Cluster Compounds

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$[Au_3Ge_{18}]^{5-}$—A Gold–Germanium Cluster with Remarkable Au–Au Interactions**

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The chemistry of anionic Group 14 Zintl ions have had a reawakening[1] with respect to the discovery of novel and larger structures and chemical reactivity. Whereas Group 10 transition metals tend to form intermetalloid clusters with Zintl ions, such as in $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt),[2] $[M@Sn_9ML]^{n-}$ (M = Ni, L = CO, $n = 3$; M = Pt, L = PPh_3, $n = 2$),[3] or $[Ni@Ge_9NiL]^{2-}$ (L = CO, PPh_3, CCPh)[4] when the corresponding M^0 complexes as reagents are used, Au^I complexes lead to an oxidation of the Zintl ion $[Pb_9]^{4-}$ and formation of the *closo*-$[Pb_{10}]^{2-}$ ion.[5] On the basis of our recent results, which showed that the Group 12 element mercury can act as a linker between the $[Ge_9]^{4-}$ Zintl ions in forming the one-dimensional polymeric structure $^1_\infty[HgGe_9]$,[6] we have extended our study to the Ge–Au system.

Herein, we report the synthesis and structural characterization of the first ligand-free anionic germanium–gold cluster in $[K([2.2.2]crypt)]_5[Au_3Ge_{18}]$ (**1**). The stability of such a cluster offers valuable clues to both the use as a catalytic seed for the growth of (germanium) nanowires[7] and the use of the cluster itself as a building block for one-dimensional systems.

Cluster compound **1** was obtained through the reaction of $[Au(PPh_3)Cl]$ with an ethylenediamine solution of the phase K_4Ge_9 in the presence of [2.2.2]crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane). After filtration, the solution was carefully layered with toluene, and dark-orange to red plate-shaped crystals were obtained after one week. Semiquantitative energy-dispersive X-ray (EDX) analyses of the crystals showed the approximate ratio of Au/Ge/K = 3:18:5. Single-crystal X-ray structure determination and refinement[8] of **1** in the triclinic space group $P\bar{1}$ showed that **1** contains the anionic cluster $[Ge_9Au_3Ge_9]^{5-}$ (Figure 1) and five $[K([2.2.2]crypt)]^+$ units per cluster. The cluster consists of a central triangular Au_3 unit with two Ge_9 subunits bonded to either side of the Au triangle with an almost linear coordination of each Au atom by two Ge atoms. EPR and magnetic measurements showed that the crystals of **1** are diamagnetic.

As shown in Figure 2, the two nine-atom cluster units possess different shapes, both having nine crystallographically

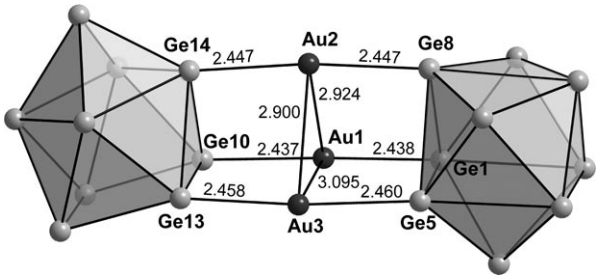

Figure 1. Structure of the cluster anion $[Ge_{18}Au_3]^{5-}$ (**1a**). Two nine-atom clusters **A** (left) and **B** (right) are linked through a gold triangle. Interatomic distances are given in Å.

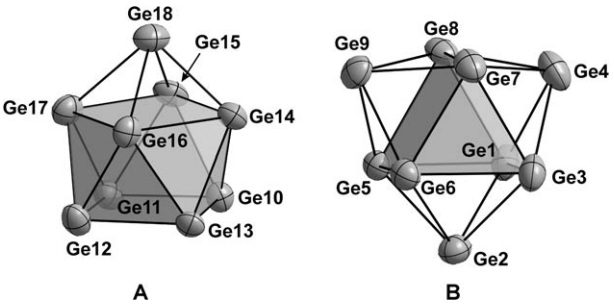

Figure 2. Structures of the two individual Ge_9 clusters **A** and **B**. Atoms are shown with a 50% occupation probability.

