

Oxidative Coupling of Deltahedral $[\text{Ge}_9]^{4-}$ Zintl Ions

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Received July 1, 1999

For the first time, a dimer of deltahedral Zintl ions is made. Interest in synthesis, isolation, and characterization of deltahedral Zintl ions from solutions dates back to the 19th century,¹ and many such species have been discovered since.^{2–6} Most of them are deltahedral, and all of them are monomeric. Well-established species among the deltahedra are the nine-atom *nido* clusters of group 14, such as Ge_9^{4-} , Sn_9^{4-} , and Pb_9^{4-} , monocapped square antiprisms with classical electron counts according to the Wade's rules.⁷ More recently, the same types of clusters were proven to exist in the neat solids that were used as precursors to the solution studies.^{8,9} In addition to these, known are also the one-electron oxidized versions, i.e., cluster radicals of the same or similar geometries but charge of 3–.^{2,3} Here we report on the coupling of deltahedral nine-atom clusters into dimers in a formal oxidative coupling reaction. Dimers of Ge_9 – Ge_9 are found in the compound $\text{Cs}_4(\text{K-crypt})_2[(\text{Ge}_9)-(\text{Ge}_9)]\cdot 6\text{en}$ (**1**), where en is ethylenediamine and crypt is 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane.

Crystals of **1** in high yield were initially made by precipitation of a solution of a precursor of nominal composition $\text{K}_2\text{CsGe}_{14}\text{B}_3$ in ethylenediamine and excess of crypt.¹⁰ Later, a precursor without boron, Cs_2KGe_9 , was used. The solutions are green-brown and form instantly upon addition of the precursor to the mixture of ethylenediamine and crypt.¹¹ It should be noted here that the solutions from which most previously known compounds of germanium clusters were crystallized were reportedly red to red-brown.^{2–4} The only other report of brownish green color was for a precursor of nominal composition “ $\text{NaGe}_{2.25}$ ” dissolved in ethylenediamine.⁵ At this stage, it is not clear what causes the different colors. Single crystals of **1** grow on the walls of the vessels and become visible by naked eye within a few hours. No other phases form. After a day, most of the crystals are of sizes that are good enough for single-crystal X-ray diffraction studies. Such crystals were selected and mounted in glass capillaries, and the structure was determined from data collected on one of them.¹²

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(11) Redistilled ethylenediamine (99.5+%), packaged under nitrogen (Aldrich), and Kryptofix 222 (98%, Acros) were used as received. All operations of the dissolution and crystallization were performed in a helium-filled glovebox.

The new compound contains dimers made of two Ge_9 clusters that are connected via an *exo* bond between two vertexes (Figure 1). The two halves are identical since there is an inversion center at the midpoint of the bond connecting them. The geometry of the Ge_9 cluster is very close to the classical monocapped square antiprism that is expected for *nido* deltahedral clusters of nine atoms. Often such shape assignments are questioned since the borderline between this shape and that of a tricapped trigonal prism is not clear. For this particular cluster, however, the established criteria unequivocally indicate monocapped square antiprism.^{2,6} For example, the two dihedral angles at the open square base are 1.08 and 1.15°, and this means that the square is virtually planar, as in an ideal monocapped square antiprism. The diagonals in the base are 3.433(1) and 3.848(1) Å for Ge6–Ge8 and Ge7–Ge9, respectively. They are somewhat different due to the shorter distances around the *exo*-bonded atom Ge6, two bonds of 2.525(1) Å, compared to the other two distances in the square, 2.640(1) and 2.628(1) Å for Ge8–Ge7 and Ge8–Ge9, respectively. This is most likely a direct result of having an *exo* bond at Ge6 instead of a lone pair and the lesser repulsion associated with that. The averaged distances within the clusters of **1** are nearly identical with those of Ge_9^{4-} clusters found in $(\text{K-crypt})_6\text{Ge}_9\text{Ge}_9$ (**2**), which contains Ge_9^{4-} and Ge_9^{2-} ,¹³ $\text{Rb}_4\text{Ge}_9\text{en}$ (**3**),⁵ and the neat Cs_4Ge_9 (**4**).^{8a} The average distances around the capping atom (d_{cap}), at the capped square (d_{csq}), at the open square (d_{osq}), and at the waist (d_{wst}) for the four compounds are (compound number in parentheses) as follow: $d_{\text{cap}} = 2.578$ (**1**), 2.563 (**2**), 2.56 (**3**), and 2.572 (**4**) Å; $d_{\text{csq}} = 2.810$ (**1**), 2.807 (**2**), 2.84 (**3**), and 2.828 (**4**) Å; $d_{\text{osq}} = 2.580$ (**1**), 2.553 (**2**), 2.57 (**3**), and 2.590 (**4**) Å; and $d_{\text{wst}} = 2.604$ (**1**), 2.595 (**2**), 2.58 (**3**), and 2.590 (**4**) Å.

