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Zintl Anions

# $[Zn_6Sn_3Bi_8]^{4-}$: Expanding the Intermetalloid Zintl Anion Concept to Ternary Systems**

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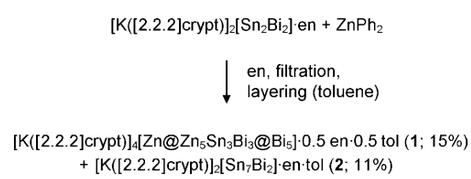
Since first reports by Joannis and Kraus[1] through the honorable work of Zintl in the 1930s[2] and first structural reports in the 1970s,[3] interest in compounds containing Zintl ions has not stopped even today, owing to their outstanding structural and electronic properties.[4] However, the size of the homoatomic molecular cages seems to be limited to nine in $[E_9]^{4-}$ (E = tetrel),[5] owing to the instability of larger deltahedral cavities.

The 21st century gave the research field a new dimension by the synthesis of intermetalloid Zintl anions with endohedral $d^{10}$ transition-metal atoms stabilizing a larger main-group-atom deltahedron (which sometimes contains additional transition-metal atoms).[6] Recent examples containing Group 13 (triel), 14 (tetrel), or 15 (pentel) elements are $[Cd@Tl_{12}]^{12-}$,[7] $[Cu@E_9]^{3-}$ (E = Sn, Pb),[8] $[Pt_2@Sn_{17}]^{4-}$,[9] $[Pd_2@E_{18}]^{4-}$ (E = Ge, Sn),[10] $[Ni(Ni@Ge_9)_2]^{4-}$,[11a] $[Zn_9Bi_{11}]^{5-}$,[11b] $[Ni_5Sb_{17}]^{4-}$,[12a] or $[As@Ni_{12}@As_{20}]^{3-}$.[12b] Very recently, $d^8$ and $d^9$ metal atoms in $[Fe@Ge_{10}]^{3-}$[13] and $[Co@Ge_{10}]^{3-}$[14] were also shown to be suitable interstitial atoms for nondeltahedral cages. Being interesting objects for the exploration of the bonding situation,[15] these anions also serve as models for doped metals and might be useful precursors for nanostructured intermetallic phases, as was realized with $[Ge_9]^{4-}$ in the formation of nanostructured Ge.[16]

Such compounds are usually prepared by treating solutions of homoatomic Zintl ions with transition-metal complexes, leading to fragmentation and rearrangement of the main-group cage incorporating the transition-metal atom or atoms, which is not yet well understood. Hence, this type of synthesis has to date been restricted to $[E_9]^{4-}$ (E = tetrel) or $[E_7]^{3-}$ cages (E = pentel) and $[Bi_4]^{5-}$ chains, whereas the smallest cages, that is, tetrahedral $[E_4]^{4-}$ or $[E_4]^{2-}$ (E = Ge, Sn)[17,18] have not yet been explored.

To contribute both to a bottom-up strategy for the formation of heterometallic and intermetalloid clusters from smaller precursors and to an expansion of the field to the unknown ternary M/14/15 systems, we are currently investigating reactions of tetrahedral Group 14/15 Zintl anions, based on our comprehensive experience in the reactivity of binary 14/16 anions.[19] The bismuth-substituted analogue of $[Sn_4]^{4-}$, $[Sn_2Bi_2]^{2-}$, exists both in the solid state as [K([2.2.2]crypt)]$_2$[$Sn_2Bi_2$]·en and in solution.[20,21] We have therefore chosen this species for preliminary investigations.

As a first result, we report the reaction with $ZnPh_2$ in 1,2-diaminoethane (en; Scheme 1) to yield [K([2.2.2]crypt)]$_4$[$Zn@Zn_5Sn_3Bi_3@Bi_5$]·0.5 en·0.5 tol (**1**; tol = toluene). Compound **1** is obtained as black crystals along with the crystalline starting material and brown crystals of [K([2.2.2]crypt)]$_2$[$Sn_7Bi_2$]·en·tol (**2**). Compound **2** contains a novel binary nine-atom cage. Both compounds were structurally characterized by single-crystal X-ray diffraction.[22,23]




***Scheme 1.*** Synthesis of **1** and **2** with yields of single-crystalline products. Note that the reactant also crystallizes upon layering with toluene.

Compound **1** contains an unprecedented ternary intermetalloid cluster anion, $[Zn@Zn_5Sn_3Bi_3@Bi_5]^{4-}$ (Figure 1), which may be described as a derivative of an 11-atom *nido* cluster: a pentagonal antiprism of a Bi-capped $Zn_5$ ring and an uncapped $Sn_3Bi_2$ ring (with statistical occupation of the atomic positions by 0.6 Sn and 0.4 Bi atoms each) enclose an endohedral Zn atom. Five additional Bi atoms cap the five $Zn_2E$ triangles ($E = Sn_{0.6}Bi_{0.4}$) between the two five-membered rings but are displaced from the centers of the triangles towards the Zn–Zn bonds.

