[(Pd–Pd)@Ge$_{18}$]$^{4-}$: A Palladium Dimer Inside the Largest Single-Cage Deltahedron

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Polyhedra with triangular faces, known as deltahedra, are among the most frequently occurring shapes in cluster chemistry. The high symmetries of their idealized geometries make them also very aesthetically pleasing. Among these deltahedra are the octahedral (O_h) transition-metal clusters and the much more diverse boranes, carboranes, and metallaboranes that include tetrahedra (T_d), trigonal and pentagonal bipyramids (D_{3h}, D_{5h}), tricapped trigonal prisms (D_{3h}), bicapped square antiprisms (D_{4d}), and icosahedra (I_h).[1] Until very recently, the icosahedron, a cluster with 12 vertices, was the largest single-cage deltahedron.[1] Not long ago, the synthesis and structure of a 14-vertex carborane deltahedron with the shape of a bicapped hexagonal antiprism (D_{6d}) was reported[2] (metallacarboranes with the same shape have been known for much longer[3]).

Another class of deltahedral clusters are the so-called Zintl anions of the heavier members of group 14. The most stable among these are the nine-atom species with the shape of distorted tricapped trigonal prisms, E$_9^{n-}$ (where E = Si, Ge, Sn, or Pb and n = 2, 3, or 4). Also known are the five-atom species with a charge of 2−, E$_5^{2-}$ (trigonal bipyramids).[4] Recent work has shown that the nine-atom clusters can be functionalized,[5] interconnected,[6] and even centered with transition metals.[7,8] Furthermore, in the case of lead, attempts to center the clusters with transition metals have led to cluster enlargement to 10- and even 12-atom species, [Ni@Pb$_{10}$]$^{2-}$ and [Pt@Pb$_{12}$]$^{2-}$, with the shapes of a bicapped square antiprism and an icosahedron, respectively.[9] Herein, we report the result from a similar reaction involving nine-atom germanium clusters, the largest single-cage deltahedron. It is made of 18 germanium atoms, has 32 triangular faces, and is centered by a dimer of palladium atoms, [Pd$_2$@Ge$_{18}$]$^{4-}$ (Figure 1).

The new anion was structurally characterized in [K(2,2,2-crypt)]$_4$-[Pd$_2$@Ge$_{18}$]·2tol synthesized by reaction of an ethylenediamine solution of K$_4$Ge$_9$ with an excess of Pd(PPh$_3$)$_4$.[10,11] The 18-vertex deltahedron is not spherical, but rather oblong, with a prolate shape. The cluster has an inversion center only, but its overall shape is very close to D_{3d} symmetry.[12] This shape and high symmetry are among those proposed as possible for a deltahedron of this size.[12] The ellipsoidal nature of the cluster provides for two foci instead of the one focus observed in the smaller clusters which tend to be spherical. This, in turn, results in two bonding molecular orbitals made of germanium hybrids that are radially pointing at the two foci instead of the one such orbital observed and prescribed by Wade's rules for spherical clusters.[13] Therefore, instead of the expected 2− charge for a deltahedron of germanium atoms, this cluster has one additional bonding orbital and, therefore, carries a charge of 4− instead (i.e., Ge$_{18}^{4-}$).[14] The two palladium atoms occupy the foci of the cluster and do not bring additional cluster bonding electrons.[9,15] Therefore, [Pd$_2$@Ge$_{18}$]$^{4-}$ carries the same charge of 4−. The role of the palladium atoms is mainly to provide central orbitals for overlap with the germanium orbitals for better bonding of the cluster which, in turn, is responsible for the stabilization of such a large deltahedron.[9,15] An attestation for this
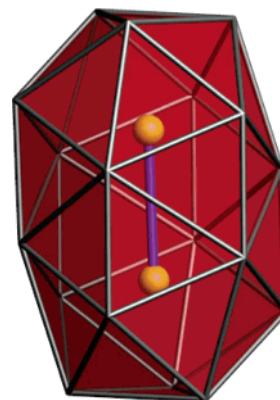