The two clusters are connected by an *exo* bond between two Ge6 atoms that are vertexes in the open squares. The distance, 2.488(2) Å, indicates a simple two-center, two-electron localized bond. It can be compared with the distance in elemental germanium, 2.445 Å, and the average Ge–Ge distances in $\text{CsNa}_2\text{Ge}_{17}$ with the clathrate-II structure, 2.494 Å,¹⁴ and in $\text{K}_4\text{Ge}_{23-x}$ with the clathrate-I structure, 2.502 Å.¹⁵ It is clearly longer than that in the element, which can be easily explained with the higher coordination number of Ge6 in the clusters, where it is surrounded by five germanium atoms and a cesium cation. On the other hand, it is shorter than the bonds in the clathrates, although the germanium atoms are only four-bonded in the latter. The reason in this case is most likely electronic since the clathrates have extra electrons provided by the alkali metals that are delocalized over the germanium antibonding band (the conduction band).¹⁴

The charge of the dimer is 6–, and this translates into 78 valence electrons ($18 \times 4 + 6$).¹⁶ This charge and number of electrons can be equally divided among the monomers and result in two Ge_9^{3-} half-dimers with 39 electrons each. This simplifica-

(12) A hemisphere of X-ray diffraction data ($2\theta_{\text{max}} = 50^\circ$) was collected at room temperature on CAD4 with Mo $K\alpha$ radiation from a single crystal of $\text{Cs}_4(\text{K-crypt})_2[(\text{Ge}_9)-(\text{Ge}_9)]\cdot 6\text{en}$ (rhombic, red-brown, $0.55 \times 0.30 \times 0.20$ mm). Crystal data: triclinic, $P1$, $Z = 1$, $a = 11.0058(8)$, $b = 12.615(1)$, and $c = 18.518(2)$ Å, $\alpha = 101.804(9)$, $\beta = 100.032(7)$, and $\gamma = 98.682(8)^\circ$, $V = 2431.3(4)$ Å³, $\mu = 70.82$ cm⁻¹, $d_{\text{calc}} = 2.07$ g·cm⁻³, $R1/wR2 = 5.58/15.35\%$ for the observed 6113 reflections ($I \geq 2\sigma$) and $R1/wR2 = 8.28/17.20\%$ for all 8494 reflections and 451 variables. All non-hydrogen atoms were refined with anisotropic displacement parameters; the hydrogens were refined as riding on the corresponding C and N atoms. The structure solution and refinement (on F^2) were done using the SHELXTL V5.1 package. The data were corrected for absorption with the aid of three ψ scans at different θ angles.

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(16) The magnetization of 13 mg of **1** was measured at field of 3 T over the range 10–295 K on a Quantum Design MPMS SQUID magnetometer. The results show temperature-independent magnetic susceptibility (ca. 2.3×10^{-3} emu·mol⁻¹), and therefore no magnetic moment due to localized spins.

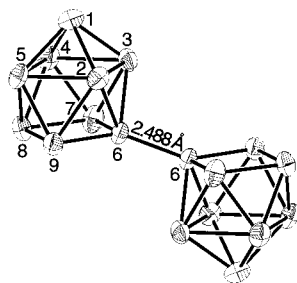


Figure 1. ORTEP drawing (50% probability level for the thermal ellipsoids) of the dimer of $[(\text{Ge}_9)-(\text{Ge}_9)]^{6-}$ found in $\text{Cs}_4(\text{K-crypt})_2[(\text{Ge}_9)-(\text{Ge}_9)] \cdot 6\text{en}$. The numbering of the germanium atoms is shown for one cluster only since there is an inversion center at midpoint of the connecting bond. Important distances: 1–2, 2.581(1); 1–3, 2.567(1); 1–4, 2.589(1); 1–5, 2.577(2); 2–3, 2.824(1); 2–5, 2.778(1); 2–6, 2.594(1); 2–9, 2.673(1); 3–4, 2.794(1); 3–6, 2.592(1); 3–7, 2.678(1); 4–5, 2.846(1); 4–7, 2.557(1); 4–8, 2.595(1); 5–8, 2.584(1); 5–9, 2.563(1); 6–7, 2.525(1); 6–9, 2.525(1); 7–8, 2.640(1); and 8–9, 2.628(1) Å.