Statistic disorder of main-group metal atoms is an intrinsic peculiarity of Sn/Bi Zintl anions and was also observed in the binary $[Sn_2Bi_2]^{2-}$ anion in the starting material.[21] Therefore, it is not surprising that both **1** and **2** exhibit Sn/Bi disorder. The compositions of **1** and **2** that represent the best crystallographic models have been confirmed by energy-dispersive X-ray spectroscopy (EDX) analyses (see the Supporting Information) and agree with the observation of diamagnetic compounds.

Quantum chemical investigations of the anion in **1** using DFT methods[24,25] further served to rationalize the atomic ratio. Interatomic distances were calculated for different atomic ratios, and those for the experimentally determined formula showed smallest deviations from the experimental values ($\Delta d_{av}$ 1.5–9.5 pm; largest $\Delta d_{av}$ for disordered Sn/Bi

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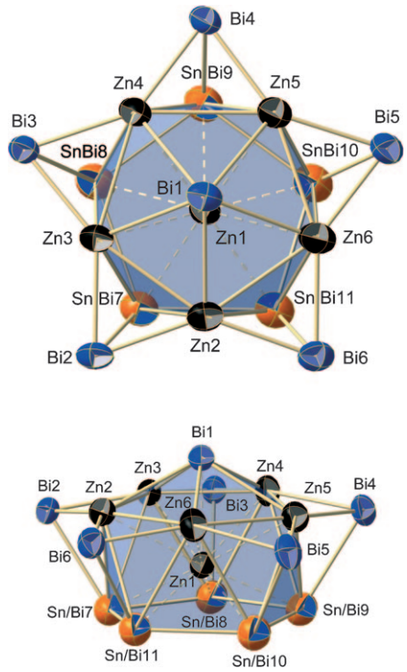


***Figure 1.*** Thermal ellipsoid plot (50% probability) of the $[Zn@Zn_5Sn_3Bi_3@Bi_5]^{4-}$ anion in **1** in top and side view. Orange/blue spheres denote $Sn_{0.6}Bi_{0.4}$ mixed sites. Selected distances [pm]: Zn1–Zn(2–6) 299.2(2)–312.8(2), Zn1–Sn/Bi(7–11) 291.50(15)–296.52(17), Zn1–Bi1 280.27(16), Zn(2–6)–Zn(2–6) 304.22(19)–313.1(2), Zn(2–6)–Sn/Bi(7–11) 320.98(19)–334.37(18), Zn(2–6)–Bi1 291.93(16)–297.2(2), Sn/Bi(7–11)–Sn/Bi(7–11) 305.81(10)–309.53(12), Zn(2–6)–Bi(2–6) 269.06(17)–270.51(16), Bi(2–6)–Sn/Bi(7–11) 299.47(11)–300.54(9).

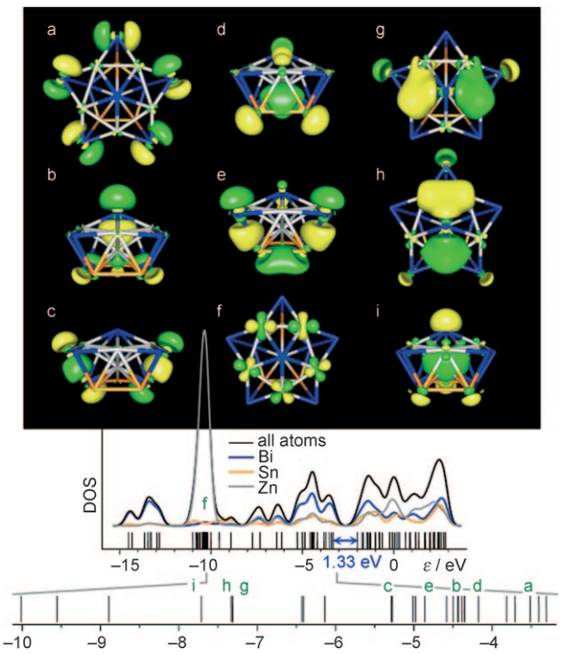


***Figure 2.*** Top: Electron density (above 0.2 $e^- Å^{-3}$) in selected molecular orbitals of **1** that represent typical MOs involving the different atom types (see text): a) HOMO−2, b) HOMO−8, c) HOMO−16, d) HOMO−5, e) HOMO−12, f) HOMO−28, g) p-type HOMO−20, h) p-type HOMO−21, i) s-type HOMO−22. Center: Density of states (DOS) of the calculated anion in **1** and energies $\varepsilon$ of the valence MOs around the HOMO–LUMO gap (1.33 eV). Bottom: enlargement of the MO scheme between HOMO (−3.309 eV) and HOMO−25 (−10.013 eV). Green letters refer to the MO pictures.

