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$[\mathrm{Ge_9{=}Ge_9{=}Ge_9}]^{6-}$: A Linear Trimer of 27 Germanium Atoms

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Nine-atom deltahedral clusters of the heavier analogues of the carbon group exist in solutions of ethylenediamine and liquid ammonia and can be crystallized from them with various countercations.[1] More recently, they have been found in neat solids as well.[2] The clusters carry a charge of 4− or 3− and have the shape of tricapped trigonal prisms elongated along one, two, or three of the prismatic edges (those parallel to the 3-fold axis of the prism). As in the well-known cagelike boranes, the bonding in these clusters is achieved by delocalized electrons. Recent studies have shown that upon oxidation these clusters couple in different modes, and various species can be crystallized with countercations of appropriate sizes and shapes. Thus, the first dimer of such clusters, $[\mathrm{Ge_9{-}Ge_9}]^{6-}$ was stabilized with a combination of naked cesium and cryptated potassium cations in $\mathrm{Cs_2(K\text{-}[2.2.2]crypt)_4[Ge_9{-}Ge_9]}$, where [2.2.2]crypt is 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]-hexacosane.[3] The tricapped trigonal prisms in this case are elongated along one edge (equivalent to a monocapped square antiprism) and are connected by a simple two-center-two-electron exo-bond between vertexes of the elongated edges in each cluster. Another example of oxidative coupling is the chain of $_\infty[-\mathrm{Ge_9}-]^{2-}$ stabilized in $\mathrm{(K\text{-}[18]crown[6])_9[Ge_9]\cdot en}$ with potassium cations sequestered by 18-crown-6 ether.[4] The shape of the clusters in the chain is the same as that in the dimer but with both vertexes of the elongated edge in each cluster involved in exo-bonding with two neighboring clusters in the chain. The existence of the dimer and the chain showed that, contrary to earlier assumptions, exo-bonds to such deltahedral ions are possible. Furthermore, it showed that the oxidation of the cluster does not affect the bonding within the cluster and its stability, but rather replaces lone pairs of electrons with bonding pairs. We followed on this idea and studied reactions of controlled soft oxidation of these clusters with $\mathrm{Ph_3E}$ where E = P, As, Sb, and Bi. The reactions with the two heavier analogues, $\mathrm{Ph_3Sb}$ or $\mathrm{Ph_3Bi}$, provided the first functionalized deltahedral Zintl ions, $[\mathrm{Ph_2E{-}(Ge_9){-}EPh_2}]^{2-}$, with two exo-bonds at the vertexes of the elongated edge of the $\mathrm{Ge_9}$ prism.[5] Here we present the product of the oxidation of the germanium deltahedral clusters with $\mathrm{Ph_3P}$ and $\mathrm{Ph_3As}$, a trimer of nine-atom clusters, $[\mathrm{Ge_9{=}Ge_9{=}Ge_9}]^{6-}$.

The new compound with this trimer, $\mathrm{(Rb\text{-}[2.2.2]crypt)_6[Ge_9{=}Ge_9{=}Ge_9]\cdot 3en}$ (**1**), was isolated from reactions of $\mathrm{Ph_3As}$ or $\mathrm{Ph_3P}$ with ethylenediamine solution of the precursor compound $\mathrm{Rb_4Ge_9}$.[6] The latter is an ionic compound made of isolated $\mathrm{Ge_9}^{4-}$ clusters and Rb cations.[2a] Upon heating to 70 °C, the color of the solution changes from brown-red (for the dissolved precursor) to extremely dark-green. After cooling and careful layering with toluene or monoglyme, we recovered needles of exactly the same dark-green color after a few days.

The trimer of clusters is linear, and the nine-atom germanium clusters are bonded with two exo-bonds to each other (Figure 1).[7] Each cluster is a tricapped trigonal prism elongated along two prismatic edges. The trigonal prism of each cluster is formed of atoms 2, 3, 4, 5, 6, and 8 (Figure 1) with elongated edges of 2−5 and 6−8, while the capping atoms are 1, 7, and 9. Thus, the lengths of the edges 2−5 and 6−8 are in the range 2.953−3.085 Å, while those of the edge 3−4 are within 2.753−2.772 Å. Like in other deltahedral nine-atom clusters,[1c,2a] the distances around the atoms that are four-bonded within the cluster (all atoms except 3 and 4, see Figure 1), 2.484−2.745 Å, are shorter than those that are five-bonded (atoms 3 and 4), 2.523−2.772 Å.

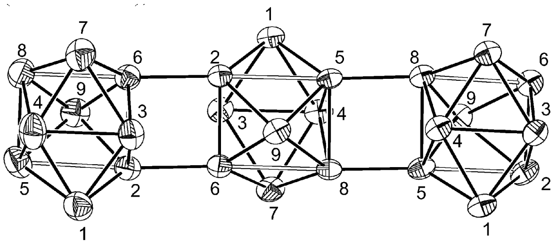

Figure 1. ORTEP drawing of the trimer $[\mathrm{Ge_9{=}Ge_9{=}Ge_9}]^{6-}$ (50% probability thermal ellipsoids). Each cluster is a tricapped trigonal prism with two elongated prismatic edges (shown as open bonds).