independent atom positions. Cluster unit **A** can be described as a monocapped square antiprism with only slight distortion from C_{4v} symmetry. The small C_{2v} distortion of **A** is expressed in the ratio of diagonal bond lengths of the open square (Ge10, Ge11, Ge12, Ge13) with d(Ge10–Ge12)/d(Ge11–Ge13) = 1.03. **B** is best described as a variant of a tricapped trigonal prism (Figure 2b). Distortion from D_{3h} symmetry is expressed in the ratio of the three prism heights d(Ge5–Ge6)/d(Ge1–Ge3)/d(Ge7–Ge8) = 1:1.02:1.05 with d(Ge5–Ge6) = 2.879 Å. A detailed investigation of bond lengths and angles shows a ratio $h/e = 1.14$ (h = mean prism height, e = mean edge length) for the distorted trigonal prism of **B** (Ge1, Ge3, Ge5, Ge6, Ge7, Ge8). This ratio lies well within the range of earlier reported clusters with 21 (Ge_9^{3-}: $h/e = 1.17$[9]) and 22 skeletal electrons ($^1_\infty[Ge_9^{2-}]$: $h/e = 1.07$; $[Ge_9–Ge_9]^{6-}$: $h/e = 1.12$[10]). Considering this and the distortion resulting from the additional three external bonds to Au atoms, a charge of 3– or 4– can be assigned to each Ge cluster. The uncertainty of the assignment of the number of electrons to homoatomic nine-atom structures was also recently examined in the case of nine-atom Sn clusters.[11] In **B** the three capping atoms Ge2, Ge4, and Ge9 are not symmetrically located above the

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rectangular sides of the trigonal prism but are shifted in the direction of the gold triangle. The distances of 2.54 Å to 2.56 Å between the three capping Ge atoms and the Ge atoms adjacent to the Au atoms (Ge1, Ge5, Ge8) are considerably shorter than those of any other Ge–Ge bond in the cap (2.62–2.64 Å). Such Ge–Ge bond shortening has also been observed in 22-skeletal-electron clusters with covalent *exo* bonds, such as $[Ph_3Sn\text{-}Ge_9\text{-}SnPh_3]^{2-}$).[12]

The gold triangle is coordinated by two Ge_3 triangles of the two Ge_9 polyhedra. In **A** one of the deltahedral faces connecting the two squares of the quadratic antiprism and in **B** the triangular face of the underlying trigonal prism are each almost coplanar with the Au_3 plane. Each Au atom is almost linearly coordinated to two Ge atoms with Ge-Au-Ge angles of 168.3° to 173.7°. The Ge–Au bond lengths range from 2.437 to 2.460 Å and are thus considerably shorter than the sum of the covalent radii (Ge: 1.22 Å, Au: 1.44 Å).

The tendency of gold to form bonds to other gold atoms is also shown to apply here. The Au–Au contacts range from 2.900 Å to 3.095 Å and are thus in the range of so-called aurophilic contacts.[13] The Au–Au and Au–Ge contacts compare well to molecular compounds with Au–Ge bonds. Such compounds are only known in the form of $GeCl_3$ complexes of gold. In the dimeric complex $[\{(Ph_3P)Au\text{-}(GeCl_3)\}_2]$, the association occurs through a short Au–Au contact of 2.960 Å.[14] Even in $[(GeCl_3)_2Au\text{-}\{(PhMe_2P)_2Au\}_2\text{-}Au(GeCl_3)_2]$, which formally contains the cationic unit $[(PhMe_2P)_2Au]^+$ and the anionic unit $[Au(GeCl_3)_2]^-$, the symmetrically substituted Au atoms exhibit short contacts with d(Au–Au) in the range from 2.88 to 2.98 Å and are almost linearly aligned.[13,15]

A preliminary density functional theoretical (DFT) analysis of the electronic structure of **1a** shows a well-separated HOMO and LUMO with an energy gap of 2.60 eV. An NBO (natural bond orbital) analysis reveals a comparable bond situation for the Au atoms in **1a** and in $[Au(PH_3)Cl]$ with a positive charge on the Au atoms of 0.24 and 0.34, respectively. The lower mean value for **1a** reflects the high negative charge of the cluster. **A** and **B** have rather similar orbital contributions to the molecular orbitals of **1a**, which is reflected by the same mean atomic charge of −0.32 per Ge atom for each cluster unit. We observe covalent orbital interactions between the Au and Ge atoms, which originate from donor orbitals of Ge atoms to empty acceptor orbitals of the Au atoms. The present calculations show only very weak Au–Au interactions; however, this aspect must be examined in more detail.[16]

The linear coordination of the Au atoms, the electronegativity difference between Ge and Au, and a similar calculated charge of the Au atoms in **1a** and $[Au^I(PH_3)Cl]$ hint at a Au^I compound in the case of **1**.[17] Thus, the chemical-bond situation is rather similar to that in the polymer $^1_\infty[HgGe_9]^{2-}$.[6] A reduction to Au^0, as is indicated by a linear P-Au-Au-P chain and a rather short Au–Au bond length of 2.625 Å in the stannaborate–gold complex $[(Ph_3P)Au\text{-}(SnB_{11}H_{11})]_2^{2-}$,[18] does not occur in **1a**.

