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$[\mathrm{Ge_9{=}Ge_9{=}Ge_9{=}Ge_9}]^{8-}$: A Linear Tetramer of Nine-Atom Germanium Clusters, a Nanorod

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A tetramer of nine-atom deltahedral germanium clusters and charge 8–, $[\mathrm{Ge_9{=}Ge_9{=}Ge_9{=}Ge_9}]^{8-}$, has been characterized as a (Rb-18C6)$^{+}$ salt (18C6 = 18-crown-6 polyether). The clusters are connected by pairs of parallel bonds, and the electrons are delocalized over the whole anion. The size of the tetramer is of nanorod dimensions, ca. 2 nm.

Recent developments in the area of deltahedral Zintl ions, i.e., borane-like anions of the heavier carbon-group elements, have brought new light to their chemistry and have changed major concepts about their reactivity. First, it was shown that nine-atom ions E_9^{4-} of group 14 (E = Ge, Sn, Pb), previously known only as crystallized from solutions, exist also in the precursor Zintl phases A_4E_9 (A = alkali metal).[1] This was unexpected[2] and, for the first time, established a connection between Zintl phases and Zintl ions.[1a] Second, contrary to the belief that exo bonds to these deltahedral clusters are not viable, dimers and chains of germanium clusters, $[\mathrm{Ge_9{-}Ge_9}]^{6-}$ and $_\infty[-\mathrm{Ge_9}-]^{2-}$, respectively, were discovered.[3,4] Next came the discovery that these clusters can exo-bond not only between themselves but also to other groups such as $\mathrm{EPh_2}$ where E = Sb or Bi and form $[\mathrm{Ph_2E{-}Ge_9{-}EPh_2}]^{2-}$.[5] These findings show that the deltahedral Zintl ions are in many respects similar to the cage-like boranes as they can also connect to each other and tolerate various substituents. The boranes are also known to fuse via edges or faces, but this has not been observed yet for the deltahedral Zintl ions. Closest to fused clusters is the trimer $[\mathrm{Ge_9{=}Ge_9{=}Ge_9}]^{6-}$ where each pair of clusters is bonded by two bonds from two neighboring vertices on each cluster.[6] Here we report the synthesis and characterization of a tetramer of such clusters, $[\mathrm{Ge_9{=}Ge_9{=}Ge_9{=}Ge_9}]^{8-}$, that is long enough to qualify for a nanorod.

The new oligomer is found in the compounds $(\mathrm{Rb\text{-}18C6})_8[\mathrm{Ge_9{=}Ge_9{=}Ge_9{=}Ge_9}]\cdot 2\mathrm{en}$ (**1**) and $(\mathrm{Rb\text{-}18C6})_8[\mathrm{Ge_9{=}Ge_9{=}Ge_9{=}Ge_9}]\cdot 6\mathrm{en}$ (**2**) where 18C6 and en stand for 18-crown-6 polyether and ethylenediamine, respectively. Both compounds crystallize from a solution of $\mathrm{Rb_4Ge_9}$ (isostructural with $\mathrm{Cs_4Ge_9}$;[1] contains isolated $\mathrm{Ge_9}^{4-}$ clusters) dissolved to saturation in ethylenediamine.[7] The structures of the two compounds were determined by single-crystal X-ray diffraction.[8] They are virtually the same and differ only by the number of solvent molecules involved in the crystallization. Both structures are made of the novel discrete tetramers of $[\mathrm{Ge_9{=}Ge_9{=}Ge_9{=}Ge_9}]^{8-}$ and rubidium cations "crowned" by 18C6, one ether molecule per cation (Figure 1). Since the cations do not reside within the planes of the crown-ether molecules but are rather removed quite a way from them, only half of their coordination spheres are occupied by the sequestering agent. Thus, they are quite open for interactions and coordinate around the germanium tetramers, capping faces and edges (Figure 1). Each cluster has two capped faces, and, in addition, the two inside clusters also have bridged edges. The Rb−Ge distances fall in the

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(7) All manipulations were performed in a nitrogen-filled glovebox with a moisture level below 1 ppm. The precursor of $\mathrm{Rb_4Ge_9}$ was made from a stoichiometric mixture of the elements (Rb, Strem, 99+ %; Ge, Acros, 99.999%) heated at 900 °C for 2 days in niobium containers that were sealed by arc-welding and were then jacketed and evacuated in fused-silica ampules. The precursor (97 mg, $\sim 9.7 \times 10^{-5}$ mol) was dissolved in 1 mL of ethylenediamine (Aldrich, 99.5+%, redistilled and packaged under nitrogen). The solution was stirred for 10 min at 50 °C, and, after cooling quickly to room temperature, an orange-brown suspension of the known $\mathrm{Rb_4Ge_9}\cdot 1.1\mathrm{en}$ formed (Somer, M.; Carrillo-Cabrera, W.; Peters, E. M.; Peters, K. von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1915). Most of this suspension dissolved after adding 106 mg of 18-crown-6 (4×10^{-4} mol, Acros, 99%) and stirring it for 15 min at 50 °C. It was left for 1 h and was then centrifuged and filtered. The resulting black-green solution (this color is associated with oligomerization) was split in two test tubes, and one of them was layered with THF and the other with toluene. Three days later crystals of **1** and **2** were recovered from the containers, respectively.