tion is quite misleading, however, since, as mentioned above, there are compounds containing monomeric species of the same formula and charge, Ge_9^{3-} .^{2,3} These latter clusters are different from the half-dimers of **1**, and the difference is very substantial. The 39 electrons of the half-dimer are made of 22 skeletal electrons ($2 \times 9 + 4$ according to Wade's rules for *nido* species), 16 lone-pair electrons, and one electron from splitting the two electrons of the *exo* bond among the two clusters. The 39 electrons of the known Ge_9^{3-} monomers, on the other hand, are distributed as follows: 21 skeletal electrons (unusual electron count midway between the *closo* and *nido* species) and 18 lone-pair electrons.^{2,3} Thus, in relation to the *nido*- Ge_9^{4-} , the latter are the result of oxidation of the delocalized cluster bonding, while the "monomers" in **1** are the result of formal oxidation of a lone pair. This, of course, is true for the monomer in the already assembled dimer and does not mean that such species were available in the solution.

The mechanism of the coupling is not clear at this stage, but nonetheless a few speculations can be made. Since all nine-atom clusters of Group 14 have charges of $4-$ in the precursors,^{8,9} it is safe to assume that, upon dissolution, initially the species entering the solution have the same charge. Next, oxidation to a radical and a subsequent coupling take place. The newly formed species precipitate together with solvated cesium and cryptated potassium cations. It is unknown for now what the oxidizing agent might be, but traces of water or oxygen in the solution are good candidates. Since the reactions are carried out with as-purchased chemicals and in open containers in a glovebox where many other liquids are handled, this is not an unlikely scenario. The oxidation of the Ge_9^{4-} clusters presumably involves skeletal orbitals rather than lone pairs since the latter are of lower energy. In solution, clusters can get close to each other, and when two vertexes are close enough, their lone pairs will interact and form bonding and

antibonding combinations. For clusters with charge of $4-$, the result will be repulsion, since both combinations will be occupied. For clusters with charge of $3-$, on the other hand, there is a better option. The two electrons of the antibonding combination would rather occupy the two lower-lying half-filled skeletal orbitals on the monomers. This *exo-to-endo* internal electron transfer from an orbital localized on the outside of the cluster (the *exo* lone pair) to a delocalized skeletal orbital (*endo* for the cluster) results in a stable dimer with a HOMO–LUMO gap of ca. 3 eV (from extended-Hückel calculations), where the cluster bonding in each half is optimized for the particular geometry with 22 electrons. This process perhaps takes place in all solutions from which cluster radicals E_9^{3-} have been crystallized (E = group 14 element).^{2,3,6} Nevertheless, in all of them the process is reversible and favors the monomers, most likely due to the availability of only large cryptated cations such as $[\text{K-crypt}]^+$. In our case, since cesium is too big to be readily cryptated, "naked" cesium cations that are much smaller than any $[\text{A-crypt}]^+$ cations are also available in the solution (A = alkali metal). They can surround the dimers closely and can coprecipitate and cocrystallize with them without breaking them back to monomers. Since the assembly is apparently insoluble in ethylenediamine, the whole process of dimerization is strongly favored.

The positioning of the cesium cations with respect to the clusters is obviously important in the formation of this compound. There are two different cesium sites in the structure. One of them caps the open square face of each Ge_9 cluster and the Ge_2 – Ge_3 edge of its partner in the dimer. This cesium atom is also coordinated by three nitrogens of three different ethylenediamine molecules. A more interesting role is played by the second cesium cation, since it not only caps faces and edges but does that of two neighboring clusters and thus "connects" the clusters into chains.¹⁷ This cesium cation caps the edge Ge_2 – Ge_9 of one cluster and the edge Ge_3 – Ge_7 of its partner in the dimer, and it serves as an *exo* atom to a Ge_4 atom from another dimer. Each two dimers are interconnected by two such cesium cations to form the chains. These cesium cations are also coordinated additionally by two nitrogens from two different ethylenediamine molecules. The positioning of the ethylenediamine molecules is such that the chains are enveloped or solvated by them, and the cryptated potassiums are located between the chains.

Acknowledgment. We thank S. Bobev for the synthesis of the precursors and the donors of the Petroleum Research Fund, administered by the ACS, for the financial support of this research.

Supporting Information Available: Figure showing the positioning of the cesium cations around the clusters (PDF). An X-ray crystallographic file, in CIF format, is available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA992269S

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