Cluster Compounds

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$[Co@Ge_{10}]^{3-}$: An Intermetalloid Cluster with Archimedean Pentagonal Prismatic Structure**

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Homoatomic clusters $[E_n]^{x-}$ of the Group 14 elements have been fascinating species since their discovery in the 19th century.[1,2] The anionic nine-atom clusters $[E_9]^{x-}$ (E = Si, Ge, Sn, Pb; $x = 3, 4$) were found to be structurally and electronically analogous to the deltahedral boranes with delocalized bonding that follow Wade's electron-counting principles.[3] They can undergo a variety of reactions, such as oligomerization and polymerization,[4] coupling with metal atoms,[5] and addition of main-group[6] or transition-metal organometallic fragments.[7] Clusters with a maximum size of 48 atoms have been realized in the form of $[Au_3Ge_{45}]^{9-}$ starting from the Zintl ion $[Ge_9]^{4-}$.[8] It is of special interest that "ligand-free" endohedral Zintl ions can also be obtained when the corresponding transition-metal complexes are used as reagents. Examples include $[Ni@Ge_9]^{3-}$ and $[(Ni@Ge_9)Ni(Ni@Ge_9)]^{4-}$,[9] $[Pd_2@Ge_{18}]^{4-}$,[10] $[Pd_2@Sn_{18}]^{4-}$,[11] $[(Ni@Sn_8)Sn(Ni@Sn_8)]^{4-}$,[12] $[Pt_2@Sn_{17}]^{4-}$,[13] $[Ni@Pb_{10}]^{2-}$, $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt),[14] and the recently reported $[Cu@E_9]^{3-}$ with E = Sn and Pb.[15] The findings on ligand-free endohedral clusters can contribute to a better understanding of bonding in clusters in the gas phase as well as in binary alloys, and progress in this field could even lead to the formation of core–shell nanoparticles. The term intermetalloid clusters[16] was introduced in this context to express that discrete or even soluble cluster ions which consist exclusively of atoms of two or more different (semi)metallic elements topologically correspond to structural units of intermetallic compounds.

Just like the discovery of endohedral metallofullerenes for fullerene chemistry, transition-metal doping brings substantial progress for the field of Group 14 Zintl clusters.[1,17] However, it should be noted that on the one hand the isolation of centered clusters from chemical reactions has, to date, been limited to late transition metals such as Ni, Pd, Pt, and recently Cu. On the other hand, many other main-group metal clusters containing d- or f-block metals have been observed in gas-phase experiments.[18] Various theoretical studies confirm that those clusters are stable with endohedral atoms.[19–21] With respect to the title compound, it is of particular interest that a high abundance of $[CoGe_{10}]^-$ cluster anions was found in laser vaporization and laser ablation experiments on binary Co/Ge mixtures.[22] Subsequent calculations were performed to predict the possible structures of endohedral $[CoGe_{10}]^-$ clusters and to explain their stability.[23]

Our group has been interested in the synthesis of intermetalloid clusters by the use of Group 14 Zintl ions.[24] Inspired by the aforementioned reports about $[CoGe_{10}]^-$, we started exploratory syntheses of endohedral $[Co@Ge_n]^{x-}$ clusters using solution chemistry methods. Herein, we report the synthesis and structural characterization of the first ligand-free cobalt-centered germanium cluster $[Co@Ge_{10}]^{3-}$ (**1a**), which cocrystallizes with the anion $[Co(C_8H_{12})_2]^-$ (**1b**) in the compound $[K(2,2,2\text{-crypt})]_4[Co@Ge_{10}][Co(C_8H_{12})_2]\cdot$tol (**1**; 2,2,2-crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, tol = toluene).

The anion **1a** was obtained through the reaction of $[Co(C_8H_{12})(C_8H_{13})]$ with an ethylenediamine solution of the phase K_4Ge_9 in the presence of 2,2,2-crypt. After filtration, the solution was carefully layered with toluene, and dark green prismatic crystals were obtained after three weeks.

