Cluster Compounds

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$[Au_3Ge_{45}]^{9-}$—A Binary Anion Containing a $\{Ge_{45}\}$ Cluster

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Dedicated to Professor Dieter Fenske on the occasion of his 65th birthday

The formation of nanostructured germanium-based materials from Zintl ions of the type $[Ge_9]^{4-}$ casts a new light on the potential of Zintl ions as precursors.[1–3] Moreover, recent investigations show that solutions of $\{Ge_9\}$ Zintl ions can lead to nanoporous materials and to a novel allotrope of germanium.[4] The synthesis of dimeric,[5] oligomeric,[6] and one-dimensional polymeric units[7] through oxidative coupling of $[Ge_9]^{4-}$ even points towards a new modification of germanium which is based on nine-atom clusters.[8] Whereas vapor-deposition processes have led to the synthesis of Ge nanowires,[9] gold particles facilitate the formation of well-defined one-dimensional structures.[10–13] A striking parallel to the metal-induced formation of Ge−Ge bonds can be found in the chemistry of Ge anions, in which the reaction of low-valent metal complexes $[ML_x]$[14] with Zintl ion clusters has yielded larger tetrel clusters that enclose the noble metal, such as $[(Pd{-}Pd)@Ge_{18}]^{4-}$[15] and $[Ni_6Ge_{13}(CO)_5]^{4-}$.[16] In the case of $[Pb_9]^{4-}$ anions, the reaction with transition-metal complexes results in clusters with higher nuclearity such as $[Pb_{10}]^{2-}$ and $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt).[17]

Our recent investigations into the reactivity of $[Ge_9]^{4-}$ Zintl ions with gold(I) compounds produced the anion $[Au_3Ge_{18}]^{5-}$ (**1a**),[18] which is composed of two $\{Ge_9\}$ clusters linked by a gold triangle. Through changes in the reaction conditions we have now managed to obtain a compound which contains a unique $\{Ge_{45}\}$ unit with four $\{Ge_9\}$ cluster units covalently linked by another nine Ge atoms. The individual clusters are connected through Ge-atom bridges and are further coordinated to three gold atoms.

The compound $[K([2.2.2]crypt)]_8K[Au_3Ge_{45}]$ (**2**) was obtained from the reaction of K_4Ge_9 with $[AuCl(PPh_3)]$ in ethylenediamine in the presence of [2.2.2]crypt.[19] Stepwise addition of the named reactants yielded diamond-shaped crystals of **2** and plate-shaped crystals of $[K([2.2.2]crypt)]_5[Au_3Ge_{18}]$ (**1**). These crystals formed over a period of two weeks from a deep red-brown solution. X-ray single-crystal structure analysis allowed the determination and refinement in the space group $Pna2_1$. The presence of eight $[K([2.2.2]crypt)]^+$ units and an additional K^+ ion that is linked to the anion indicates a net charge of 9− for the cluster. The asymmetric unit contains two independent cluster units $[Au_3Ge_{45}]^{9-}$ (**2a**), sixteen $[K([2.2.2]crypt)]^+$ units, and two K^+ ions.

The two individual $\{Ge_{45}\}$ clusters **A** and **B** are very similar in terms of structural characteristics. Therefore, the structure discussion below will focus on one of the clusters (**A**) and will point out significant differences where appropriate. Full structure optimization of those units using the program TURBOMOLE on the basis of density functional theory (DFT, BP86/SV(P)) including COSMO solvation in ethylenediamine ($\varepsilon_r = 13.82$) confirms the experimental structure and leads to species with a maximum deviation of interatomic distances of 0.143 Å.

The structural unit, made up of three Au atoms and 45 Ge atoms, consists of four polyhedral $\{Ge_9\}$ units, labelled **I** to **IV**, which are interconnected to nine further Ge atoms (Figure 1 a). Three structurally almost identical $\{Ge_9\}$ subunits **I** to **III** are each bonded to two Au atoms. Hence, the three Au atoms and the three clusters **I** to **III** form a cyclic unit with almost threefold symmetry. Also, clusters **I** to **III** form one *exo* bond each to the adjacent Ge atoms Ge51, Ge52, and Ge53, respectively. These Ge atoms act as a bridge to the Au atoms and establish covalent contacts to the atoms Ge54, Ge55, and Ge56, respectively. Therefore, the atoms Ge51, Ge52, and Ge53 are roughly in a tetrahedral environment with two Au atoms and two Ge atoms. The K^+ ion which is not trapped by [2.2.2]crypt is positioned almost symmetrically within the center of the three $\{Ge_9\}$ units **I** to **III** with the shortest K−Ge contacts ranging from 3.476 to 3.575 Å (all standard deviations for interatomic distances mentioned herein are below 0.005 Å).

