Cluster Compounds

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$[Zn_9Bi_{11}]^{5-}$: A Ligand-Free Intermetalloid Cluster**

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One of the most important aspects of metal clusters is that they provide a window into the rather ill-defined area of chemistry that lies between isolated molecular species and solid-state compounds with extended structures.[1] Small, cage-like clusters have been relatively well studied and are found to generally follow established rules for electron counting and isolobal relationships.[2] Their structures and bonding are fairly well understood and can be rationalized within the context of these rules. However, this is not the case for large clusters with high nuclearities (more than 12 atoms) and dimensions beyond that of the nanometer. These species lack such a cohesive foundation, and furthermore, many of them seem to disobey traditional electron-counting rules, which ultimately makes the discussion of their structure and bonding very difficult. In addition, only a handful of such clusters have been structurally characterized, most of them limited to the field of precious-metal cluster chemistry.[1b] This scarcity is all the more valid for main-group-element species, for which the first example, $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$, was isolated by Schnöckel and co-workers only a few years ago.[3] These authors coined the term metalloid cluster for such species in which the metal–metal contacts in the cluster outnumber the metal–ligand contacts, and in which the cluster atoms exhibit close packing, as in bulk metals. More species have been discovered since, and the cluster chemistry of Group 13 has been enriched by the isolation of species with Al_n ($n = 7$, 12, 14, 50, 69) and Ga_m ($m = 9$, 10, 19, 22, 24, 26, 84) metal cores.[4,5]

Similarly, large metal-centered clusters of Group 14 elements have also been extensively studied in recent years. The synthetic approach towards these species involves reactions of nine-atom deltahedral clusters of Group 14 elements, known as Zintl ions, with various transition-metal complexes. Some of the species isolated by this route are: $[Ni(Ni@Ge_9)_2]^{4-}$,[6] $[Pd_2@Ge_{18}]^{4-}$,[7] $[Ni_2Sn_{17}]^{4-}$,[8] $[Ni@Pb_{10}]^{2-}$,[9] $[Pt@Pb_{12}]^{2-}$,[10] and a single cluster of a Group 15 element, $[As@Ni_{12}@As_{20}]^{3-}$.[11] These species are also metalloid clusters, although, as they involve more than one metal, they may be more appropriately referred to as intermetalloid

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clusters.[12] Nonetheless, the two types of atoms in each of these clusters have two very specific coordination environments; that is, one type of atom centers the cluster, while the other type makes up the cage. Herein, we report the synthesis and structure of a new 20-atom intermetalloid cluster, $[Zn_9Bi_{11}]^{5-}$, with extensive amalgamation of the two types of atoms, as in a true intermetallic compound.

The novel cluster was synthesized during an exploration of the reactivity of ethylenediamine (en) solutions of K_5Bi_4 towards various organometallic compounds, $ZnPh_2$ (Ph = phenyl) in this case, in the presence of 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (2,2,2-crypt). The K_5Bi_4 precursor contains tetrameric zigzag $[Bi_4]^{(4+\delta)-}$ oligomers,[13] but its ethylenediamine solutions exhibit double-bonded $[Bi{=}Bi]^{2-}$ dimers and $[Bi_4]^{2-}$ squares,[14,15] which can further fragment upon reaction with transition-metal complexes, as seen in $[Bi_3M_2(CO)_6]^{3-}$ (M = Cr, Mo).[16] A similar reaction carried out with $ZnPh_2$ resulted in the isolation of $[K(2,2,2\text{-crypt})]_5[Zn_9Bi_{11}]\cdot 2\,en\cdot tol$ (tol = toluene), which exhibits naked heterometallic $[Zn_9Bi_{11}]^{5-}$ clusters (Figure 1). Apparently, both phenyl groups at the zinc atoms were "replaced" in this case. This reaction is analogous to the previously studied reactions of deltahedral $[Ge_9]^{4-}$ clusters with EPh_3 (E = Sb, Bi) and $E'Ph_4$ (E′ = Ge, Sn), where one phenyl group is replaced by the cluster, yielding $[Ph_2E\text{-}Ge_9\text{-}EPh_2]^{2-}$ and $[Ph_3E'\text{-}Ge_9\text{-}E'Ph_3]^{2-}$, respectively.[17]

