formed. After workup of the reaction mixture, the anionic cluster **4**, which crystallizes together with $[Li(thf)_6]^+$ as counterion, could be isolated in the form of red crystals.

As shown in Figure 1, the molecular structure of **4** consists of two $\{Ge_9R_3\}$ units which are connected by a central gold atom. The $[Li(thf)_6]^+$ salt of **4** crystallizes in the trigonal crystal system in the space group $R\bar{3}$, whereby the gold atom is located at the center of inversion. The central $\{Ge_{18}Au\}$ unit has D_{3d} symmetry, and since the $Si(SiMe_3)_3$ ligands are twisted by 37.7° against the mirror plane, the symmetry of the whole cluster is reduced to C_{3i}. The steric demand of the six $Si(SiMe_3)_3$ ligands is so large that the ligands are interlocked,[14] totally shielding the central gold atom against the exterior (Figure 2).

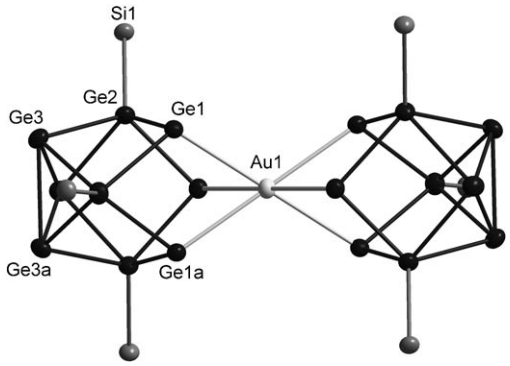

Figure 1. Molecular structure of **4** (without the $SiMe_3$ groups; vibrational ellipsoides with 50% propability). Selected bond lengths [pm] and angles [°]: Au1-Ge1 268.76(6), Ge1-Ge1a 296.09(6), Ge1-Ge2 251.57(9), Ge2-Si1 237.86(16), Ge2-Ge3 255.87(9), Ge3-Ge3a 263.58(6); Ge1-Ge2-Ge3 83.309(21), Ge1-Au1-Ge1a 66.862(14).

The gold atom is bound trigonal-antiprismatic to six germanium atoms and owing to the high coordination

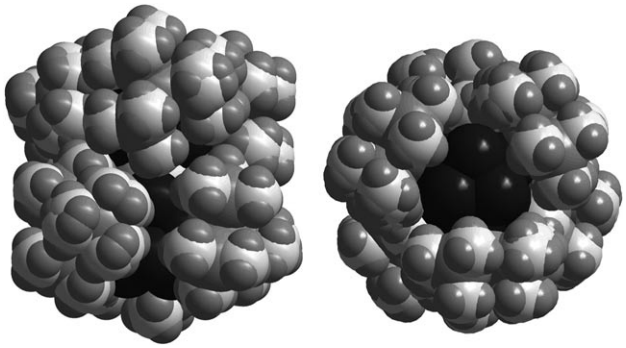

Figure 2. Space-filling model of **4**; left: side view; right: view along the threefold axis.

[*] Dipl.-Chem. C. Schenk, Dr. A. Schnepf
Institut für Anorganische Chemie der Universität Karlsruhe (TH)
Engesserstrasse, Geb. 30.45, 76128 Karlsruhe (Germany)
Fax.: (+49) 721-608-4854
E-mail: Schnepf@chemie.uni-karlsruhe.de

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number, a Au–Ge bond length of 269 pm results, which represents the longest Au–Ge bond observed in a molecular compound so far. The observed long Au–Ge bond fits well in the row of known Au–Ge bond lengths: a bond length of 238 pm is found for the Au–Ge bond in $[Au(GeCl_3)\{(o\text{-}Tol)_3P\}]$.[15] For coordination number 2, a slightly longer Au–Ge bond length of 242 pm is found in $[Au(GeCl_3)_2]^-$, [15] and in the gold-bound Zintl anion $[Au_3Ge_{18}]^{5-}$ (**1**) the Au–Ge bond length averages 245 pm.[11] For coordination number 3, the Au–Ge bond lengths in $[Au(GeCl_3)_3]^{2-}$ vary between 241 and 253 pm.[16]