Single-crystal X-ray structure determination and refinement of the crystal in the triclinic space group $P\bar{1}$ showed the presence of one $[Co@Ge_{10}]$, one $[Co(C_8H_{12})_2]$, and four [K(2,2,2-crypt)] units (see Figure S1 in the Supporting Information). The four positive charges of the alkali metals per formula unit are compensated by one $[Co(C_8H_{12})_2]^-$ unit (see below) and one $[Co@Ge_{10}]$ cluster, consequently a charge of 3− is assigned to the endohedral cluster. The outstanding structural feature of the compound is the shape of the $[Co@Ge_{10}]^{3-}$ anion. Unlike all other reported one-metal-atom-centered Group 14 Zintl ions (Figure 1), $[Co@Ge_{10}]^{3-}$ exhibits a D_{5h} pentagonal prismatic structure. The only comparable clusters are the $[Pd@Bi_{10}]^{4+}$ ion with a D_{5d} pentagonal antiprism structure[25] in $Bi_{14}PdBr_{16}$ and the organometallic tin compound $Sn_{10}R_{10}$ (R = 2,6-diethylphenyl) with a D_{5h} pentagonal prismatic structure.[26]

The $[Co@Ge_{10}]^{3-}$ ion in **1** consists of ten Ge atoms with one Co atom at the center (Figure 2). Virtual D_{5h} symmetry of

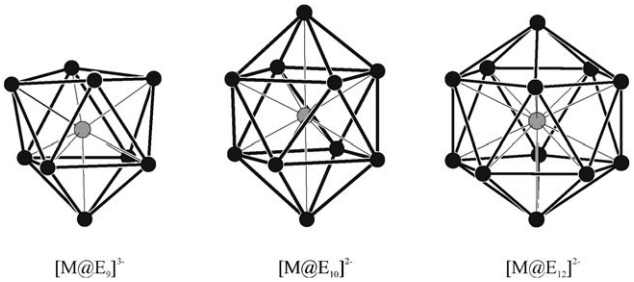

Figure 1. Known structures of reported Group 14 Zintl ions centered by one metal atom. E and M see text.

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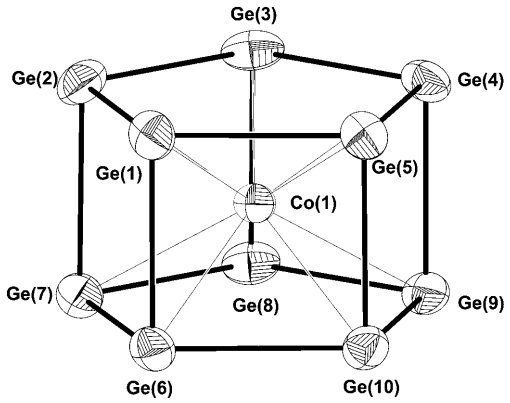

Figure 2. Structure of the $[Co@Ge_{10}]^{3-}$ ion (**1a**). Thermal ellipsoids are shown at 50% probability level. For selected bond lengths and angles, see reference [27].

the pentagonal prism is observed; the maximum deviation of the atoms from a mean plane through the five Ge atoms in each pentagon is 0.01 Å. The bond angles in each pentagon are very close to the ideal 108°, and their sum (540°) fits perfectly for a planar pentagon. Furthermore, the interatomic distances within the two pentagons are almost equal, and the two pentagons are parallel to each other (dihedral angle 0.3°). All bond angles in the five side faces of the prism are $90 \pm 0.7°$. A pentagonal prism with D_{5h} symmetry possesses two different edge lengths: the lengths of the ten equivalent edges of the two pentagonal faces *e* and the five heights *h* connecting the two pentagonal faces. The *h*/*e* ratio in the cluster $[Co@Ge_{10}]^{3-}$ is 1.06 and thus deviates only slightly from the *h*/*e* ratio of a perfect pentagonal prism. Therefore the structure of the $[Co@Ge_{10}]^{3-}$ anion represents an Archimedean polyhedron. The Ge–Ge bonds[27] of 2.5015(6) to 2.5269(7) Å in the pentagons are longer than the single bond in the organogermanium ring *cyclo*-$(GePh_2)_5$ (2.45 Å)[28] and slightly shorter than those in homoatomic nine-atom Zintl ions $[Ge_9]^{x-}$ ($x = 3, 4$) with $d_{Ge-Ge} \geq 2.533$ Å.[29,30] They are in the range of Ge–Ge single bonds observed in binary or ternary intermetallic compounds, such as $MgCo_6Ge_6$ with $d_{Ge-Ge} = 2.501$ Å.[31] The bond lengths between the two pentagons are in the range of 2.6003(6) to 2.6218(6) Å and are comparable with those found in other transition-metal-centered Zintl ions.[32] The Co–Ge bonds in **1a** range from 2.4792(7) to 2.5247(7) Å. They are longer than the sum of covalent radii (2.38 Å)[33] and than many reported Co–Ge covalent bonds;[34] in fact, they represent typical values observed in intermetallic compounds containing Co and Ge.[35]

