Cs_6Ge_8Zn: A Zintl Phase with Isolated Heteroatomic Clusters of Ge_8Zn

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The number of compounds with large deltahedral clusters in the solid state has grown immensely in the last few years. The increase is due exclusively to examples from the heavier analogs of the boron group.[1,2] Recently, we extended the area into the carbon group by the synthesis of the first large cluster of this group (larger than four atoms[3]) in the solid state, Ge_9^{4-} in A_4-Ge_9 (A = Rb or Cs).[4] The cluster has the shape of a monocapped square antiprism, a group 14 analog of the *nido*-$B_9H_9^{4-}$ in the solid state. Ge_9^{4-} was previously known only as crystallized from solutions with cryptated alkali metal countercations.[5] The silicon analog, unknown before, was also recently characterized in the solid state.[6] Perhaps the major issue in the stability of deltahedral clusters of group 14 is their charge to size ratios. According to Wade's rules developed for the isoelectronic boranes,[7] the charge of the cluster is independent of the nuclearity, and therefore, large clusters have relatively small negative charges. As a consequence of this, only a few countercations are needed, and they may not be enough to efficiently shield and separate the large clusters. In cluster solution chemistry, the problem has been solved by the use of large countercations such as cryptated alkali metals or large organic cations. In the solid state, the answer is to use larger alkali metals such as Rb and Cs for countercations, or alternatively to increase the charge of the cluster by substitution with electron-poorer atoms. The latter approach, an attempt to substitute a germanium atom by zinc in Ge_9^{4-}, led to the synthesis of the title compound.

Fusion of the elements in the indicated proportions at 900 °C in a welded Ta-container followed by slow cooling (5 °C/h) yields nearly a single phase of Cs_6Ge_8Zn.[8] The plate-like crystals of the compound are brittle, black, and with coal-like luster. Single-crystal studies unveiled a new type of cluster formation, a dimer of corner-sharing trigonal bipyramids (Figure 1).[9] The clusters are ordered in layers perpendicular to the *b* axis (Figure 2). Although all clusters are Ge_8Zn and have very similar geometries, they are of two crystallographically different types. The clusters of type A have only a horizontal mirror plane (C_m) while the clusters of type B have an additional
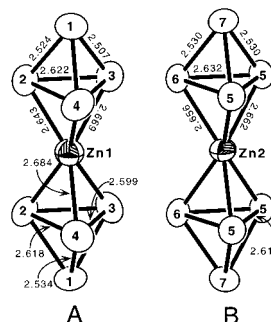

Figure 1. The two crystallographically different clusters of Ge_8Zn^{6-} in Cs_6Ge_8Zn drawn with thermal ellipsoids at 90% probability (the *b* axis is vertical). Clusters A (C_m) have only a horizontal mirror plane through the zinc, while clusters B (C_{2v}) have an additional vertical one containing Ge6.
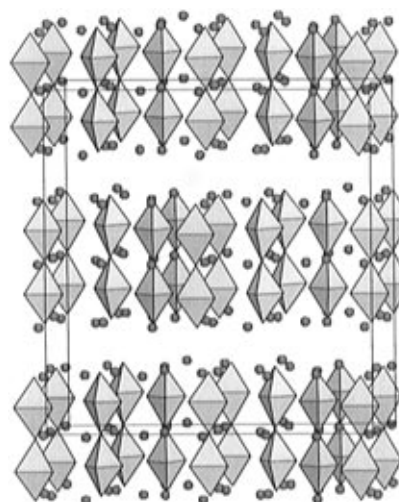

Figure 2. Shown are three layers of isolated clusters of Ge_8Zn^{6-} packed with cesium cations (isolated spheres) in Cs_6Ge_8Zn. The view is along the *c* axis with *b* vertical, and the unit cell is outlined.

vertical mirror plane (C_{2v}). There are eight A-type and four B-type clusters per unit cell. Both have pseudo D_{3h} symmetry with very similar bond distances. The two trigonal bipyramids, the smallest *closo*-deltahedra, share the apical zinc atom and are eclipsed. The Zn–Ge distances, $d_{av} = 2.664$ Å, are quite short and correspond to an average bond order of 0.45 on the basis of the sum of Pauling's single bond radii of the two elements, 2.455 Å.[10] The Ge–Ge distances to the apical germanium, $d_{av} = 2.524$ Å, are even shorter despite the similar sizes of zinc and germanium. One likely explanation lies with the different coordination numbers, six for the zinc and three for the apical germanium. The distances within the bases of the bipyramids, $d_{av} = 2.618$ Å, are also longer, and this is normal for trigonal bipyramids. All known trigonal bipyramidal clusters have longer equatorial distances, sometimes by as much as 0.31 Å.[11] Similarly, in the monocapped square antiprisms of Ge_9^{4-}, the distances to the capping atom and within the open square (both four-bonded atoms), 2.572 and 2.590 Å, respectively, are shorter than those within the capped square (five-bonded atoms), 2.830 Å.[4] Considering the short Zn–Ge distances in Ge_8Zn, it is reasonable to expect that the cluster may stay intact if extracted in solution.[12]