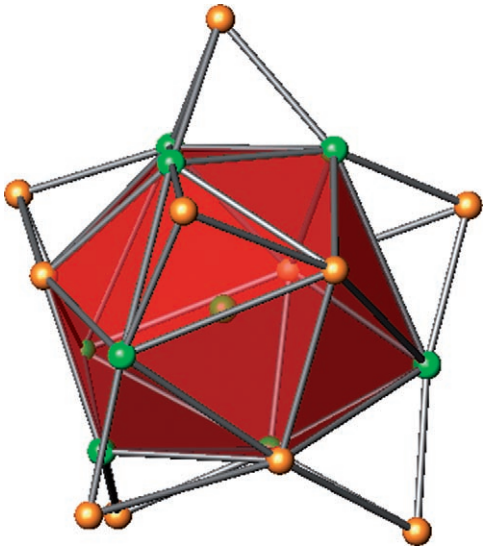

Figure 1. The $[Zn_9Bi_{11}]^{5-}$ cluster: a central zinc atom (green) within a Zn_8Bi_4 icosahedron (red) is capped by seven bismuth atoms (orange), that is, $[Zn@(Zn_8Bi_4)@Bi_7]^{5-}$. Interatomic distances [Å]: Zn_{cen}–Zn_{ico} 2.832(2)–3.594(3), Zn_{cen}–Bi_{ico} 2.822(2)–2.928(2), Zn_{ico}–Bi_{ico} 2.876(2)–3.755(2), Bi_{ico}–Bi_{ico} 3.2051(8), Zn_{ico}–Zn_{ico} 2.894(2)–3.762(2), Bi_{cap}–Zn_{ico} 2.598(1)–2.768(1), Bi_{cap}–Bi_{ico} 3.1072(8)–3.3121(9); the subscripts cen, ico, and cap denote cluster atoms in the central, icosahedral, and capping sites, respectively.

The ligand-free cluster has a central zinc atom which, as in numerous aluminum and gallium metalloid species,[18] is 12-coordinate in an icosahedral environment, albeit a distorted one in this case, owing to the very different atomic radii of zinc and bismuth. The icosahedron consists of eight zinc and four bismuth atoms, that is, Zn_8Bi_4. If not for one of the four bismuth atoms (in the bottom triangle of the icosahedron in Figure 1), it would have a pseudo-threefold axis (vertical in Figure 1 and perpendicular to the page in Figure 2a). Seven of the 20 triangular faces of the icosahedron are capped by bismuth atoms that form a second shell, and the formula of the cluster can be written as $[Zn@(Zn_8Bi_4)@Bi_7]^{5-}$. One of the capping bismuth atoms is along the imaginary threefold axis (top in Figure 1), while the other six are split into two sets of three atoms that are related by the imaginary threefold axis. This arrangement results in a pseudo-threefold axis for the entire cluster, as shown in Figure 2a.

