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Tri-metallic deltahedral Zintl ions: experimental and theoretical studies of the novel dimer $[(Sn_6Ge_2Bi)_2]^{4-}$†

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We report the synthesis, characterization, and computational rationalization of the first trimetallic deltahedral Zintl ions. The novel nine-atom clusters were structurally characterized as dimers of $[(Sn_6Ge_2Bi)_2]^{4-}$ with Ge–Ge intercluster bonds. They are synthesized either by reacting bimetallic clusters $(Sn_{9-x}Ge_x)^{4-}$ with $BiPh_3$ or by direct extraction from precursors with nominal composition "$K_4Ge_4Sn_4Bi$".

The deltahedral Zintl ions have been attracting renewed attention in recent years as it has been realized that they have unique and potentially very rich chemistry.[1] The list of different types of reactions is growing rapidly and now includes their coupling into oligo- and polymers,[2] functionalization with organic[3] and organometallic groups,[4] centering with transition-metal atoms and subsequent fusion of clusters,[5] *etc*. The most recent addition to this list was their ability to exchange cluster atoms for exo-bonded atoms. For example, the reaction of Ge_9^{4-} clusters with $SbPh_3$ or $BiPh_3$ at higher temperatures produces the "doped" monomers of $(Sb_2Ge_7)^{2-}$ and dimers of $[(BiGe_8)_2]^{4-}$ with Ge–Ge intercluster bonds.[6] These new deltahedral bi-metallic anions join a very short list of such species, namely $[Sn_2Bi_2]^{2-}$, $[Sn_2Sb_2]^{2-}$, $[Pb_2Sb_2]^{2-}$, $[InBi_3]^{2-}$, $[GaBi_3]^{2-}$, $[In_4Bi_5]^{3-}$, $[TlSn_9]^{3-}$, and $[Tl_2Te_2]^{2-}$.[7] In addition, even fewer tri-metallic, although non-deltahedral, anions are known: $[Zn_6Sn_3Bi_8]^{3-}$, $[Eu@Sn_6Bi_8]^{4-}$, $[Pd_3Sn_8Bi_6]^{4-}$ and $[Ni_2Sn_7Bi_3]^{3-}$.[8] Such heteroatomic species have garnered much interest as potential precursors towards heteroatomic bulk materials, thin films, and zero- and one-dimensional nanoformations.[9–11]

The successful "n-doping" of Ge_9-clusters with Sb and Bi prompted similar studies with Sn_9^{4-}. However, none of the analogous reactions with $SbPh_3$ and $BiPh_3$ were successful; they all resulted in formation of a tin mirror on the walls of the flasks. At the same time, the reaction with $BiPh_3$ produced crystals containing the known Bi_4^{2-} squares indicating that the negatively charged tin in Sn_9^{4-} is more reducing than the negatively charged bismuth in Bi_4^{2-}. Next, we attempted a

strategy used in the recent synthesis of Ni-centered Sn_9-clusters, namely direct extraction of the clusters from a ternary precursor with appropriate composition, "K_4Sn_9Ni" in that case.[5m] Thus, a precursor with nominal composition "K_4Sn_8Bi" was synthesized and then dissolved in ethylenediamine. Unfortunately, the only heteroatomic species were the well-known and extensively exploited tetrahedral $[Sn_2Bi_2]^{2-}$ and $[SnBi_3]^-$ (based on electrospray mass spectrometry).[7a] At the same time, the Ge-analogue "K_4Ge_8Bi" did not produce any mixed-atom anions, thus behaving exactly as the corresponding "K_4Ge_9Ni" precursor.[5m] All this led to the idea to combine the two precursors into one and to eventually extract nine-atom tri-metallic species by avoiding the otherwise stable bimetallic anions $[Sn_2Bi_2]^{2-}$ and $[SnBi_3]^-$. This resulted in the extraction of the first deltahedral tri-metallic Zintl ions $[Sn_6Ge_2Bi]^{3-}$ from a quaternary precursor with a nominal composition "$K_4Sn_4Ge_4Bi$". They were structurally characterized in a dimer of $[(Sn_6Ge_2Bi)_2]^{4-}$ with a Ge–Ge intercluster bond (Fig. 1). It should be pointed out that the three pairs of elements Ge–Sn, Bi–Ge, and Bi–Sn are immiscible in the bulk and do not form solid solutions (the corresponding ternary phase diagram is not available).[12] The reproducible synthesis of the title tri-metallic ion with the three elements already bonded to each other provides a potential precursor for metastable heteroatomic bulk phases of these three elements.