In compound **1** the $[Co@Ge_{10}]^{3-}$ cluster ion (**1a**) co-crystallizes with the ion $[Co(C_8H_{12})_2]^-$ (**1b**), which is formed by the reduction of the starting material $[Co(C_8H_{12})(C_8H_{13})]$. The coordination of the two 1,5-cyclooctadiene (cod) ligands is rather similar to that observed in $[K([18]crown\text{-}6)]_2[\eta^5\text{-}C_5H_5][Co(C_8H_{12})_2]$ (**2**)[36] and $[Li(thf)_2][Co(C_8H_{12})_2]$.[37] Cluster **1b** appears in two orientations in crystals of **1**, and all the atomic parameters can be well refined with a 1:1 ratio. The Co–C and C–C distances in **1b** are in full agreement with those in **2**. To show the presence of the two cobalt species **1a** and **1b** in **1**, ^{59}Co NMR spectra of crystals of **1** in DMF were recorded (see the Supporting Information). The spectra show two resonances at $\delta_1 = -731$ ppm and $\delta_2 = -1680$ ppm. The latter resonance can be assigned to **1b** and is in agreement with a chemical shift of $\delta = -1737$ ppm observed for **2**.[36] Therefore, the signal at $\delta_1 = -731$ ppm is assigned to the cobalt center $[Co@Ge_{10}]^{3-}$.

The mechanism of the formation of the $[Co@Ge_{10}]^{3-}$ cluster cannot be established at this stage. The assembly of two $[Ge_5]^{2-}$ ions, as obtained by extraction of binary germanium–alkali-metal alloys,[38,39] and one Co^+ ion is a possible route. However, more complex redox reactions involving the anion $[Ge_9]^{4-}$, such as they occur during the formation of the $[Au_3Ge_{45}]^{9-}$ ion,[8] cannot be ruled out.

The $[Co@Ge_{10}]^{3-}$ ion features a unique pentagonal prismatic structure that is different from the conventional deltahedral structures observed for most Zintl ions. A related η^5-coordinating *cyclo*-Pb_5 unit was observed in the triple-decker complex $[(CO)_3Mo{-}Pb_5{-}Mo(CO)_3]^{4-}$ and has formally been described as a 2π-aromatic *cyclo*-$[Pb_5]^{2-}$ ligand bound to two $[Mo(CO)_3]^-$ fragments.[24] At first glance, a description of **1a** as a Co^I complex with two *cyclo*-$[Ge_5]^{2-}$ units suggests an analogy to the *cyclo*-$[Pb_5]^{2-}$ ligand. However, in **1a** bonding interactions exist between the Ge atoms of the two coplanar pentagons, and a description of the Ge_{10} cage as an analogue to pentaprismane $C_{10}H_{10}$ is more appropriate.

DFT calculations were performed on the $[Co@Ge_{10}]^{3-}$ ion, the isoelectronic $[Ni@Ge_{10}]^{2-}$ ion, and the empty $[Ge_{10}]^{2-}$ cluster. An overview of the results of various structure optimizations is given in the Supporting Information. For the $[Co@Ge_{10}]^{3-}$ ion, the optimization of a pentagonal prismatic structure with D_{5h} symmetry led to a ground state, consistent with the experimental data presented herein. The calculated interatomic distances are in good agreement with those observed.[40] The calculated gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO gap) of the D_{5h} symmetric $[Co@Ge_{10}]^{3-}$ ion is 2.27 eV. A natural charge of −1.05 calculated for Co supports the assumption of a d^{10} configuration. Interestingly, according to recently reported quantum chemical calculations for the isoelectronic species $[Ni@Ge_{10}]^{2-}$, $[Cu@Ge_{10}]^-$, and $[Zn@Ge_{10}]$[41] as well as for the empty cluster $[Ge_{10}]^{2-}$,[42] the D_{4d} symmetric bicapped square antiprism is predicted to be the lowest-energy structure (B3LYP/6-31G(d) gas-phase calculations).[43] With SCI-PCM/B3LYP/cc-pVTZ(-NR) we found that the optimization of a D_{4d} bicapped square antiprism led to a stationary state 13.3 kcal mol^{-1} above the D_{5h} minimum for the $[Co@Ge_{10}]^{3-}$ ion, but this stationary state shows two imaginary frequencies (43.0 i cm^{-1}) and does not represent a ground or a transition state. However, for the $[Ge_{10}]^{2-}$ ion, a ground state with *closo* D_{4d} structure was found. Optimization of a D_{5h} pentagonal prism led to a stationary state showing five imaginary frequencies (between −73.1 and 49.1 i cm^{-1}) 62.4 kcal mol^{-1} above the D_{4d} minimum. For the $[Ni@Ge_{10}]^{2-}$ ion, the D_{4d} bicapped square antiprism seems to be the energetically most favorable structure (among those considered herein), even though the frequency calculation led to two very low imaginary frequencies. The D_{5h} pentagonal