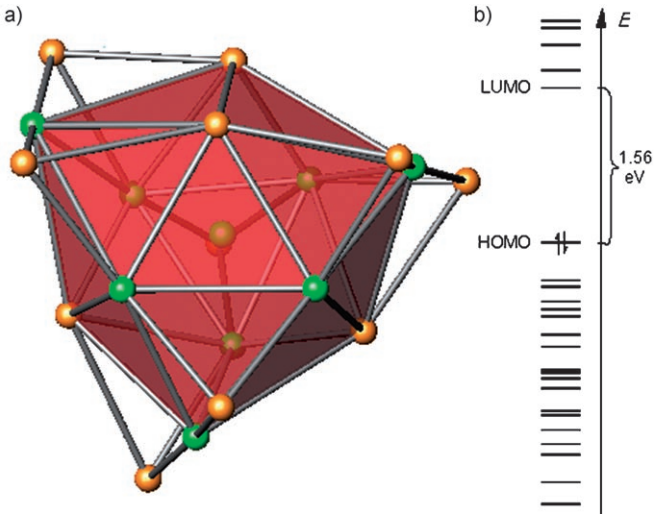

Figure 2. a) View of the $[Zn_9Bi_{11}]^{5-}$ cluster along the pseudo-threefold axis. b) Part of the molecular orbital diagram of $[Zn_9Bi_{11}]^{5-}$; the energy of the HOMO/LUMO gap is indicated.

The "packing" of the atoms in $[Zn_9Bi_{11}]^{5-}$ resembles the distorted cubic close packing (ccp) found in intermetallic compounds and alloys, as well as in some homoatomic metalloid clusters. There are no known zinc–bismuth binary intermetallic phases, which makes comparison of the structure and bonding of the cluster and with those of a bulk material impossible. To our knowledge, no molecular zinc–bismuth species have been reported either. There are, however, several ternary phases with formally anionic zinc–bismuth extended structures, such as $BaZnBi_2$,[19] $Ca_9Zn_4Bi_9$,[20] LiZnBi,[21] and $SrZnBi_2$.[22] The average Zn–Bi distance of 2.840 Å in these compounds compares well with the corresponding distances in $[Zn_9Bi_{11}]^{5-}$ (Figure 1).

Electronically, the Zn_8Bi_4 icosahedron is equivalent to an icosahedron made of 12 atoms of a Group 13 element. Formally, two atoms of the Group 12 element zinc (providing 2 electrons each; total of 4 electrons), and one atom of the Group 15 element bismuth (providing 5 electrons) average as three atoms of a Group 13 element (providing 3 electrons each; total of 9 electrons). Therefore, the Zn_8Bi_4 icosahedron is a heteroatomic version of the homoatomic Al_{12} and Ga_{12} icosahedra, both geometrically and electronically.

Density functional theory (DFT) calculations using the observed geometry and charge of the $[Zn_9Bi_{11}]^{5-}$ cluster

revealed a gap of 1.56 eV between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), with tightly packed molecular orbitals in both the full and empty manifolds (Figure 2b). This orbital distribution indicates a good stability for the cluster and suggests a relative inertness towards both oxidation and reduction. As previously mentioned, rationalization of the bonding and electronic requirements of the homoatomic metalloid clusters has been an elusive goal and an insurmountable obstacle in the majority of cases. The situation is not very different for the heteroatomic intermetalloid cluster $[Zn_9Bi_{11}]^{5-}$, and we can offer only a possible explanation to rationalize the bonding within this species. The bonding in deltahedral closo clusters is accomplished by $2n+2$ delocalized electrons, where n is the number of vertices,[2a] which is 12 in the case of an icosahedron. Furthermore, an additional 2 electrons per vertex are associated with either an exo bond or a lone pair. Thus, the total number of electrons needed for an icosahedron is 50, that is, $(2\times12+2)+2\times12$. The eight zinc and four bismuth atoms of the Zn_8Bi_4 icosahedron provide a total of $8\times2+4\times5=36$ electrons. An additional 2 electrons are provided by the central zinc atom, and 5 more electrons come from the charge of the cluster. This totals 43 electrons, which is 7 electrons short of 50. These 7 electrons must be provided by the seven capping bismuth atoms, which apparently, behave as one-electron ligands to the icosahedron. This hypothesis implies that each bismuth atom keeps its remaining 4 electrons in the form of two lone pairs. While this type of bonding may seem unusual, it is clear from the DFT calculations that this electron count corresponds to a very stable cluster.