The electrospray mass spectrum of the ethylenediamine solution of the precursor "$K_4Sn_4Ge_4Bi$" showed the presence of all possible nine-atom clusters with one bismuth atom, *i.e.* $[Sn_{8-n}Ge_nBi]^{3-}$ for $n = 0$–8, and a couple of combinations
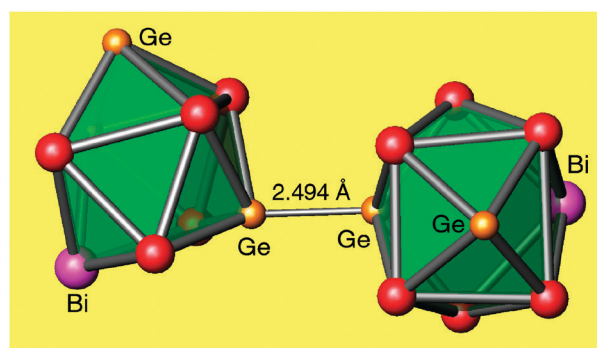
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Fig. 1 The trimetallic dimer $[(Sn_6Ge_2Bi)_2]^{4-}$ with a normal 2-center–2-electron Ge–Ge intercluster bond (Sn-red, Ge-orange, Bi-purple).

with two bismuth atoms (figure in ESI†). Upon layering with toluene containing 2,2,2-crypt, the solution produced crystals of $[K(2,2,2\text{-crypt})]_4[(Sn_6Ge_2Bi)_2]\cdot1.5en$ after a few weeks.‡ The dimer is made of identical but crystallographically different clusters that can be viewed either as distorted tricapped trigonal prisms or monocapped square antiprisms. In the former, the prism in each cluster is made of the six tin atoms, while the two Ge- and one Bi-atoms cap the three rectangular faces of the prism (in Fig. 1 the 3-fold axis in the left-hand cluster points at the reader while it is vertical in the right-hand cluster). Viewed as a monocapped square antiprism, the open square is made of the exo-bonded germanium and the one bismuth and two tin atoms. The second Ge-atom is capping the opposite square. Overall, the two clusters are close to being perpendicular to each other with respect to the intercluster bond. The latter is 2.494(2) Å and compares well with the Ge–Ge intercluster bonds in the known dimers $[(Ge_9)_2]^{6-}$, $[(SbGe_8)_2]^{4-}$, and $[(BiGe_8)_2]^{4-}$ with distances of 2.488(2), 2.487(2), and 2.569(3) Å, respectively.[2a,6]

The clusters do not show any compositional disorder, and the reason for this is most likely the existence of an exo-bond which, as seen in previous instances, "orients" the clusters and "pins" the various atoms in specific positions.[3g,5m,6] As a result of this, the refined thermal ellipsoids of the cluster atoms are very well behaved (figure in ESI†) and the distances within the clusters are very distinct at the different atom types. Thus, those around the two Ge-atoms are in the narrow range of 2.670(2)–2.801(2) Å and are significantly shorter than the distances at the Bi-vertex, 2.948(2)–3.018(1) Å. The range of Sn–Sn distances is significantly wider, 2.865(2)–3.347(2) Å, because of the presence of both 4- and 5-connected vertices.

The discovery of the unprecedented tri-metallic deltahedral cluster instigated further attempts for its synthesis by other methods. The fact that the ES-MS showed clusters with a bismuth atom and varying Sn/Ge ratios suggested that it might be possible to replace an atom in the bi-metallic nine-atom Sn/Ge clusters with a bismuth atom by a reaction with $BiPh_3$ in analogy with the same exchange in homoatomic germanium clusters.[6] Thus, $(Sn_{9-x}Ge_x)^{4-}$ clusters were first extracted in ethylenediamine from a precursor of nominal composition $K_4Ge_{4.5}Sn_{4.5}$ and were then reacted with excess of $BiPh_3$. The ES-MS of the reaction (figure in ESI†) was virtually identical to the one from the dissolved aforementioned precursor $K_4Sn_4Ge_4Bi$. Furthermore, while the Bi-for-Ge exchange in Ge_9-clusters occurs at higher temperatures only, the current reaction works equally well at room temperature. Upon layering with toluene and 2,2,2-crypt, the reaction solution produced exactly the same crystalline compound $[K(2,2,2\text{-crypt})]_4[(Sn_6Ge_2Bi)_2]\cdot1.5en$ as obtained from the direct precursor solution.§