The three nine-atom building blocks **I** to **III** can be best described as tricapped trigonal prisms. Polyhedral edge lengths ranging from 2.502 to 3.078 Å indicate delocalized skeletal cluster bonds as often observed in $\{Ge_9\}$ clusters.[1] The trigonal prisms **I** to **III** have distorted C_{2v} symmetry and structural arguments indicate 20-electron *closo* clusters with one covalent *exo* bond.[20]

The remaining 15-atom cluster unit can be divided into a polyhedral nine-atom unit **IV** (Ge41–Ge49), three triply coordinated Ge atoms (Ge57, Ge58, Ge59), and a Ge triangle (Ge54, Ge55, Ge56). The polyhedron **IV** shows the approximate symmetry of a capped square antiprism (Figure 1 b). This aspect is where significant differences between the

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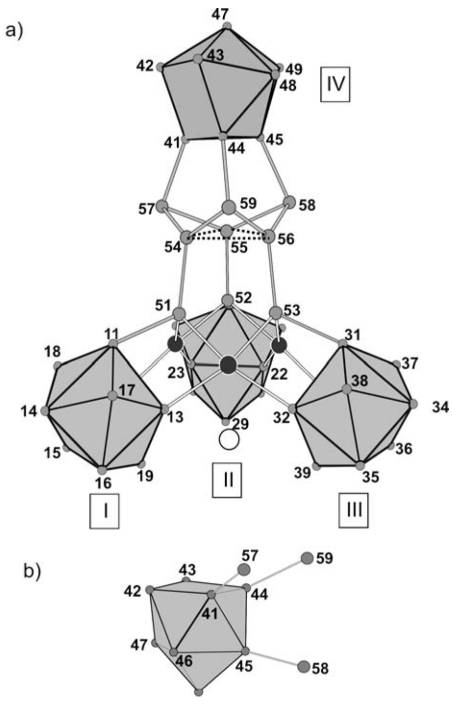

Figure 1. a) One of the two independent cluster anions $[Ge_{45}Au_3]^{9-}$ (**2a**). The four $\{Ge_9\}$ subunits are highlighted as polyhedra; Ge atoms gray, Au atoms black, K atoms white; the Ge atoms are numbered. b) Structure detail of **2a**: the quadratic antiprismatic cluster **IV** with three Ge–Ge *exo* bonds.

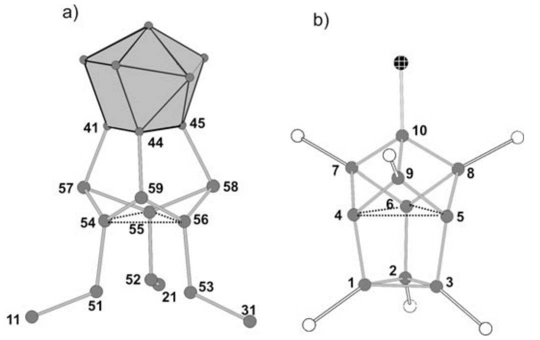

Figure 2. a) The central unit of Ge atoms in **2a** compared to b) the $\{Ge_{10}\}$ cluster in $[Ge_{10}(SitBu_3)_6I]^+$ (**3a**). Ge atoms gray, Si atoms white, I atom cross-hatched.

clusters **A** and **B** can be found: In **A** the capped quadratic antiprism **IV** is hardly distorted with the ratio of the diagonals of the uncapped square d_1/d_2 being 1.02 and hence almost ideal. However, cluster **B**, with $d_1/d_2 = 1.18$ and an angle of 13° along the smaller diagonal d_2 of the quadratic face, exhibits a far greater distortion. Taking into account that both subunits **IV** in **A** and **B** form three Ge–Ge *exo* bonds each, the overall distortion of the nine-atom cluster is surprisingly small.[5,6] DFT structure optimization without symmetry restrictions (see below) leads to an almost undistorted cluster with local C_{4v} symmetry.

