DOI: 10.1002/anie.200900133

The Shape of Germanium Clusters To Come

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cage compounds · cluster compounds · germanium ·
Zintl anions

The venerable field of Zintl ions of Group 14 elements,[1] which for a long time held mainly an academic interest, has recently yielded two breakthrough developments. The first was the oxidative coupling of the long-known Ge_9^{4-} cluster anions in an ionic liquid, resulting in a new crystalline germanium modification with the clathrate II structure,[2] which fulfilled the long-held dream of using homoatomic polyanions of post-transition elements as building blocks for new element structures. The implications of this discovery for semiconductor applications are self-evident. The second was the ascent of a new class of transition-metal-centered soluble cluster ions such as $[Ni@Pb_{10}]^{2-}$,[3] $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt),[4] and very recently $[Cu@Sn_9]^{3-}$ and $[Cu@Pb_9]^{3-}$.[5] These anions are usually synthesized from the binary Zintl phases $M^{I}_4Tt_9$ (M^{I} = Na–Cs; Tt = Ge, Sn, Pb) with an organometallic complex of the transition metal in a polar solvent, which is just as likely to result in anions containing two or even three metal atoms, such as $[Ni_2@Sn_{17}]^{4-}$,[6] $[Pt_2@Sn_{17}]^{4-}$,[7] $[Pd_2@Sn_{18}]^{4-}$,[8] and $[(Ni\text{-}Ni\text{-}Ni)@(Ge_9)_2]^{4-}$.[9] The term intermetalloid clusters was proposed to describe these endohedral Zintl ions.[10] They are exciting models for doped materials and, in analogy to the homoatomic polyanions, potential building blocks for cluster-assembled nanomaterials. The transition-metal atoms have closed-shell d^{10} configurations and do not change the electron count for the main-group-element cage; they serve as templates that stabilize larger cages such as icosahedra, which seem to be inaccessible as empty homoatomic cage anions of heavier Group 14 elements in the condensed phase.

All of these new intermetalloid clusters have one thing in common: their shape is deltahedral or at least derived from a deltahedron. The nine-atom cages are tricapped trigonal prisms, the ten-atom cages bicapped quadratic antiprisms, and the twelve-atom species are icosahedra (Figure 1), which lends additional credence to the long-held assumption that the Wade–Mingos formalism[11] should be applicable to ligand-free tetrel clusters.[12] Of course, it is known from NMR spectroscopy studies that in contrast to boranes and carboranes the polyhedral skeletons of these heavy-atom cages are highly flexible. Sn_9^{4-} [13] and $[Ni@Pb_{10}]^{2-}$ [3] show only a single resonance at room temperature, so that no hard and fast correlation between the shape of the anions and the electron count can be expected. The limitations of the analogy between polyhedral boranes and bare post-transition-element clusters has led to the recent proposal of an alternative approach, the so-called jellium model for spherical clusters.[14] Nevertheless, in spite of well-founded reservations, the beauty of a unified formalism for boranes and positively or negatively charged clusters of post-transition elements remains alluring, and the didactic value of the analogies is undeniable. Moreover, even when in clusters with two endohedral transition metal atoms the simple Wade–Mingos model has to fail, the tetrel skeleton still adopts a polyhedral shape with all triangular faces and with the vertices having as similar angles as possible, which is the very definition of a deltahedron. The magnificent deltahedron found for $[Pd_2@Ge_{18}]^{4-}$ [15] (Figure 2) as well as the (very flexible) structure of $[Pt_2@Sn_{17}]^{4-}$ [7] both bear witness to this trend. Consequently, deltahedra were what was to be expected for new endohedral Group 14 clusters.

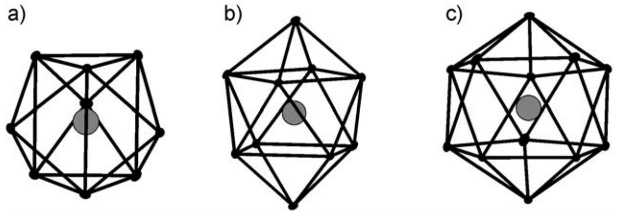

Figure 1. Deltahedral structures adopted by a) $[Cu@Sn_9]^{3-}$ (● Cu, ● Sn),[5] b) $[Ni@Pb_{10}]^{2-}$ (● Ni, ● Pb)[3] and c) $[Pd@Pb_{12}]^{2-}$ (● Pd, ● Pb).[4]