Figure 1. The structure of [Pd$_2$@Ge$_{18}$]$^{4-}$, the largest single-cage deltahedron. The shape of the deltahedron is prolate with a pseudo-D_{3d} symmetry (the pseudo 3-fold axis is vertical) and has two foci that are occupied by the palladium atoms. The Pd–Pd distance is 2.831(1) Å.
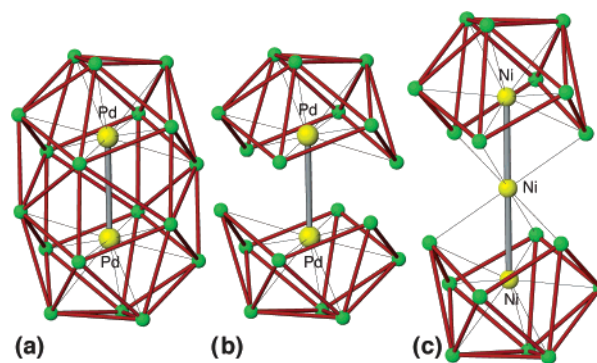
Figure 2. Ball-and-stick drawings of (a) [Pd$_2$@Ge$_{18}$]$^{4-}$; (b) [Pd$_2$@Ge$_{18}$]$^{4-}$, shown as made of two Pd-centered Ge$_9$ clusters by simply removing the bonds between the halves; and (c) the recently characterized [Ni$_3$@(Ge$_9$)$_2$]$^{4-}$ made of the same halves as (b) but separated further by the third nickel atom.

is the relatively large HOMO−LUMO gap of 2.67 eV calculated for the cluster.[16] The Pd−Pd distance of 2.831(1) Å is longer than the range of observed single-bond distances, 2.53−2.70 Å,[17] and indicates weak interactions at best. Perhaps the distance is "imposed" by the Ge−Ge distances of the cluster.

The new 18-atom deltahedron is most likely formed by fusion of two Pd-centered 9-atom deltahedra (Figure 2a and b). It has been shown that Ni and Pt can center 9-atom clusters of germanium or tin with the addition of a ligated Ni or Pd vertex, forming [Ni@(Ge$_9$Ni−PPh$_3$)]$^{2-}$, [Ni@(Sn$_9$Ni−CO)]$^{2-}$, and [Pt@(Sn$_9$Pt−PPh$_3$)]$^{2-}$.[7] This additional (tenth) vertex caps one of the triangular bases of the otherwise tricapped trigonal prismatic Ni-centered 9-atom germanium clusters and opens it to a great extent. (We have characterized [Ni@Ge$_9$]$^{3-}$ with the shape of such an elongated tricapped trigonal prism.[8]) Such a cluster looks very much like each
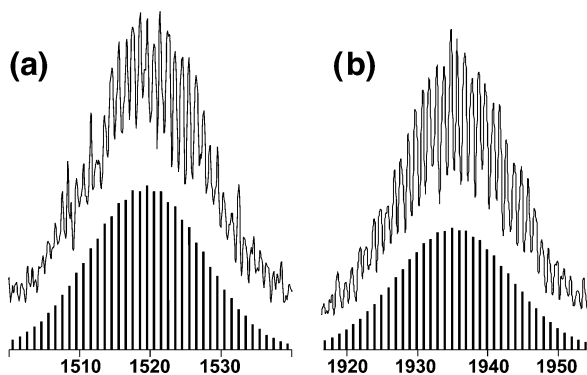
Figure 3. The mass spectrometry peaks corresponding to (a) $[Pd_2@Ge_{18}]^-$ and (b) $\{[K(2,2,2\text{-crypt})][Pd_2@Ge_{18}]\}^-$. The calculated theoretical isotope distributions are shown under each peak.

of the two halves of $[Pd_2@Ge_{18}]^{4-}$ shown in Figure 2b. These two halves are "generated" by simply omitting the bonds that stitch them together in Figure 2a. Note that they are staggered with respect to each other in order to produce triangular faces when connected into the large cluster. Recently, we characterized a very similar formation of such two halves positioned in a similar way but encompassing a linear formation of three nickel atoms, $[Ni_3@(Ge_9)_2]^{4-}$ (Figure 2c).[8] The additional nickel atom in this case keeps the two 9-atom clusters further apart and prevents Ge–Ge interactions between them. Thus, the sequence shown in Figure 2a–c can be viewed as the opening (cracking) of a large ellipsoidal cluster (an egg) by adding more central atoms.