While the interatomic distances within **IV** are typical for polyhedral Ge clusters, the bond lengths of the three Ge–Ge *exo* bonds of **IV** (distances to Ge57, Ge58, and Ge59: 2.482–2.490 Å) as well as contacts of those atoms to the Ge54-Ge55-Ge56 triangle with separations between 2.479 and 2.514 Å indicate a covalent-bond character. Ge–Ge contacts within the three-membered ring of the fivefold-coordinated Ge atoms are considerably longer (2.785–2.834 Å for **A** and 2.777–2.798 Å for **B**).[21] The bond character of the Ge54-Ge55-Ge56 triangle compares well to a similar triangle of Ge atoms (Ge4-Ge5-Ge6) in the cationic cluster $[Ge_{10}(SitBu_3)_6I]^+$ (**3a**, Figure 2), which shows a comparable atomic arrangement with the difference that bridging Ge atoms Ge7 to Ge9 in **3a** are fourfold-coordinated, whereas the corresponding atoms Ge57 to Ge59 in **2a** are threefold-coordinated. The contacts within the three-membered rings Ge4 to Ge6 in **3a** have been described as a three-center, two-electron bond;[22] these contacts (3.254–3.264 Å) are considerably longer than their counterparts Ge54 to Ge56 in **2a**. Therefore, the description of a three-center, two-electron bond applies even better for **2a**.

The three gold atoms Au1, Au2, and Au3 are each coordinated by four Ge atoms in a trapezoid fashion (angular sum 359°, Ge-Au-Ge angles 79–113°). Furthermore, the Ge–Au contacts of 2.479 to 2.565 Å are considerably shorter than the sum of the covalent radii (Ge: 1.22 Å, Au: 1.44 Å) and just slightly longer than the Au–Ge contacts in **1a**,[18] and are in the range of other compounds containing Au–Ge contacts.[23]

The assumption that each *exo* bond reduces the charge of a polyhedral homoatomic cluster by one[24] leads to the following formal electron count: 1) Clusters **I** to **III** are derived from a *closo* $[Ge_9]^{2-}$ cluster in which one *exo* bond yields one negative charge per cluster, and the 22-electron *nido* cluster **IV** with three *exo* bonds retains also a single negative charge. 2) According to the (8-*N*) rule, the twofold- (2b) and threefold-bonded (3b) Ge atoms carry a double and a single negative charge, respectively. 3) The central three-membered Ge54-Ge55-Ge56 ring with fivefold-bonded Ge atoms forms a three-center, two-electron bond, which leads to an overall charge of +1 for the triangle. Hence, **2a** can be described as a gold complex of the polyanion $\{([Ge_9]^-)_4(3b\text{-}Ge^-)_3(2b\text{-}Ge^{2-})_3([Ge_3]^+)\}$.[23] The counterbalance of the $[Ge_{45}]^{12-}$ anion cluster is formally given by nine K^+ ions and the assumption of an Au^I complex.

To gain insight into the chemical bonding of **2a** and especially to learn about the nature of the planar coordination of the Au atoms, which is generally indicative of Au^{III} complexes, we undertook a computational investigation. Au^I usually prefers linear or (distorted) tetrahedral coordination. However, in the chemistry of Ag^I an example of a related planar tetracoordinate complex exists: D_{2h}-symmetric $[Ag(P_4)_2]^+$.[25] Also in the related $[Au^I\{P_3M(tppme)\}_2]^+(PF_6)^-$ (M = Co, Rh, Ir, tppme = 1,1,1-tris(diphenylphosphanylmethyl)ethane),[26] the dihedral angle between the $\{AuP_2\}$ planes is on average 51°, thus between tetrahedral and planar. Since the $[Ge_4]^{4-}$ ion is isoelectronic with P_4 and $[P_3M(tppme)]$, we calculated the model compound $[Au(Ge_4)_2]^{n-}$.[27] The structure was optimized in D_{2d} and D_{2h} symmetry with a charge of $n = 7$ and $n = 5$, which would amount to two $[Ge_4]^{4-}$ ions as well as Au^+ and Au^{3+}, respectively. For comparative studies, structure optimizations were conducted also for the $[AuCl_4]^-$

ion in D_{2d} and D_{4h} symmetry as well as for $[Au_2Cl_6]$ with planar and tetrahedral coordination.