sites), whereas structures with more Bi or Sn atoms showed significant and unacceptable deviations and ranges of the calculated bond lengths ($\Delta d_{av} = -1.5$ to 40.4 or −17.7 to 30.3 pm) at the given, unambiguous charge. Additionally, relative energies of the two possible isomers with a $Sn_3Bi_2$ five-membered ring suggest a Sn-Bi-Sn-Sn-Bi arrangement to be favored by 11.1 kJ mol$^{-1}$ over the alternative Sn-Sn-Sn-Bi-Bi atomic sequence. The cocrystallization of **1** and **2** serves to keep the overall Sn:Bi ratio near 1:1, as provided in the starting material.

Analysis of the molecular orbitals (MOs) indicates that different characteristics of the bonding within the cluster result from the different types of atoms involved, as illustrated for typical MOs in Figure 2. Bismuth atomic orbitals (AOs) mainly contribute to MOs that host external, nonbonding electron density, mainly at Bi1–6 (Figure 2 a,b), or represent low delocalization (two- or three-center bonds, Figure 2 c). MOs with high AO contributions of Sn atoms show low to medium delocalization, in most cases in combination with Bi (and Zn) AOs (Figure 2 d,e). Of these, MOs with dominant main-group-metal p AO contributions are found between the HOMO energy level (−3.31 eV) and −10.01 eV, while MOs that are dominated by s AO contributions of Bi and Sn are lower in energy (−12.82 to −14.54 eV). Zinc 3d AOs are localized in 30 nonbonding MOs (Figure 2 f) in the energy range of −10.21 to −11.00 eV, whereas the six 4s AOs (with some Bi/Sn contribution) form six highly delocalized cluster orbitals at −5.27, −6.41 and −6.42, −7.31 and −7.32, (Figure 2 g,h), and −7.71 eV (Figure 2 i). As expected, an increasing number of nodal planes in these six MOs (zero to three) run through the cluster at increasing energy.

Both experimental and quantum chemical observations show that in spite of rather similar behavior of the two main-group metals within the deltahedral *nido* cluster, which may be attributed in part to their identical electronegativity (1.7),[26] only Bi serves as an additional, external ligand owing to its higher tendency for localization of electron density into nonbonding external MOs, which differentiates it clearly from the Group 14 metal.

For exploration of the charge distribution in **1**, natural charges were calculated by means of a natural population analysis (NPA).[27a] The result demonstrates a moderate polarity within the $Zn_6Sn_3Bi_2$ centered pentagonal antiprism, with natural charges of 0.67 (Zn1), 0.89 to 0.91 (Zn2–6), and −0.30 to −0.44 (Sn/Bi7–11). Thus the negative charge of the anion is predominantly localized at the capping Bi1 atom (−1.60), succeeded by the five external Bi atoms (−1.02 to −1.17).

The structure of the anion in **1** is related to that of the binary $[Zn_9Bi_{11}]^{5-}$ anion mentioned above,[11b] in which a Zn-centered $Zn_8Bi_4$ icosahedron is surrounded by seven addi-

  

tional face-capping Bi atoms. This arrangement, however, differs from the unique and very regular *nido* cluster in **1**. As in the binary cluster, and consistent with the charge localization within the highest occupied orbitals, the anion in **1** exhibits a distinct HOMO–LUMO gap (1.33 eV), which indicates a relatively high redox stability of the semimetallic, intermetalloid cage. So far, $[Zn_9Bi_{11}]^{5-}$ is the only intermetalloid Zintl anion that has allowed for a correlation of structural features with its cluster electron number according to Wade–Mingos rules. Following the same formalism, this is also possible for the anion in **1**: $2n+4$ electrons are expected to accomplish the bonding within an *n*-vertex *nido* cluster.[15a] With two extra electrons ("exo") per vertex, the total electron number needed for a ligand-free *nido* cage is $(2\times11+4)+(2\times11)=48$. The atoms of the $Zn_5Sn_3Bi_3$ cage provide $(5\times2)+(3\times4)+(3\times5)=37$ electrons, and the central zinc atom and the charge add another two and four electrons, respectively. The resulting sum of 43 is missing five electrons. As is the case for $[Zn_9Bi_{11}]^{5-}$, the Wade–Mingos rules can be satisfied by considering the five external Bi ligands as one-electron donors to the cage, which are not part of the deltahedral cage and hence do not necessarily need to participate as three-electron donors. However, although population analyses (both NPA and Mulliken analysis)[27b] give some evidence for this uncommon donor behavior,[28] the electron-counting procedure is still a formalism and does not serve to represent the complicated situation within this multinary, intermetalloid cluster.