The bonding of the gold atom to the $\{Ge_9\}$ unit in **4** leads to a significant distortion of the arrangement of the nine germanium atoms when compared to the arrangement in the anionic reactant **3**. The difference is best seen by an inspection of the bond length between gold-bound germanium atoms (Ge1), which is elongated by 28 pm from 268 pm in **3** to 296 pm in **4**. In contrast, the other Ge–Ge bond lengths between ligand-bound (Ge2) and gold-bound or naked germanium atoms (Ge1 and Ge3) are essentially undistorted. This bond length amounts to 253 pm in **3**, and bond lengths of 252 and 256 pm are found in **4**. Furthermore, the Ge–Ge bond length between naked germanium atoms decreases by 4 pm to 264 pm, and the Si–Ge bond length in **4** (238 pm) is comparable to that in **3**, in which a Ge–Si bond length of 236 pm is found. The observed distortion in **4** is in contrast to the results of the gold-bound Zintl anion $[Ge_{18}Au_3]^{5-}$ (**1**), in which two essentially undistorted $\{Ge_9\}$ units are found with respect to the starting material $[Ge_9]^{4-}$; thus, a different bonding situation is to be expected. The observed elongation in the Ge1-Ge1a-Ge1b three-membered ring in **4** is comparable to the situation found in $[Ni_3Ge_{18}]^{4-}$, in which an additional transition-metal atom (Ni) is present inside the $\{Ge_9\}$ unit.

A first insight into the bonding situation of **4** could be established using DFT calculations[17] on the model compound $[AuGe_{18}H_6]^-$ (**4′**), for which a similar arrangement as in **4** was calculated. The shared electron numbers (SENs)[18] of the two-center bonding components of an Ahlrichs–Heinzmann population analysis follow the trend in the bond lengths well. Consequently, the smallest two-center bonding component with an SEN of 0.62 is found between gold and germanium. With respect to this small two-center bonding component indicating a weak bond, the question arises whether **4** is stable in solution and would not dissociate into, for example, $[Ge_9R_3]^-$ and $[AuGe_9R_3]$. To answer this question, we dissolved crystals of $[Li(thf)_6]$-**4** in THF, and transferred the ions by electrospray ionization (ESI) into the gas phase, after which only the molecular peak of **4** could be detected (Figure 3), thus showing that **4** is stable in solution.

Furthermore, gas-phase dissociation experiments[19] that have been performed in a similar way with the metalloid cluster species **3**[20] show that the weakest bond inside **4** is the gold–germanium bond, as the primary product of the dissociation is the anionic species $[Ge_9R_3]^-$.[21]

Besides two-center bonding components, three- and also four-center bonding components are found inside **4′**, with SENs between 0.15 and 0.33, thus showing that the bonding electrons are delocalized over the whole cluster core. The

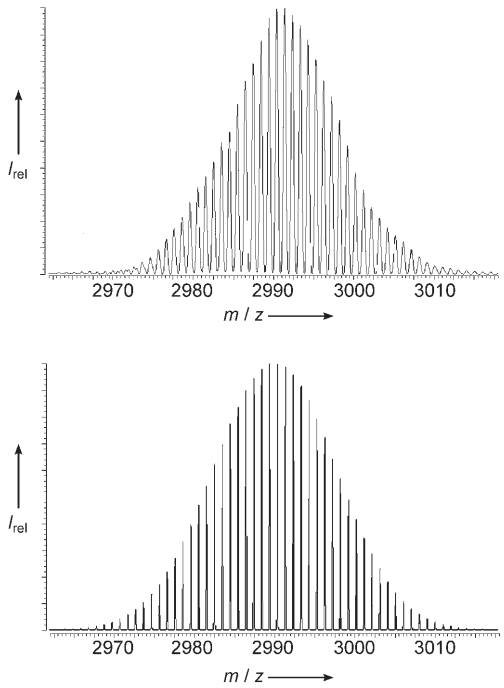

Figure 3. Measured (top, ESI mass spectrum) and calculated (bottom) isotopic pattern of the molecular peak of $[AuGe_{18}\{Si(SiMe_3)_3\}_6]^-$ (**4**).