Most interesting and nontrivial to rationalize in the new species is the character of the bonds between the clusters and the resulting charge of 6−. The end clusters have two exo-bonds each, while the middle cluster has four such bonds (Figure 1). This type of connectivity with two bonds between the clusters is quite unexpected, almost as unexpected as a single exo-bond between such clusters was prior to the discovery of $[\mathrm{Ge_9{-}Ge_9}]^{6-}$.[3] As in the latter, the oxidation of these clusters does not involve cluster-bonding electrons but rather the higher-energy lone-pair electrons, specifically the lone pairs at the atoms of the elongated prismatic edges. The four intercluster bonds are nearly equidistant in the narrow range 2.579−2.601 Å. These bond lengths are significantly longer than the two-center-two-electron intercluster bonds of 2.488(2) and 2.486(1) Å found in the dimer $[\mathrm{Ge_9{-}Ge_9}]^{6-}$ and the chain $_\infty[-\mathrm{Ge_9}-]^{2-}$, respectively,[3,4] and indicate that the bond order for the bonds in the trimer is lower than one. Furthermore, a bond order of one for each exo-bond would have resulted in a charge of 4− for the trimer and not the observed 6− because the central cluster would have been neutral and the end ones would have carried charges of 2− each.

Fenske−Hall and extended-Hückel molecular orbital calculations were carried out for the trimer to find the origin of the 6− charge. The results showed that the clusters needed 22 bonding electrons each (the same as for clusters with one elongated edge), confirmed the overall charge, and showed that it was distributed almost evenly among the three clusters resulting in a diamagnetic trimer (in agreement with measurements).[8] It was quite clear that this "unexpected" charge originated from the unusual way the clusters were bonded. Thus, the exo-bonds are not "radial" to the clusters as they are in the boranes, the dimers $[\mathrm{Ge_9{-}Ge_9}]^{6-}$,[3] the chains

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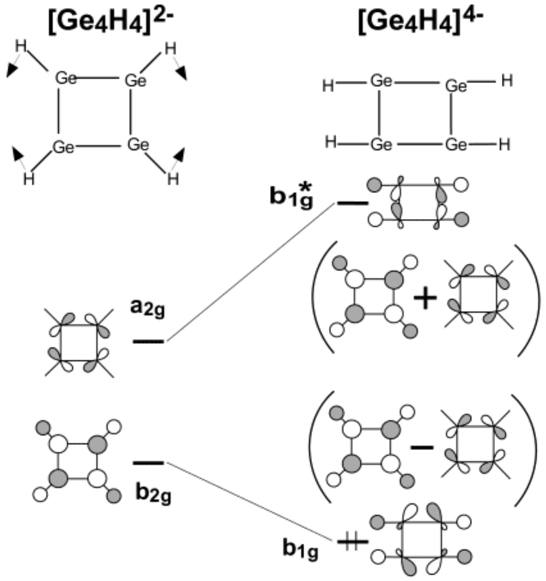

Figure 2. Correlation (Walsh) diagram between two specific molecular orbitals in a square of germanium with four radially pointing exo-bonds (left, D_{4h}) and the same square with the exo-bonds parallel to a pair of Ge−Ge edges (right, D_{4h}). The two orbitals on the left are of different symmetry, b_{2g} and a_{2g}, and cannot mix, but the two orbitals on the right are of the same symmetry, b_{1g}, and mix to form stabilized and destabilized combinations.

$_\infty[-Ge_9-]^{2-}$,[4] and the ligated clusters $[Ph_2Bi-(Ge_9)-BiPh_2]^{2-}$,[5] but are rather "parallel" to the elongated edges of the prisms. This changes quite drastically the intercluster interactions between the outward-pointing hybrid orbitals. Focusing on the central cluster, the effect of this is that one molecular orbital of lone-pair type that would have been empty for a cluster with four radially positioned exo-bonds becomes stabilized and filled by mixing with a cluster-type orbital for the observed arrangement of four parallel exo-bonds. The same effect was observed for a modeled trimer of octahedral clusters connected in the same way. To study the effect in more detail, the model was simplified even further to a planar cluster of four germanium atoms with four hydrogen ligands (Figure 2). The cluster with radial exo-bonds is a typical *arachno*-species $[Ge_4H_4]^{2-}$ (D_{4h}) with $2n + 6 = 14$ cluster-bonding and $4 \times 2 = 8$ exo-bonding electrons. However, the Walsh diagram, part of which is shown in Figure 2 (the full diagram is available as Supporting Information), shows that upon bending of the exo-bonds to become parallel to two Ge−Ge edges (D_{2h}), two orbitals of different symmetry, b_{2g} and a_{2g}, in the former, become of the same symmetry, b_{1g}, and mix in the latter. Naturally, one of the combinations is stabilized and the other destabilized. The stabilized combination, basically a combination of lone pairs pointing at the available space vacated by moving the exo-bonds away from the radial positions, is filled, and the species become $[Ge_4H_4]^{4-}$ with two additional electrons. This is exactly the same effect that is observed in many systems upon symmetry reduction such as linear to bent AH_2, or planar to pyramidal AH_3, etc., systems where the higher symmetry prevents mixing of orbitals that are otherwise allowed to mix in the lower symmetry to produce similarly a stabilized lone pair in the vacated space.