The $[Zn_9Bi_{11}]^{5-}$ cluster should be viewed as a part of the small family of "molecular alloys" that have been recently synthesized by similar reactions of Zintl ions with transition-metal reagents.[6–11] This handful of novel species represent intermediates in the eventual generation of intermetallic and alloy-like precipitates. As such, these species can provide important insight into how metal atoms aggregate in solution to initially form metastable clusters, before the ultimate oxidation to form neutral nanoparticles and then bulk solids. The true intermetalloid character of $[Zn_9Bi_{11}]^{5-}$ is expressed in the extensive amalgamation of zinc and bismuth, as would be expected in an eventual zinc–bismuth alloy or intermetallic compound. Such clusters may provide a clue as to what a binary zinc–bismuth phase may look like. Their oxidation may actually lead to metastable intermetallic compounds that are otherwise inaccessible. The discovery of this and other similar species may help develop a greater understanding of this ever-expanding area of chemistry and may lay a stronger foundation for unifying views on the bonding and geometry of metalloid and intermetalloid clusters.

Experimental Section

All manipulations were carried out under an inert atmosphere using standard Schlenk-line and/or glove-box techniques. Ethylenediamine (Acros, 99%) was distilled over sodium metal and stored in a gas-tight ampoule under nitrogen. K_5Bi_4 was synthesized according to a reported procedure.[13] A stoichiometric mixture of the elements (K: 99+%, Strem; Bi: 99.998%, Alfa-Aesar) was heated at 700°C over 2 days, inside a sealed niobium container jacketed in an evacuated fused-silica ampoule. 2,2,2-crypt (Acros, 98%) and $ZnPh_2$ (Strem, 99%) were used as received.

$[K(2,2,2\text{-crypt})]_5[Zn_9Bi_{11}]\cdot2\,en\cdot tol$: K_5Bi_4 (144 mg, 0.139 mmol) and 2,2,2-crypt (242 mg, 0.643 mmol) were weighed out into a test tube inside a glove box and dissolved in ethylenediamine (approximately 3 mL). The resulting dark greenish-blue solution was stirred for 5 min, after which $ZnPh_2$ (36 mg, 0.163 mmol) was added. The reaction mixture was stirred for 2 h, filtered, and the filtrate layered with toluene to allow for crystallization. After several days, very thin black-green plates of $[K(2,2,2\text{-crypt})]_5[Zn_9Bi_{11}]\cdot2\,en\cdot tol$ (estimated yield 5–10%) were obtained, alongside a black amorphous precipitate.

Single-crystal X-ray diffraction data for $[K(2,2,2\text{-crypt})]_5[Zn_9Bi_{11}]\cdot2\,en\cdot tol$ were collected on a Bruker APEX-II diffractometer with a CCD area detector at 100 K with $Mo_{K\alpha}$ radiation. The crystal was selected under Paratone-N oil, mounted on a fiber, and positioned in the cold nitrogen stream on the diffractometer. The structure was solved and refined (on F^2) with the aid of the SHELXTL V6.12 package.[23] Crystal data: $M_r=5177.39$, $P2_1/c$, $a=31.0930(8)$, $b=27.5755(7)$, $c=17.3825(4)$ Å, $\beta=90.869(2)°$, $V=14902.1(6)$ Å^3, $Z=4$, $\rho_{calcd}=2.308$ g cm^{-3}, $\mu(Mo_{K\alpha})=14.557$ cm^{-1}, $R1/wR2=5.38/10.63\%$ for the observed data. CCDC 606635 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Single-point DFT calculations were performed on the cluster by employing the atomic positions elucidated by single-crystal X-ray diffraction. The Becke3-parameter hybrid functional[24] with Lee–Yang–Parr correlation[25] (B3LYP) was used in conjunction with the LanL2DZ basis set.[26] Computations were executed with the Gaussian 98 package, revision A.11.3,[27] on Notre Dame's "Bunch-o-Boxes" Beowulf cluster.

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