The energy difference between the planar and the tetrahedral coordination of these compounds delivers good evidence for the oxidation state of the gold atoms. In the chlorides, with an undisputed Au^{III} atom, the two structures differ by about 144 ($[AuCl_4]^-$) and 289 $kJ\,mol^{-1}$ ($[Au_2Cl_6]$), very clearly favoring the all-planar structures. The Au–Ge model compounds show no such simple behavior: In $[Au(Ge_4)_2]^{7-}$, the D_{2h} conformation is preferred over the D_{2d} conformation by only 6 $kJ\,mol^{-1}$; in $[Au(Ge_4)_2]^{5-}$, the D_{2d} conformation is preferred by about 13 $kJ\,mol^{-1}$ over the D_{2h} structure. Such small differences are negligible, thus indicating that both conformations are approximately isoenergetic. Investigations of bond orders in the $\{Ge_4\}$ moieties indicate that Au^{III} oxidizes both $[Ge_4]^{4-}$ entities to $[Ge_4]^{3-}$ and in turn is itself reduced to Au^I. Also, the partial charges of the Au atoms are similar with an average of $+0.10$ in the $[Au(Ge_4)_2]^{7-}$ compounds while those in the $[Au(Ge_4)_2]^{5-}$ conformers are $+0.18$ and $+0.30$ for the two isomers. For comparison, the partial charge of the gold atoms in **2a** is calculated to be $+0.35$, whereas in contrast, the charge in $[AuCl_4]^-$ and $[Au_2Cl_6]$ is on average $+0.69$.

In conclusion, the calculated very small energy differences between planar- and tetrahedral-coordinated $[Au(Ge_4)_2]^{n-}$ as well as the calculated partial charges for $[Au(Ge_4)_2]^{n-}$ and **2a** support the assignment of an oxidation state of $+1$ to the Au atoms in **2a** and the electron count for the $\{Ge_{45}\}$ cluster anion given above. Moreover, the unusual, almost planar coordination for Au^I may be easily rationalized given the right coordination environment. It appears that the nature of the Au–Ge cluster **2a** enforces the planar coordination of the three Au^I atoms, which is also supported by the complete structure optimization of **2a**.

The optimization led to Au–Ge and Ge–Ge bond lengths which are in excellent agreement with the measured ones although the calculated bond lengths are somewhat too long (which is a common problem for DFT methods; see Table 1). There are two distinct Au–Ge contacts: Six longer contacts occur to Ge atoms that are part of the clusters **I** to **III** with a mean separation of 2.554 Å, and shorter contacts to Ge atoms that have two homoatomic bonds (Ge51 to Ge53) with a mean value of 2.491 Å. The highest and lowest values differ in calculation and experiment by at most 0.111 and 0.052 Å for the longer and shorter contacts, respectively. The Au–Ge interaction is therefore well-represented by the model. The Ge–Ge contacts have a maximum deviation of 0.143 Å, and SENs (shared electron numbers) of Ge–Ge contacts that are considerd to be "single" bonds are between 0.9 and 1.1. For comparison, the SEN is 1.24 for Ge_2H_6 and 1.68 for Ge_2H_4. For the Ge54-Ge55-Ge56 triangle the calculated Ge–Ge bond lengths (ca. 2.8 Å) are also in excellent agreement with the experiment. The computed SENs of about 0.71 in these bonds are too small for single bonds, but there is also a significant three-center contribution of 0.26 shared electrons to the bonding in the Ge54-Ge55-Ge56 triangle, thus supporting a three-center, two-electron interaction (Table 1).

The 45 covalently bonded Ge atoms in **2a**, together with the recently described clusters $[Ge_9{=}Ge_9{=}Ge_9]^{6-}$ and $[Ge_9{=}Ge_9{=}Ge_9]^{8-}$,[6] provide new insight into the structural chemistry of germanium. The observed homoatomic coordination of germanium atoms and the wide variety of bond types in those anions are rather unexpected. In some aspects these systems share similarities with the triel elements boron and gallium as well as with partial structures in metal borides and gallides, which include Wade clusters along with three- and two-center, two-electron bonds.

Table 1: Comparison of observed (**2a**, cluster **A**) and calculated distances between selected atoms and associated shared electron numbers (SEN).

	Distance [Å] (observed)	Distance [Å] (calculated)	SEN
Ge54-Ge55	2.834 (**A**)	2.838	0.72
Ge54-Ge56	2.785 (**A**)	2.843	0.71
Ge55-Ge56	2.819 (**A**)	2.841	0.70
Ge54-Ge55-Ge56			0.26
Au-$Ge_{cluster}$	2.554[a]	2.654[a]	0.52
Au-(2b-Ge)	2.491[a]	2.531[a]	0.30

[a] Mean value.

Experimental Section

All manipulations and reactions were performed in an argon atmosphere using standard Schlenk techniques. Solids were weighed in a glove box in an argon atmosphere. Ethylenediamine (Merck) was distilled over calcium hydride and used immediately after collection. $[AuCl(PPh_3)]$ and K_4Ge_9 were synthesized according to known procedures.[18,28] [2.2.2]crypt was dried in vacuo for 8 h.