This expectation is one reason why the very regular pentagonal prismatic structure of $[Co@Ge_{10}]^{3-}$ reported by Wang et al.[16] comes as a major surprise (Figure 3): three

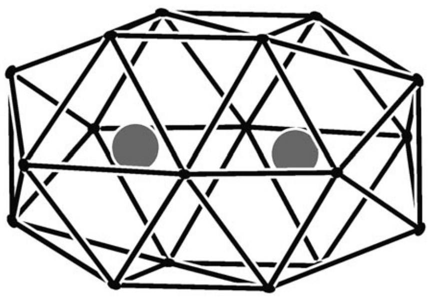

Figure 2. Deltahedral structure adopted by $[Pd_2@Ge_{18}]^{4-}$ (● Pd, ● Ge).[15]

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decidedly dissimilar angles at the vertices (108° and 2 × 90°), and not a single triangle in sight! The second reason why this intermetalloid cluster is remarkable is the transition metal inside the pentagonal prism. To date, only the late transition metals of Group 10 and copper could be successfully inserted into ligand-free non-carbon tetrel cages and isolated as bulk compounds, in spite of the claim that "most transition-metal atoms in the periodic table" should fit into cages like the icosahedral stannaspherene Sn_{12}^{2-}, which was characterized by photoelectron spectroscopy in the gas phase.[17] However, it has to be emphasized that gas-phase experiments set the pace for the development of endohedral tetrel cluster chemistry: in our case, $[Co@Ge_{10}]^{-}$ was discovered as early as 2001 by laser vaporization of Co/Ge mixtures.[18] The endohedral nature of the cluster was demonstrated by a double laser ablation technique, and the structure was calculated to be a bicapped quadratic antiprism. If the concept of the closed-shell character of the encapsulated transition-metal atoms holds true, then the reported cluster should consist of a Co^{-} ion inside a Ge_{10}^{2-} cage. This formulation is nicely supported by the natural charge of −1.05 calculated for Co by the authors.

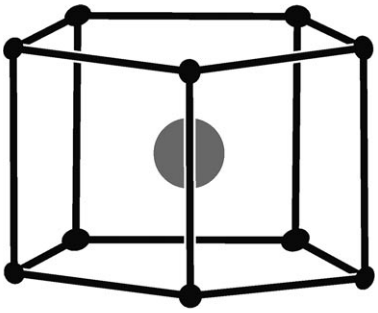

Figure 3. Pentagonal prismatic structure of $[Co@Ge_{10}]^{3-}$ (● Co, ● Ge).

Interestingly, practically simultaneously to the preparation of $[Co@Ge_{10}]^{3-}$, a detailed theoretical study on metal-centered ten-vertex germanium clusters was published, which included the isoelectronic species $[Ni@Ge_{10}]^{2-}$, $[Cu@Ge_{10}]^{-}$, and $[Zn@Ge_{10}]$.[19] For all of these, the lowest-energy structures were calculated to be the bicapped square antiprisms predicted by the Wade–Mingos rules, which had also resulted earlier for the empty Ge_{10}^{2-} cage.[20] The Fässler group repeated the calculations for $[Ni@Ge_{10}]^{2-}$ and Ge_{10}^{2-} with a slightly different basis set and confirmed the *closo* D_{4d} shape for these anions;[16] however, using the same methods, the experimentally observed prismatic structure with approximate D_{5h} point symmetry was calculated for $[Co@Ge_{10}]^{3-}$. The energetic difference between this minimum and the bicapped square antiprism is rather small (13.3 kcal mol^{-1}); still smaller is the difference for the inverted situation for $[Ni@Ge_{10}]^{2-}$, where the pentagonal prismatic shape lies only 5.33 kcal mol^{-1} above the D_{4d} minimum. Some kind of border seems to have been crossed when moving from Group 10 to Group 9 endohedral atoms, and the encapsulated transition-metal atom clearly is not as innocent a template as it was assumed to be from the earlier results.

As was pointed out above, insights into intermetalloid cluster chemistry of Group 14 elements emerge equally from gas-phase experiments, calculations, and synthesis in the condensed phase. In this light, the just recently published theoretical investigations on Ge_n clusters ($n = 9$–24) encapsulating hafnium atoms should be carefully considered. It is found that the dominant growth behavior of the $[Hf@Ge_n]$ clusters is based on pentagonal prisms, and that fullerene-like structures begin to emerge starting with $n = 14$.[21] Consequently, there is hope that $[Co@Ge_{10}]^{3-}$ will not remain a freak in intermetalloid germanium cluster chemistry but may be only the first of the nondeltahedral clusters to come.

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