Any deductions about the mechanism of formation of this trimer should account for the fact that (a) the trimers exist in solution,[6] that is, they are not assembled upon crystallization; (b) the reaction with the heavier triphenylbismuth and antimony derivatives provides the disubstituted species $[Ph_2E-(Ge_9)-EPh_2]^{2-}$ instead.[5] The different outcome of the latter reactions is perhaps due to the lower stability of the heavier diphenylpnictides $[Ph_2Sb]^-$ and $[Ph_2Bi]^-$ as free anions and their apparent preference to bond as ligands to the clusters.[9] The same species, on the other hand, are more stable as free anions for the lighter phosphorus and arsenic. Thus, in analogy with the reaction of lithium with triphenylphosphine to produce phenyllithium and lithium diphenylphosphide, a proposed scenario for the reaction at this preliminary stage is

$$3Ge_9^{4-} + 3Ph_3E \rightarrow [Ge_9{=}Ge_9{=}Ge_9]^{6-} + 3[Ph_2E]^- + 3Ph^-$$

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Supporting Information Available: An X-ray crystallographic file in CIF format, and figures showing the full correlation Walsh MO diagram for the transformation of $[Ge_4H_4]$ from D_{4h} to D_{2h} and the UV−vis spectra of the trimers in solution and in the solid state (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) All operations were carried out in inert atmosphere or under vacuum. The precursor compound Rb_4Ge_9 (isostructural with Cs_4Ge_9[2a]) was made from the elements heated at 900 °C for 2 days in sealed (by arc-welding) niobium containers that were jacketed in evacuated fused-silica ampules. Inside a drybox, 108 mg of it was placed in a test tube and was covered with 1 mL of ethylenediamine and 200 mg of Kryptofix 222. After being stirred for a few minutes, the color of the solution became intense brown-red (UV−vis: 368, broad peak from 450 to 500 with a broad shoulder extending to 650−700), indicative of Ge_9^{4-} and Ge_9^{3-}. Next, Ph_3As was added, and the solution was heated to 70 °C. After a few hours, the color changed to dark-green (UV−vis: 494, 641, and 825 nm). After being cooled to room temperature, the solution was filtered and carefully layered with 3 mL of monoglyme. Needle- and wedgelike crystals of exactly the same dark-green color (UV−vis: somewhat red-shifted to 503, 655, and 838 nm) formed after a few days (ca. 32 mg of product, which is approximately 61% yield based on the amount of dissolved precursor). The virtually identical absorption spectra prove the existence of the trimers in the solution. The compound can be synthesized also by oxidation of an ethylenediamine solution of the same precursor with Ph_3P or elemental As and Sb at the same temperature followed by layering with toluene. The elemental As and Sb in the latter two reactions are reduced to the well-known anions E_7^{3-}: $3Ge_9^{4-} + 14E \rightarrow [Ge_9{=}Ge_9{=}Ge_9]^{6-} + 2E_7^{3-}$.

(7) X-ray diffraction data were collected from a dark-green brick of **1** ($0.39 \times 0.30 \times 0.19$ mm) with graphite-monochromated Mo Kα radiation on a Bruker APEX diffractometer with a CCD area detector at 100 K. The structure was solved by direct methods in $P2_1/n$ and refined on F^2 (full matrix, absorption corrections with SADABS) using the SHELXTL V5.1 package. Crystal data: $a = 15.246(2)$, $b = 47.223(7)$, and $c = 26.657(4)$ Å, $\beta = 98.373(3)°$, $V = 18987(5)$ Å^3, $Z = 4$, $\mu = 57.90$ cm^{-1}, $d_{calc} = 1.72$ g/cm^3, R1/wR2 = 7.28/14.48% for the observed data ($I \geq 2\sigma_I$). All 27 Ge atoms of the trimer are unique and not disordered. The six [2,2,2]-crypt molecules around the Rb cations, on the other hand, show different degrees of disorder around the central rubidium.

(8) The molar magnetic suscpetibility of the compound (measured on 12 mg) is negative and temperature independent within 50−250 K: −0.035 emu/mol.

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