prism corresponds to a ground state only 5.33 kcal mol^{-1} above the D_{4d} stationary point. The computational results show that with the adopted methods, it is rather difficult to locate the global minimum for these anionic clusters unambiguously. It should also be noted that the calculated lowest (real) vibrational frequencies of these cluster anions are rather low (between 45 and 65 cm^{-1} in most cases), indicating that the potential energy surfaces of these species are rather flat and that the clusters are quite flexible. In summary, only a small energetic difference between the D_{5h} pentagonal prism and the D_{4d} *closo* structure is calculated for the endoheral clusters $[Co@Ge_{10}]^{3-}$ and $[Ni@Ge_{10}]^{2-}$, while the D_{4d} *closo* structure is clearly favored for the empty cluster $[Ge_{10}]^{2-}$.

The electron localization function (ELF)[44] for the $[Co@Ge_{10}]^{3-}$ ion is shown in Figure 3. Apart from core basins and striking monosynaptic valence basins of the Ge atoms ① (representing the lone pairs), two further kinds of valence

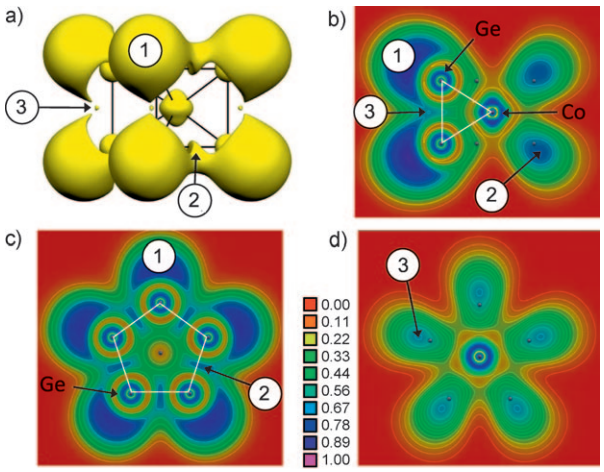

Figure 3. ELF representations for the D_{5h} pentagonal prismatic $[Co@Ge_{10}]^{3-}$ anion. ELF isosurface with $\eta(r) = 0.635$ (a) and ELF values on a plane including the Co atom and two Ge atoms that are adjacent along a prism height (b), on a plane including the five Ge atoms of a pentagon (c), and on a plane parallel to the pentagons including the Co atom (d). See text for details.

basins are found. There are valence basins between neighboring Ge atoms in the five-membered rings ②, and there are valence basins with a smaller volume between Ge atoms that are adjacent along the prism heights ③. There are no distinct basins for the Co–Ge bonds, indicating the strongly delocalized character of the bonding between the Co and Ge atoms.

The ion $[Co@Ge_{10}]^{3-}$ represents a novel binary cluster with a unique pentagonal prismatic structure that is rather different from the conventional deltahedral structures of transition-metal-centered Group 14 Zintl ions observed to date. Interestingly, the neat intermetallic solid $CoGe_2$[45] contains a rather similar Co–Ge unit. In $CoGe_2$, Co is surrounded by eight Ge atoms in an arrangement that is best described as intermediate between a square antiprism and a cube (regardless of Co–Co interactions; Figure S3 in the Supporting Information) with Co–Ge and Ge–Ge separations of 2.460 and 2.789–3.021 Å, respectively. In this light, the $[Co@Ge_{10}]^{3-}$ ion is best regarded as a true intermetalloid cluster with strongly delocalized bonds.[16]

Experimental Section

All manipulations and reactions were performed in an argon atmosphere using standard Schlenk or glovebox techniques. K_4Ge_9 was synthesized by heating the elements K and Ge at 650 °C for 20 h in a stainless steel tube. Ethylenediamine (Merck, 99 %) was distilled over CaH_2 and stored in an argon-filled Schlenk tube. 2,2,2-crypt (Merck) was dried under vacuum for 8 h.