Au atoms can serve as a link between anionic cluster units, thus giving rise to promising expectations for even larger nanostructures made up of Zintl ions. Moreover, the synthesis of **1** supplements the series of reactions of Ge_9 clusters including low-valent Ni and Pd metals in $Ni_3@Ge_{18}$ and $Pd_2@Ge_{18}$[19,20] as well as oxidative-coupling reactions to form $[Ge{=}Ge{=}Ge]^{6-}$[21] and $[Ge{=}Ge{=}Ge{=}Ge]^{8-}$.[22] In this context it is interesting to point out that the interaction of silicon or germanium with gold nanoparticles plays an important role in the formation of low-dimensional Si or Ge nanostructures.[23,24] Current techniques to obtain semiconducting nanowires involve the vapor–liquid–solid (VLS) whisker-growth mechanism,[25,26] in which gold metal has proven to be a capable catalyst to seed wire growth.[27] However, virtually nothing is known about Ge–Au interactions at the metal-cluster–nanowire interface. Ongoing investigations show that even larger clusters with up to 45 germanium atoms and three gold atoms can be isolated from the same reaction as reported here.[28] The anion $[Au_3Ge_{18}]^{5-}$ represents the first binary cluster of the elements Au and Ge. This is especially interesting since the binary-phase diagram does not hint at the existence of binary Au–Ge compounds but forms a eutectic mixture at 28% germanium.[29] Furthermore, the anion shows a most exciting result for Au chemistry: the aurophilic character can be observed in the direct vicinity of highly negatively charged Zintl anions.

Experimental Section

All manipulations and reactions were performed under argon with standard Schlenk techniques. Solids were weighed in a glove box in an argon atmosphere. An alloy of the nominal composition K_4Ge_9 was synthesized from the elements by heating for 8 h at 650 °C in stainless-steel tubes. Ethylenediamine (Merck) was distilled over calcium hydride and used immediately after collection. $[Au(PPh_3)Cl]$ was synthesized according to known procedures[30] from $HAuCl_4$ (Chem-Pur) and PPh_3 (Merck) and dried under vacuum for 8 h. [2.2.2]Crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, Merck) was also dried in vacuo for 8 h. The phase K_4Ge_9 (122 mg, 0.15 mmol) was dissolved in ethylenediamine (3 mL) and stirred for two hours. The intense red-brown solution was then separated from the residue by filtration onto $[Au(PPh_3)Cl]$ (75 mg, 0.15 mmol). This mixture was stirred for another hour and filtered onto [2.2.2]crypt (236 mg, 0.6 mmol). After stirring for 1.5 h and filtration, the intensely brown-red solution was carefully layered with toluene. Dark orange to red plate-shaped crystals were obtained in approximately 20% (40 mg) yield after one week. Repeated syntheses showed that the formation of **1** strongly depends on the concentration of the reactants.

EDX analyses of the crystals were carried out on a JEOL-SEM 5900LV spectrometer. EPR spectra were obtained on a JEOL JES-RE2X spectrometer, and magnetic measurements were carried out on a MPMS XL Squid Magnetometer (Quantum Design).

Crystal structure determination: Single crystals of **1** were fixed on glass capillaries. The structure was solved by direct methods (SHELXS-97[8a]) and refined by full-matrix least-squares calculations against F^2 (SHELXL-97[8b]). The Au, Ge, and K atoms and the cryptand units coordinating to K1, K3, and K4 were refined with anisotropic displacement parameters. The cryptand units coordinating to K2 and K5 show a disorder that could not be resolved by using a split model and were refined with isotropic displacement parameters using restraints for some bond lengths. Residual electron density indicates a disordered solvent molecule, which could not be resolved by using even split positions, so the PLATON SQUEEZE procedure was used.[8c] Crystal size: $0.4 \times 0.2 \times 0.02$ mm^3; unit cell parameters at 120 K: $a = 15.090(1)$, $b = 19.911(1)$, $c = 25.967(1)$ Å, $\alpha = 111.326(3)$, $\beta = 92.123(2)$, $\gamma = 93.120(2)$°, $V = 7243.3(4)$ Å^3; triclinic, space group