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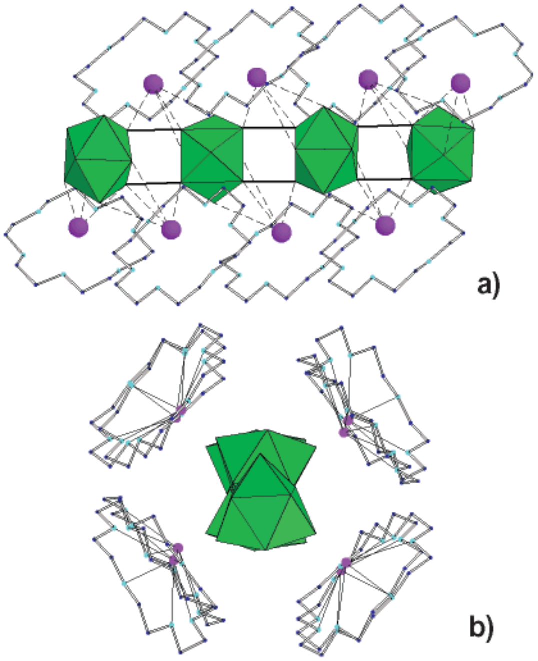

Figure 1. Two views of the tetramer of [Ge9=Ge9=Ge9=Ge9]$^{8-}$ surrounded with eight rubidium cations (purple) "crowned" by 18-crown-6 polyether: (a) shown are the Rb−Ge interactions; (b) the view along the nanorod's axis clearly shows how the crown-ether molecules "protect" the tetramer on the outside.

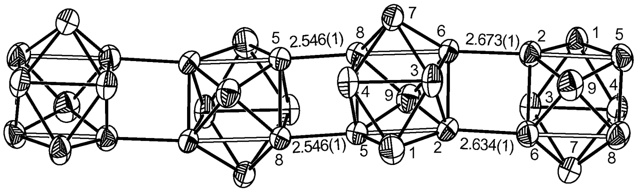

Figure 2. ORTEP drawing of the tetramer [Ge_9=Ge_9=Ge_9=Ge_9]$^{8-}$ (90% probability thermal ellipsoids). Each cluster is a tricapped trigonal prism with two elongated prismatic edges (shown as open bonds).

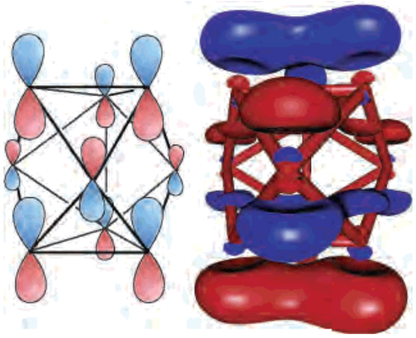

Figure 3. The HOMO of one of the nine-atom clusters of the tetramer. It is formed explicitly of p_z orbitals (left, from extended-Hückel MO calculations). The largest contribution is from the atoms of the elongated edges and the corresponding vertex that caps those edges. Notice that the orbital is (a) π-bonding within the triangular bases of the trigonal prism, (b) σ-antibonding between the bases, and (c) σ-bonding bewteen the capping atoms and those at the bases. Most importantly, the orbital extends outside the cluster as extensions of the elongated edges. All this is confirmed by the shape of the orbital calculated by DFT (right).[10]

range 3.5−4.2 Å. The coordination of eight (Rb-18C6) cations around the tetramer provides a positively charged and protective outer shell around the negatively charged core of 36 germanium atoms.