$[K(2,2,2\text{-crypt})]_4[Co@Ge_{10}][Co(C_8H_{12})_2]\cdot$toluene: K_4Ge_9 (85 mg, 0.105 mmol) was weighed into a Schlenk tube inside a glovebox and dissolved in ethylenediamine (1 mL). The color of the solution changed from dark red to dark green after it was stirred for half an hour. The solution was filtered onto a mixture of $[Co(C_8H_{12})(C_8H_{13})]$ (42 mg, 0.15 mmmol) and 2,2,2-crypt (150 mg, 0.4 mmol) and stirred for 3 h. The dark green solution was filtered and layered with toluene to allow for crystallization. After three weeks, some black-green prismlike crystals formed on the bottom of the Schlenk tube, alongside some black amorphous precipitate (for the precipitate, EDX analysis indicated the presence of K, Ge, and Co). The semiquantitative energy-dispersive X-ray spectroscopy (EDX) analysis of the crystals showed the presence of the elements K, Co, and Ge, with an approximate atomic ratio K/Co/Ge = 2:1:5.

^{59}Co NMR spectra were recorded on a Bruker AMX400 spectrometer with samples of 5 mM solutions of single crystals of **1** in DMF. The observed frequency was ^{59}Co (94.9 MHz), and ^{59}Co was referenced to $K_3[Co(CN)_6]$ in D_2O at $T = 298$ K as external standard. A total of 500 scans were accumulated for the ^{59}Co NMR spectrum.

Single-crystal X-ray diffraction data for $[K(2,2,2\text{-crypt})]_4[Co@Ge_{10}][Co(C_8H_{12})_2]\cdot$tol (**1**) were collected on an Oxford Diffraction Xalibur3 diffractometer at 150 K with $Mo_{K\alpha}$ radiation. The crystal was selected under perfluoropolyalkylether and mounted on a glass fiber. The structure was solved by direct methods and refined on F^2 using the SHELXTL V6.1 package.[57] Crystal data: $M_r = 2814.60$, space group $P\bar{1}$, $a = 16.1892(7)$, $b = 16.7138(9)$, $c = 24.0583(14)$ Å, $\alpha = 74.012(5)$, $\beta = 73.940(5)$, $\gamma = 79.200(4)°$, $V = 5970.0(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.566$ g cm^{-3}, $\mu = 2.953$ mm^{-1}, 38698 measured reflections, 20348 independent reflections, $R_{int} = 0.0203$; $R_1 = 0.0371$ and $wR_2 = 0.0946$ for $I > 2\sigma(I)$, $R_1 = 0.0604$ and $wR_2 = 0.1087$ for all data. CCDC-702927 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. The disorder of the 1,5-cyclooctadiene ligands and the toluene molecule is successfully described as rotational disorder with 1:1 ratio. All heavy atoms except the carbon atoms of the cod ligands were refined using anisotropic thermal parameters.

Computational methods: DFT calculations were performed using the GAUSSIAN 03 package of programs (Revision D.01).[46] Natural charges were calculated using Version 3.1 of the NBO program[47] as implemented in GAUSSIAN 03. The highly negatively charged clusters were found to be unstable in the gas phase, with positive energy eigenvalues for occupied orbitals. Therefore the self-consistent isodensity polarizable continuum model (SCI-PCM)[48] was used in all calculations to account for solvation effects (dielectric constant ε_r(ethylendiamine) = 12.9). With this method, negative energy eigenvalues were calculated for all occupied orbitals of the studied species. All DFT calculations were carried out using the B3LYP functional, that is, Becke's hybrid three-parameter exchange functional[49] with the Lee–Yang–Parr correlation functional.[50] Computations were performed using three highly symmetric structures, the D_{5h} symmetric pentagonal prism, the pentagonal antiprism with D_{5d} symmetry, and the D_{4d} symmetric bicapped square antiprism. The symmetries were maintained during the structure optimization processes. Preliminary structure optimizations for $[Co@Ge_{10}]^{3-}$ and $[Ge_{10}]^{2-}$ were carried out with 6-31G(d) basis sets. Further optimizations for $[Co@Ge_{10}]^{3-}$ and

$[Ge_{10}]^{2-}$ as well as optimizations for $[Ni@Ge_{10}]^{2-}$ were performed at the SCI-PCM/B3LYP/cc-pVTZ(-NR) level of theory using nonrelativistic all-electron correlation-consistent polarized valence triple zeta basis sets. These basis sets (cc-pVTZ for Ge[51] and cc-pVTZ-NR for Co and Ni[52]) were obtained from the EMSL Basis Set Exchange.[53] Harmonic vibrational frequencies were calculated numerically for the optimized structures to characterize the nature of the stationary point on the potential energy surface.

The electron localization function (ELF)[44] was calculated with the program DGrid.[54] Representation of the results was obtained with the programs XCrySDen[55] and MOLEKEL.[56]

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