(1) (a) Corbett, J. D. In *Chemistry, Structure and Bonding of Zintl Phases and Ions*; Kauzlarich, S., Ed.; VCH Publishers: New York, 1996. (b) Corbett, J. D. *Structure Bonding* **1997**, *87*, 157. (c) Corbett, J. D. *Chem. Rev.* **1985**, *85*, 383.

(2) Belin, C.; Tillard-Charbonnel, M. *Prog. Solid State Chem.* **1993**, *22*, 59.

(3) Tetrahedral clusters E_4^{4-} in the solid state are known for all elements of group 14 except carbon.

(4) Queneau, V.; Sevov, S. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36/16*, in print.

(5) Belin, C. H. E; Corbett, J. D.; Cisar, A. *J. Am. Chem. Soc.* **1977**, *99*, 7163.

(6) Queneau, V.; Sevov, S. C. Unpublished research.

(7) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(8) The product is a single phase according to a comparison of the Guinier powder X-ray photograph with a powder pattern calculated on the basis of the refined structure.

(9) The structure was solved by direct methods from data collected on CAD4 diffractometer with Mo Kα radiation ($2\theta_{max} = 50°$) at 20 °C. Crystal data: *Fmm2*, Z = 12, a = 22.090(2), b = 23.421(4), and c = 12.467(2) Å, R1/wR2 = 7.95/14.4% and GOF = 1.14 for 2990 independent reflections with $I \geq 2\sigma_I$ and 119 variables. The data were corrected for absorption ($\mu = 220.1$ cm^{-1}) with the aid of the average of three ψ scans. The largest positive and negative peaks in the difference Fourier map were +2.23 (1.35 Å from Cs2) and −2.40 (1.16 Å from Cs3) e/Å^3, respectively.
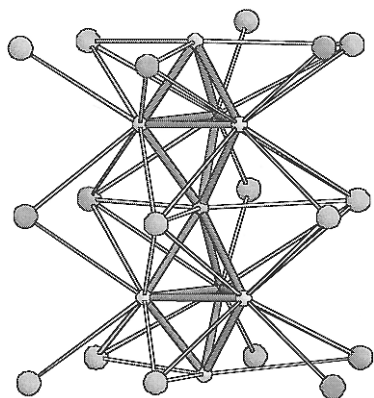
(10) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(11) Some examples of such clusters are Tl_5^{7-} (Dong, Z. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 3429), Sn_5^{2-} (Edwards, P. A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 903), and Bi_5^{3+} (Corbett, J. D. *Inorg. Chem.* **1968**, *7*, 198), with differences between the average equatorial and apical distances of 0.22, 0.23, and 0.31 Å, respectively.

Figure 3. The coordination of the cesium cations (larger spheres) around the clusters of Ge_8Zn^{6-}. They are hexagonally positioned around the apical Ge and central Zn atoms and form close-packed layers with them. All faces of the cluster are capped by cesium, and each Ge atom has two "*exo*" cesiums. (The *exo* cations of the apical germaniums are in the adjacent layers and are not shown.)

The clusters are packed very efficiently with the cesium cations and form slabs perpendicular to the *b* axis (Figure 2). Each slab is shifted with respect to the adjacent one by a half of a unit cell along the *c* axis. The cations are at the "levels" of the zinc and apical germanium atoms along *b* (Figure 2) and form close-packed layers with them (Figure 3). In a slab, each cesium atom caps one or two faces of two clusters and is *exo*-positioned to one or two atoms of a third cluster. Thus, each cation is shared by three clusters in a slab, and since each cluster is surrounded by eighteen cations (Figure 3), the stoichiometry is six cesiums per a cluster of Ge_8Zn. The "coordination" of the cations around this vertex-fused dimer is strikingly reminiscent of the positioning of ligands around chains of corner-shared octahedral clusters of transition metals, for example, in the Ti_5Te_4 structure type.[13]

The electronic features of the cluster can be understood with the aid of extended-Hückel calculations and Wade's rules. According to the latter, the number of skeletal electrons needed for delocalized bonding in two *closo*-clusters of five atoms each (the two trigonal bipyramids) is $2(2 \times 5 + 2) = 24$. When the electrons of the eight lone pairs on the germanium atoms (zinc with this geometry would not have a lone pair) are added, the total becomes 40. Since each germanium and zinc atoms bring four and two electrons, respectively, the number of available electrons is $8 \times 4 + 2 = 34$. In order to satisfy the bonding requirements, therefore, the cluster needs six additional electrons, and these come from the six cesium cations.