The tetramer is a rodlike formation with a length of about 2 nm and diameter of ca. 0.4 nm, i.e., a nanorod with an aspect ratio of about 5. These nanorods, in both compounds, are made of two crystallographically different Ge_9 clusters and their images generated by inversion centers (Figure 2). The four Ge_9 clusters are quite similar and can be viewed as tricapped trigonal prisms where the triangular bases are made of atoms 4−5−8 and 2−3−6 while the capping atoms are 1, 7, and 9. The prisms are elongated along two of the three prismatic edges parallel to the 3-fold axis, in this case edges 2−5 and 6−8. The average distance for these edges is 2.982 Å while it is 2.793 Å for the "normal" edges 3−4. It is exactly the atoms of the elongated edges, i.e., atoms 2, 5, 6, and 8, that are exo-bonded to the neighboring clusters. Furthermore, the exo bonds are not radial to the clusters, as might have been expected, but are virtually collinear with the elongated edges (Figures 1 and 2). The reason for this is the geometry of the monomer and, subsequently, the shape of the HOMO, i.e., the orbital that is accessible for oxidative coupling. Studies of the molecular orbitals of a similar cluster but with three elongated edges, Bi_9^{5+}, have already revealed the shape and character of this orbital.[9] It is made predominantly of p_z orbitals (z along the 3-fold axis) with larger participation of the atoms at the elongated edges and the one capping them, and almost no contribution of p_x,p_y (Figure 3). Thus, large parts of the orbital are found outside the cluster as extensions to the elongated edges (Figure 3) and, therefore, the observed coupling along z is easily understood. It should be pointed out that coupled in the same way but along one edge are the clusters in the dimers of [Ge_9−Ge_9]$^{6-}$ and the infinite chains of $_\infty$[−Ge_9−]$^{2-}$.[3,4] Also, the Ph_2E groups in [Ph_2E−Ge_9−EPh_2]$^{2-}$ (E = Sb, Bi) are attached along one elongated edge and the Ge−E exo bonds are also collinear with that edge.[5]

The clusters in the tetramer are stacked in such a way that the "normal" edges of the trigonal prisms, edges 3−4, alternate with respect to the plane defined by the exo bonds. Had they all been on one side, the clusters would have been automatically three-connected along all three edges forming a columnar tetramer of stacked tricapped trigonal prisms elongated presumably along all three edges. Such a structure might be accessible judging from the fact that already known are examples of clusters coupled along one and two edges,

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(8) Several crystals of **1** and **2** were placed on a micro slide and were covered with oil (Paratone-N) inside the glovebox. The slide was taken out, and, under a microscope, crystals were picked with thin glass fibers. For the best ones, X-ray diffraction data were collected with graphite-monochromated Mo Kα radiation at 100 K on a Bruker APEX diffractometer with a CCD area detector. The structures were solved by direct methods and were refined on F^2 using the SHELXTL V5.1 package. Crystal data for compound **1**: platelike; dichroic; 0.18 × 0.08 × 0.02 mm; triclinic; $P\bar{1}$; a = 15.120(1) Å, b = 16.250(1) Å, and c = 18.717(1) Å, α = 83.30(1)°, β = 83.01(1)°, γ = 78.00(3)°; V = 4445.2(5) Å^3; Z = 1; μ = 82.2 cm^{-1}; ρ_{calc} = 2.066 g·cm^{-3}; R1/wR2 = 5.76/13.15% for 10334 observed reflections ($I \geq 2\sigma_I$). Crystal data for compound **2**: platelike; dichroic; 0.11 × 0.10 × 0.03 mm; triclinic; $P\bar{1}$; a = 13.571(1) Å, b = 15.885(2) Å, and c = 22.645(3) Å, α = 99.355(3)°, β = 97.813(3)°, γ = 101.257(3)°; V = 4652(1) Å^3; Z = 1; μ = 78.6 cm^{-1}; ρ_{calc} = 2.06 g·cm^{-3}; R1/wR2 = 6.49/12.01% for 6622 observed reflections ($I \geq 2\sigma_I$).

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$[Ge_9-Ge_9]^{6-}$ and $[Ge_9{=}Ge_9{=}Ge_9{=}Ge_9]^{8-}$, respectively, and based on the specifics of the HOMO as discussed above. One problem with such a columnar tetramer might be the relatively low negative charge of 6− calculated for it. Formations with more reasonable charge-to-size ratios would be columnar pentamers which would have a charge of 8− and higher columnar oligomers.

The charge of the tetramer is easily verified by calculations.[10] As in the trimer,[6] this charge is equally distributed among the clusters. The intercluster bonding by two parallel bonds was initially considered to be unusual, and detailed electronic structure calculations and Wilson plots were performed for the trimer and various models of it.[6] The conclusions for the latter are valid for the tetramer as well. It should be pointed out that the exo-bond distances, 2.546−2.673 Å, are comparable to the distances within the clusters, 2.517−2.747 Å. This and the collinear exo bonds and prismatic edges lead to delocalization of the bonding electrons over the whole tetramer and not only in each monomer. Thus, the exo bonds can be described not as localized 2-center-2-electron bonds but rather as participating in a system of delocalized bonding. The tetramer should not be viewed as made of four clusters of delocalized bonding that are bonded via localized bonds but rather as one monolithic formation where the delocalization is over the whole tetramer involving both the intra- and intercluster bonds.

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Supporting Information Available: Two views of the packing of the tetramers in the structure of **1** and an X-ray crystallographic file for the two structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) DFT calculations were performed on the tetramer (with the observed geomtery) using the B3LYP functional (A. D. Becke, *J. Chem. Phys.* **1996**, *104*, 1040) with 3-21G basis set.