$P\bar{1}$ (No. 2), $Z=2$, $\rho_{calcd}=1.878\ g\,cm^{-3}$, $\mu=6.904\ mm^{-1}$; data collection: Oxford-Diffraction Xcalibur3 Diffractometer, $Mo_{K\alpha}$ radiation, $\theta_{max}=20.86°$, 29141 measured reflections, 14346 independent reflections, $R_{int}=0.031$, $R_1=0.053$ and $wR_2=0.121$ for reflections with $I>2\sigma(I)$, $R_1=0.096$ und $wR_2=0.130$ for all data. CCDC-606528 (**1**) 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.

Calculations: Single-point DFT calculations with the LanL2DZ basis set and B3LYP functional were performed on the cluster **1a** by using the atomic positions deduced from the single-crystal X-ray analysis. Full structure optimization was run for $[Au(PH_3)Cl]$, leading to a P-Au-Cl angle of 180.0° as well as Au–P and Au–Cl bond lengths of 2.389 and 2.373 Å, respectively, and is in agreement with earlier studies.[31] Computations were executed with the Gaussian 03 package, Revision C.[32]

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[1] T. F. Fässler, *Coord. Chem. Rev.* **2001**, *215*, 347.
[2] E. N. Esenturk, J. Fettinger, B. W. Eichhorn, *J. Am. Chem. Soc.* **2006**, *128*, 9178.
[3] B. Kesanli, J. Fettinger, D. R. Gardner, B. W. Eichhorn, *J. Am. Chem. Soc.* **2002**, *124*, 4779.
[4] D. R. Gardner, J. C. Fettinger, B. W. Eichhorn, *Angew. Chem.* **1996**, *108*, 3032; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2852; E. N. Esenturk, J. Fettinger, B. W. Eichhorn, *Polyhedron* **2006**, *25*, 521; J. M. Goicoechea, S. C. Sevov, *J. Am. Chem. Soc.* **2006**, *128*, 4155.
[5] A. Spiekermann, S. D. Hoffmann, T. F. Fässler, *Angew. Chem.* **2006**, *118*, 3538; *Angew. Chem. Int. Ed.* **2006**, *45*, 3459.
[6] A. Nienhaus, R. Hauptmann, T. F. Fässler, *Angew. Chem.* **2002**, *114*, 3352; *Angew. Chem. Int. Ed.* **2002**, *41*, 3213.
[7] J. Hu, T. W. Odom, C. M. Lieber, *Acc. Chem. Res.* **1999**, *32*, 435.
[8] a) G. M. Sheldrick. SHELXS-97, Program for the Solution of Crystal Structures, Universität Göttingen **1997**; b) G. M. Sheldrick. SHELXL-97, Program for the Refinement of Crystal Structures, Universität Göttingen **1997**; c) PLATON: A. L. Spek, *Acta Crystallogr. Sect. C* **1990**, *34*, 46; SQUEEZE: P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194.
[9] M. Hunziker, T. F. Fässler, *Inorg. Chem.* **1994**, *33*, 5380.
[10] a) C. Downie, Z. Tang, A. M. Guloy, *Angew. Chem.* **2000**, *112*, 346; *Angew. Chem. Int. Ed.* **2000**, *39*, 338; b) R. Hauptmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2266; c) A. Nienhaus, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1752.
[11] J. Ronsdahl, T. F. Fässler, L. Kloo, *Eur. J. Inorg. Chem.* **2005**, 2888.
[12] A. Ugrinov, S. C. Sevov, *Chem. Eur. J.* **2004**, *10*, 3727.
[13] See also contributions in: *Gold—Progress in Chemistry, Biochemistry and Technology* (Ed.: H. Schmidbaur), Wiley, Chichester, **1999**.
[14] H. Schmidbaur, *Chem. Soc. Rev.* **1995**, *24*, 391; H. Schmidbaur, *Gold Bull.* **2000**, *33*, 3.
[15] A. Bauer, H. Schmidbaur, *J. Am. Chem. Soc.* **1996**, *118*, 5324.
[16] P. Pyykkö, *Angew. Chem.* **2004**, *116*, 4512; *Angew. Chem. Int. Ed.* **2004**, *43*, 4413.