1, **2**: The phase with the nominal composition K_4Ge_9 (122 mg, 0.15 mmol) was dissolved in ethylenediamine (4 mL) and stirred for two hours at room temperature. The intense red-brown solution was then separated from the residue by filtration onto $[AuCl(PPh_3)]$ (75 mg, 0.15 mmol). This mixture was stirred for another 14 h at room temperature, then filtered onto [2.2.2]crypt (236 mg, 0.6 mmol). After two weeks, dark red platelike crystals of **1** (ca. 15% yield) and diamond-shaped, dark red to black crystals of **2** (ca. 5% yield) formed in the dark red solution. Further dilution with ethylenediamine (10 mL) yielded exclusively crystals of **2**. EDX analyses of the crystals were carried out on a JEOL-SEM 5900 LV spectrometer.

Single crystals of **2** were fixed on glass capillaries. Crystal size: $0.4\times0.2\times0.1\ mm^3$. Unit cell parameters at 120 K: $a=69.30(1)$, $b=25.071(5)$, $c=31.607(6)$ Å, $\alpha=\beta=\gamma=90°$, $V=54\,915$ Å^3; space group $Pna2_1$ (no. 33), $Z=8$, $\rho_{calcd}=1.747\ g\,cm^{-3}$, $\mu=6.625\ mm^{-1}$. Data collection: Oxford-Diffraction Xcalibur3 diffractometer; $Mo_{K\alpha}$ radiation, $\theta_{max}=20.83°$; 387296 measured reflections, 28884 independent reflections; $R_1=0.077$ and $wR_2=0.212$ for $I>2\sigma(I)$, $R_1=0.103$ and $wR_2=0.224$ for all data. The structure determination (SHELXS-97[29]) and refinement (SHELXL-97[30]) were carried out using direct methods and full-matrix least-squares calculations against F^2. The crystals diffracted poorly, which can be understood in terms of the large unit cell parameters and poor crystal quality. All Au, Ge, and K atoms could be directly localized, and their refinement was carried out with anisotropic displacement parameters. The remaining electron density obtained through differential Fourier syntheses could only be approximately assigned to the atomic positions of the [2.2.2]crypt molecules. Therefore, the electron density surrounding the potassium atoms was fitted with a known structural fragment [K([2.2.2]crypt)] and refined as a fixed group. Refinement of the hydrogen atoms was carried out using fixed positions. Remaining electron densities in the cavities of the structure hinted towards disordered molecules of ethylenediamine and were treated with the PLATON SQUEEZE routine.[31] The Flack parameter deviates significantly from zero and indicates a racemic twin problem or the existence of a center of inversion. The non-centrosymmetric model was confirmed by the PLATON ADDSYM routine,[23] in particular for the Au, Ge, and K atoms. Therefore, final refinement was carried out in $Pna2_1$ using racemic twinning. The Flack parameter refines to 0.36(1). A series of other crystals of **2** yielded the same unit cell parameters within the range of the standard deviations. However, their refinement led to the same or poorer results. CCDC-617258 (**2**) 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.

All calculations were performed with the program TURBOMOLE, version 5.8.0.[32] The geometries were optimized at the (RI)-BP86 level[33–36] with the SV(P) basis set[37] in ethylenediamine solution ($\varepsilon_r = 13.82$) using the COSMO model.[38] To acquire partial charges, a population analysis based on occupation numbers[39,40] was performed. Further details of the calculations are given in the Supporting Information.

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[19] [2.2.2]crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane.

[20] The units **I** to **III** have two identical prism heights and one prism height elongated by 7 to 10%. This longest prism height is adjacent to the Ge−Ge *exo* bond. The homoatomic *exo* cluster contacts (Ge11−Ge51, Ge21−Ge52, Ge31−Ge53) range from 2.583 Å to 2.617 Å and can be considered as slightly elongated covalent bonds between Ge atoms.

[21] The arrangement of the Ge atoms Ge51 to Ge59 can also be understood as starting from a tricapped trigonal prism. Here the three capping atoms have moved upwards to establish a link to cluster **IV**. A similar “blossoming” of a monocapped square antiprism has been described for the nine-atom $\{In_4Bi_5\}$ cluster in $Ba_5In_4Bi_5$. S. Ponou, T. F. Fässler, G. Tobías, E. Canadell, A. Cho, S. C. Sevov, *Chem. Eur. J.* **2004**, *10*, 3615.

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