The binary precursor clearly influences the formation of heteroatomic Zintl anions by providing a different number of cluster electrons than homoatomic Zintl anions, as outlined above. However, it is not yet possible to explain the formation of **1** in detail. A fresh solution of $[K([2.2.2]crypt)]_2[Sn_2Bi_2]\cdot en$ in 1,2-diaminoethane shows one signal in the $^{119}Sn$ NMR spectrum (−1650.5 ppm). However, crystallization of **2** within a few days indicates a slow transformation of $[Sn_2Bi_2]^{2-}$ into more stable anionic cages. Thus, we anticipate a fragmentation of the precursor in 1,2-diaminoethane, as reported for $K_5Bi_4$;[29] this process becomes even more complicated in the presence of transition-metal complexes.[30]

Ongoing studies employing different binary Group 14/15 anions will provide further insight into the formation and stability of multimetalloid Zintl anions.

## Experimental Section

General: All manipulations and reactions were performed in an argon or nitrogen atmosphere using standard Schlenk or glovebox techniques. 1,2-Diaminoethane (en; Aldrich, 99%) was distilled over $CaH_2$, and toluene (tol, technical grade) was distilled over sodium. Both were stored in argon-filled flasks. [2.2.2]crypt[20] (Merck) and $ZnPh_2$ (Arcor Organics, 95%) were dried in vacuum for 13 h. The precursor $[K([2.2.2]crypt)]_2[Sn_2Bi_2]\cdot en$ was prepared according to the literature procedure.[21]

Synthesis of **1** and **2**: $[K([2.2.2]crypt)]_2[Sn_2Bi_2]\cdot en$ (193 mg, 0.125 mmol) was dissolved in en (3 mL) to form a dark reddish-brown solution. Separately, $ZnPh_2$ (36 mg, 0.163 mmol) was suspended in en (1 mL). The yellow suspension was added to the dark reddish-brown solution while the mixture was stirred powerfully for 3 h. Then, the dark brown reaction solution was filtered through a standard glass frit and carefully layered with toluene (5 mL). After two days, black, wedge-shaped crystals of $[K([2.2.2]crypt)]_4[Zn_6Sn_3Bi_8]\cdot0.5\,en\cdot0.5\,tol$ (**1**) formed at the wall of the Schlenk tube in 15% yield (17 mg, $4.037\times10^{-6}$ mol). Compound **2** $[K([2.2.2]crypt)]_2[Sn_{6.96}Bi_{2.04}]\cdot en\cdot tol$ formed after one week in 11% yield (7 mg, $3.131\times10^{-6}$ mol). Semiquantitative energy-dispersive X-ray spectroscopy (EDX) analyses of several crystals confirmed the composition of **1** and **2** (see the Supporting Information). Crystalline starting material $[K([2.2.2]crypt)]_2[Sn_2Bi_2]\cdot en$ was also recovered.

Single-crystal X-ray diffraction: Data were collected on a Stoe IPDS 2T diffractometer at 100 K with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$). The structure was solved by direct methods and refined with full-matrix least squares against $F^2$ using SHELXS-97 and SHELXL-97.[23]

Quantum chemical methods: The DFT investigations[24] were undertaken with the program system TURBOMOLE[25] using the RIDFT program[31] with the Becke–Perdew 86 (BP86) functional[32] and the gridsize m3. Basis sets were of def2-TZVP quality (TZVP = triple zeta valence plus polarization).[33] Effective core potentials were used for Sn (ECP-28) and Bi atoms (ECP-60)[34] to consider relativistic corrections and to reduce the computational effort. The high negative charge was compensated for by employment of the COSMO model.[35] DOS values were obtained upon a Mulliken population analysis.[27b]

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[22] X-ray data for $C_{76.5}H_{152}N_9O_{24}K_4Zn_6Sn_3Bi_8$ (**1**): monoclinic, $P2_1/n$, $a = 15.442(3)$, $b = 28.506(6)$, $c = 27.937(6)$ Å, $\beta = 90.47(3)$, $V = 12297(4)$ Å$^3$, $Z = 4$, $R_1$ ($I > 2\sigma(I)$) = 0.0582, $wR_2$ (all data) = 0.1022, *GooF* (all data) 0.950, max. peak/hole 1.24/−2.42. X-ray data for $C_{45}H_{88}N_6O_{12}K_2Sn_{6.96}Bi_{2.04}$ (**2**): hexagonal, $P6_3/m$, $a = 12.1635(17)$, $c = 26.336(5)$ Å, $V = 3374.4(10)$ Å$^3$, $Z = 2$, $R_1$ ($I > 2\sigma(I)$) = 0.0562, $wR_2$ (all data) = 0.1451, GooF (all data) = 1.112, max peak/hole 2.09/−1.11. For more details, see the Supporting Information. CCDC 733155 (**1**) and 733156 (**2**) contain 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.

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