[17] For **1a** to have a net charge of −5, clusters **A** and **B** must formally be fourfold negatively charged. Indeed, the shape of cluster **A** is very similar to a number of Ge *nido* clusters, as in $(Cs^+)_4[Ge_9^{4-}]$.[33] Cluster **B** with three nearly equal prism heights compares well to the 22-electron *nido* cluster $([Bi_9]^{5+})_2$-$([BiX_5]^{2-})_8([Bi_2X_8]^{2-})_2$.[34] A similar distortion of a 22-skeletal-electron cluster with the same *h*/*e* ratio of 1.14 is also found in the fourfold negatively charged tin cluster in $[K^+([18]crown-6)]_3(K^+)[Sn_9]^{4-}$.[35]
[18] S. Hagen, I. Pantenburg, F. Weigand, C. Wickleder, L. Wesemann, *Angew. Chem.* **2003**, *115*, 1539; *Angew. Chem. Int. Ed.* **2003**, *42*, 1501.
[19] J. M. Goicoechea, S. C. Sevov, *Angew. Chem.* **2005**, *117*, 4094; *Angew. Chem. Int. Ed.* **2005**, *44*, 2.
[20] J. M. Goicoechea, S. C. Sevov, *J. Am. Chem. Soc.* **2005**, *127*, 7676.
[21] A. Ugrinov, S. C. Sevov, *J. Am. Chem. Soc.* **2002**, *124*, 10990; L. Yong, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1149.
[22] A. Ugrinov, S. C. Sevov, *Inorg. Chem.* **2003**, *42*, 5789; L. Yong, S. D. Hoffmann, T. F. Fässler, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1977.
[23] T. Hanrath, B. A. Korgel, *J. Am. Chem. Soc.* **2002**, *124*, 1424.
[24] A. M. Morales, C. M. Lieber, *Science* **1998**, *279*, 208.
[25] R. S. Wagner, W. C. Ellis, K. A. Jackson, S. M. Arnold, *J. Appl. Phys.* **1964**, *35*, 2993.
[26] R. S. Wagner, W. C. Ellis, *Appl. Phys. Lett.* **1964**, *4*, 89.
[27] Y. Wu, P. Yang, *J. Am. Chem. Soc.* **2001**, *123*, 3165.
[28] X-ray diffraction structure analysis of crystals from subsequent reactions which were different in shape and appearance contained $[K([2.2.2]crypt)]_8K[Ge_{45}Au_3]$ and led to the orthorhombic space group $Pna2_1$ with $a=69.30$, $b=25.07$, $c=31.61$ Å. A. Spiekermann, S. D. Hoffmann, T. F. Fässler, I. Krossing, U. Preiss, unpublished results.
[29] Ternary Au–Ge phases have been reported: A_3AuGe_4 (A = alkali metal) contains tetrahedral Ge_4 units. Describing these units as stable $[Ge_4]^{4-}$ ions leads to the assumption that the gold atoms should be described as Au^I. The Au–Ge bond lengths are slightly longer (about 0.13 Å) than in **1**.[29a] In NaAuGe the Au–Ge contacts are considerably longer (2.67 Å),[29b] and shorter contacts (2.41 Å) are observed in K_4Au_7Ge;[29c] see: a) U. Zachwieja, J. Wlodarski, *Z. Anorg. Allg. Chem.* **2004**, *630*, 993; b) U. Zachwieja, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1173; c) U. Zachwieja, *Z. Anorg. Allg. Chem.* **1995**, *621*, 975.
[30] S. Ahrland, K. Dreisch, B. Norén, A. Oskarsson, *Mater. Chem. Phys.* **1993**, *35*, 281.
[31] P. Schwerdtfeger, H. L. Hermann, H. Schmidbauer, *Inorg. Chem.* **2003**, *42*, 1334.
[32] Gaussian 03 (Revision C.02): M. J. Frisch et al., see the Supporting Information.
[33] V. Quéneau, S. C. Sevov, *Angew. Chem.* **1997**, *109*, 1818; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1754.
[34] A. Hershaft, J. D. Corbett, *Inorg. Chem.* **1963**, *2*, 979; H. Von Benda, A. Simon, W. Bauhofer, *Z. Anorg. Allg. Chem.* **1978**, 53.
[35] R. Hoffmann, T. F. Fässler, *Angew. Chem.* **1999**, *111*, 526; *Angew. Chem. Int. Ed.* **1999**, *38*, 543.