Extended-Hückel calculations were performed on the cluster with idealized D_{3h} geometry and with distances equal to the corresponding average distances of the real clusters.[14] Calculations were also carried out on a model of $H_3Ge-Zn-GeH_3$ with Ge–Zn distance of 2.45 Å, a single bond distance according to Pauling's single bond radii of the two elements.[10] The calculated bond overlap populations for the Zn–Ge bond in the cluster and in the model are 0.2992 and 0.6186 per bond,

respectively, and indicate relatively strong bonding interactions between the zinc and the six germanium atoms in the former. The HOMO–LUMO gap for 40 electrons is *ca.* 3 eV with the zinc p_x and p_y orbitals constituting the major part of the LUMO. The zinc p_z and s orbitals mix substantially with orbitals of appropriate symmetry from the two germanium caps and bring stabilization to the system. This is very similar to interactions of an interstitial atom and a cluster, and theoretically has been described before.[15] Thus, the electron count can be rationalized as the sum of the two caps since the central atom brings no new orbitals. Each cap can be considered as a *nido*-species and therefore with $2n + 4 = 12$ bonding electrons. When the eight lone pairs are added, the total becomes 40 again. Magnetic measurements show that the compound is diamagnetic, i.e., a closed-shell Zintl phase.[16]

Vertex-fused formations are not very common in main group cluster systems. A few such examples are known for molecular clusters with aluminum or silicon as the central atom and two caps of *nido*-carboranes derived from icosahedra or pentagonal bipyramids.[17] Some geometrical similarities in the solid state can be found in the mixed alkali metal compounds $A'_7A''E_8$ (E = Ge, Si) where the smaller alkali metal caps parallel faces of two (staggered) E_4 tetrahedra.[18] Another comparison can be made with the zinc-centered bicapped square antiprisms of In_{10} in $K_8In_{10}Zn$.[19] When the bonds between the two squares in such a cluster are disregarded, the resulting shape is a similar dimer of square bipyramids sharing a vertex, the zinc atom. Moreover, the corresponding compound was also made in an attempt to substitute with zinc an atom of the empty cluster of In_{11}^{7-}.[20] The "failed" substitution in that cluster and in Ge_9^{4-}, and the "successful" substitution with Hg in the former to form $[In_{10}Hg]^{8-}$,[21] can be explained with the different "stability" of lone pairs on zinc and mercury. In both cases, zinc secures coordination for which a lone pair is not required.

(12) Tetrahedra of E_4^{4-} do not exist in solutions and have not been crystallized from them with alkali metals, cryptated or not.

(13) Simon, A. In *Solid State Chemistry: Compounds*; Cheetham, A. K., Day, P., Eds.; Oxford University Press: Oxford, 1992.

(14) The H_{ii} values for Zn were iterated to self consistency by the aid of parameters from the following: Munita, R.; Letelier, J. R. *Theor. Chim. Acta* **1981**, *58*, 167.

(15) Burdett, J. K.; Canadell, E. *J. Am. Chem. Soc.* **1990**, *112*, 7207.

(16) The magnetization of 25 mg of sample from quenched stoichiometric reaction was measured at 3 T over a temperature range of 6–295 K on a Quantum Design MPMS SQUID magnetometer. The raw data, temperature independent susceptibility fluctuating between -5.1 and -5.4×10^{-4} emu/mol (adjusted for holder contribution), was corrected for core diamagnetism (-2.5×10^{-4} emu/mol) and for diamagnetism of the electron pairs on cluster orbitals (-1.8×10^{-4} emu/mol). The final numbers are between -0.8 and -1.1×10^{-4} emu/mol.

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(20) Sevov, S. C.; Corbett, J. D. *Inorg. Chem.* **1991**, *30*, 4875.

(21) Sevov, S. C.; Ostenson, J. E.; Corbett, J. D. *J. Alloys Compd.* **1993**, *202*, 289.