appearance of a four-center bonding component inside the Au1-Ge1-Ge1a-Ge1b trigonal pyramid is most unusual. The appearance of covalent bonds between gold and germanium (two-center and multicenter bonding components) shows that the gold atom is an essential part of the cluster compound. Therefore, describing **4** as two $\{Ge_9R_3\}$ units that are connected by a gold atom is only correct from a topological point of view. With respect to the bonding situation, **4** is better described as a $\{AuGe_{18}\}$ cluster in which six germanium atoms are bound to one ligand each.[22]

In terms of the formation of **4**, we assume a similar reaction sequence as proposed for the formation of the cluster compound $[Ni_3Ge_{18}]^{4-}$.[10] In the first step, a metathesis reaction between the metalloid cluster compound $Li[Ge_9R_3]$ and the gold reagent $[AuCl(PPh_3)]$ takes place, whereby the neutral intermediate $[(PPh_3)Au(Ge_9R_3)]$ (not yet isolated) and LiCl are formed. Afterwards, the triphenylphosphane ligand is substituted by a further anionic germanium cluster **3**, leading to the metalloid cluster compound **4**.

The naked germanium atoms in **4** are as easily accessible (Figure 2, right), as is the case for **3**. Consequently, a subsequent reaction with the gold reagent seems feasible, that is, the formation of a linear chain of formula $[AuGe_9R_3]_n$ might be possible. Taking into account the strong delocalization of bonding electrons inside **4**, which might be spread over the whole chain, such a linear chain can be considered as a one-dimensional conductor, which would be totally shielded against the exterior by the $Si(SiMe_3)_3$ units (in the form of a molecular cable[23]). Experiments to realize such a concept are underway. The results presented herein show that the chemistry of metalloid Group 14 cluster compounds can open the way to new and unusual compounds and materials.

Experimental Section

4: At room temperature, [Li(thf)$_4$]-**3** (282 mg, 0.167 mmol) was dissolved in THF (ca. 100 mL). A solution of [AuCl(PPh$_3$)] (32 mg, 0.08 mmol) in THF was added dropwise over a period of 2 h. During this time the reaction mixture changed color from orange to red, and a white precipitate of LiCl was formed. The solution was filtered and after concentration in vacuum was stored at −28 °C, after which red crystals of [Li(thf)$_6$]-**4** were obtained (60 mg, 0.017 mmol, 19.6 %).

Crystal structure data for [Li(thf)$_6$]-**4**: $AuGe_{18}Si_{24}O_6C_{78}LiH_{210}$ $M_r = 3429.14\ g\,mol^{-1}$, crystal dimensions $0.1 \times 0.05 \times 0.05\ mm^3$, rhombohedral, space group $R\bar{3}$, $a = 15.6521(18)$ Å, $\alpha = 97.237(17)°$, $V = 3743.3(7)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.525\ g\,cm^{-3}$, $\mu_{Mo} = 4.767\ mm^{-1}$, $2\Theta_{max} = 51.90°$, 26552 measured, 4845 independent reflections ($R_{int.} = 0.0963$), absorption correction: numerical (min./max. transmission 0.7298/0.6726), $R_1 = 0.0389$, $wR_2 = 0.0662$, Stoe-IPDS-II diffractometer ($Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), 150 K). The structure was solved by direct methods and refined against F^2 for all observed reflections. Programs used: Shelxs und Shelxl.[24] CCDC-634299 contains 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.

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[22] If **4** is considered as consisting of a Au$^-$ center and two neutral {Ge$_9$R$_3$} units, every {Ge$_9$R$_3$} unit exhibits 21 cluster bonding electrons. This perception is in accord with the results of a population analysis,[17] in which the gold atom possesses the maximum negative charge. According to Wade's rules, a cluster of nine atoms with 21 bonding electrons would range between a *closo* ($2n + n = 20$) and a *nido* ($2n + 4 = 22$) cluster. As the arrangement of the nine germanium atoms inside the {Ge$_9$R$_3$} unit of **4** can be considered neither as *closo* (tricapped trigonal prism) nor as *nido* (monocapped square antiprism), a description of **4** with Wade's rules seems not to be reasonable. This observation is in contrast to the results with the Zintl anions, for which the structures often fit Wade's rules;[11] thus, there is a significant difference between metalloid cluster compounds and Zintl anions.
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