The new cluster stays intact in solutions. This was confirmed by electrospray mass spectrometry in both negative- and positive-ion modes of a solution of $[K(2,2,2\text{-crypt})]_4[Pd_2@Ge_{18}]\cdot2\text{tol}$ in DMF.[18] The negative-ion mode shows a sequence of different cluster charges coupled with a different number of $[K(2,2,2\text{-crypt})]^+$ cations, that is, $[Pd_2@Ge_{18}]^-$ (m/z = 1519.82), $\{[K(2,2,2\text{-crypt})]\text{-}[Pd_2@Ge_{18}]\}^-$ (1935.41), and $\{[K(2,2,2\text{-crypt})]_2[Pd_2@Ge_{18}]\}^-$ (2351.00) (see Supporting Information). Shown in Figure 3 are the first two anions and the corresponding calculated isotope distributions. Clearly, the match is excellent. The positive-ion mode shows a very strong peak of $\{K[K(2,2,2\text{-crypt})][Pd_2@Ge_{18}]\}^+$ (1974.51) which also matches perfectly the theoretical isotope distribution (Supporting Information).

An 18-atom cluster with exactly the same shape has been observed before, but as a part of an extended three-dimensional framework of Cd/Sn in $Na_{49}Cd_{58.5}Sn_{37.5}$.[19] However, six of the vertices are partially occupied, and the cluster is not a complete deltahedron. Also, it is bonded within the complex framework via 12 of its vertices and cannot be isolated as discrete species.

Supporting Information Available: X-ray crystallographic file in CIF format, two ORTEP views of the 18-atom cluster, extended mass spectra in negative- and positive-ion modes, and complete ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) All operations were carried out under an inert atmosphere or vacuum using standard Schlenk-line or glovebox techniques. Ethylenediamine (Acros, 99%) was distilled over sodium metal, collected, and redistilled over K_4-Sn_9 and/or K_4Pb_9 intermetallics. 2,2,2-Crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]-hexacosane, Acros, 98%) and Pd(PPh₃)₄ (Acros, 99%) were used as received after carefully drying them under vacuum. K_4Ge_9 was synthesized by heating a stoichiometric mixture of the elements (K: 99+%, Strem; Ge: 99.999%, Alfa Aesar) at 900 °C for 2 days in sealed niobium containers jacketed in evacuated fused silica ampules. K_4-Ge_9 (70 mg, 0.086 mmol) and 2,2,2-crypt (129 mg, 0.344 mmol) were dissolved in 2 mL of ethylenediamine (red solution) in a test tube inside a glovebox. $Pd[P(C_6H_5)_3]_4$ (130 mg, 0.112 mmol) was added, and the reaction mixture was stirred for 3 h. The resulting dark brown solution was filtered and layered with toluene. It yielded nicely shaped black brick-like crystals of $[K(2,2,2\text{-crypt})]_4[Pd_2@Ge_{18}]\cdot2\text{tol}$ after 2 days (ca. 56% crystalline yield).

(11) Single-crystal X-ray diffraction data of $[K(2,2,2\text{-crypt})]_4[Pd_2@Ge_{18}]\cdot2\text{tol}$ were collected on a Bruker APEX diffractometer with a CCD area detector and Kα radiation at 100 K. The structure was solved by direct methods and was refined on F^2 using the SHELXTL V5.1 package. Crystal data: monoclinic, $P2_1/n$, a = 15.324(3), b = 27.519(5), and c = 15.849(3) Å, β = 115.333(3)°, V = 6041(1) Å³, Z = 4, $R1/wR2$ = 4.97/12.02% for the observed data ($I \geq 2\sigma(I)$), $R1/wR2$ = 7.79/13.28% for all data.

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(14) Smaller deltahedral clusters have n tangential and 1 radial bonding orbitals and require $2(n + 1)$ bonding electrons. Each vertex can be viewed as sp-hybridized with the two hybrid orbitals pointing radially in- and outward, while the two pure p-orbitals are tangential to the surface of the cluster. Each germanium vertex provides two cluster bonding electrons (the other two electrons occupy the outward pointing lone pair type sp hybrid), that is, $2n$ electrons from n vertices. This results in a charge of $2-$ per cluster, Ge_n^{2-}. The elongated 18-vertex deltahedron has n tangential and two radial bonding orbitals (the latter pointing at the two foci). These $n + 2$ orbitals need $2(n + 2)$ bonding electrons, that is, the charge of the clusters is $4-$, Ge_{18}^{4-}.

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