The new dimer is isoelectronic with the known homo- and hetero-atomic dimers $[(Ge_9)_2]^{6-,2a}$ and $[(EGe_8)_2]^{4-}$ (E = Sb, Bi),[6] respectively. The Sb- and Bi-atoms in all three heteroatomic species are found at one and the same position, namely diagonally across from the exo-bonded atom in the open square of the monocapped square antiprism. Furthermore, the positioning and bonding of the two germanium atoms in $[(Sn_6Ge_2Bi)_2]^{4-}$ are exactly the same as in the previously characterized $[(Sn_7Ge_2)\text{–HC}{=}\text{CHPh}]^{3-,3g}$ where one of them

is exo-bonded while the other one is naked. The naked Ge-atom is the capping atom of the monocapped square antiprism while the exo-bonded Ge-atom is part of the open square. In addition, the exo-bonded Ge-atoms in $[(Sn_8Ge)\text{–CH}{=}\text{CH}_2]^{3-}$ and $[(Sn_8Ge)\text{–CH}{=}\text{CH}(CH_2)_2]^{3-}$ are also found at exactly that same position.[3g] Lastly, the two substituents in $[CH_2{=}\text{CH–}(Sn_7Ge_2)\text{–CH}{=}\text{CH}_2]^{2-}$ are bonded to the two germanium atoms which, in this case, are diagonally positioned within the uncapped square of the prism.[3g]

Relativistic DFT calculations,[13] taking into account both scalar and spin–orbit effects,[14] were performed on a monomer of $[Sn_6Ge_2Bi]^{3-}$, the dimer $[(Sn_6Ge_2Bi)_2]^{4-}$, and a hypothetical vinyl-substituted monomer of $[(Sn_6Ge_2Bi)\text{–CH}{=}\text{CH}_2]^{2-}$. It should be noted that the calculations were carried out without prior knowledge of the shape of the cluster, the location of the different atoms, and the nature and location of the exo-bond in the dimer. Explored first was the potential energy surface (PES) based on the 250 possible conformers of the nine-atom trimetallic cluster $[Sn_6Ge_2Bi]^{3-}$ generated by the different possible positioning of the Sn, Ge, and Bi atoms. Each starting geometry was then optimized without any symmetry restrains, and the nature of every stationary point on PES was characterized by the analytical second derivatives of the potential energy. Four low-energy isomers were found for the preferred conformations (Fig. 2). The isomer at the global minimum turned out to be exactly the observed one where a trigonal prism of six tin-atoms is capped by two germanium and one bismuth atoms. This validated further the accuracy of the structural refinement in terms of atom assignments, and all subsequent calculations were carried out using the global minimum conformation.

Next, the exo-bond in the dimer was simulated by a bond to a vinyl group in a hypothetical $[(Sn_6Ge_2Bi)\text{–CH}{=}\text{CH}_2]^{2-}$. The purpose was to identify the nature and position of the exo-bonded atom and predict the nature of eventual organic functionalization of these tri-metallic clusters. The results indicated that a cluster with and exo-bonded Ge atom, i.e. with a bond Ge–CH=CH$_2$, is more stable than those with exo-bonded Sn and Bi atoms by 14.72 and 27.63 kcal mol^{-1}, respectively.

Lastly, evaluated theoretically were the various exo-bonding schemes between the monomers in the dimer. The calculations indicated and confirmed that the isomer with a Ge–Ge exo-bond (calculated at 2.530 Å) is the most stable. It is more stable by 6.46 kcal mol^{-1} than the next in stability which happens to be with a Ge–Sn external bond (Table S, ESI†).

In summary, we have synthesized the first tri-metallic deltahedral ion and a potential precursor towards otherwise inaccessible ternary solid phases. The ions can be produced by
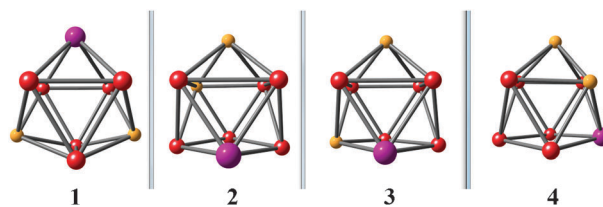
Fig. 2 The four shapes corresponding to energy minima from the relativistic DFT calculations (Sn-red, Ge-orange, Bi-purple). The global minimum corresponds to structure **1**, while **2**, **3**, and **4** are higher in energy by 1.00, 1.11, and 1.35 kcal mol^{-1}, respectively.

two methods, namely by treatment of the known bimetallic clusters $[Sn_{9-x}Ge_x]^{4-}$ with $BiPh_3$ or by direct extraction from the corresponding quaternary intermetallic precursor "$K_4Ge_4Sn_4Bi$". Both methods are reproducible with reasonable yields. The relativistic DFT calculations confirmed the shape of the monomer, the positions of the different types of atoms, and the preferred position of the exo-bond in the dimers.

Notes and references

‡ All manipulations were carried out under a nitrogen atmosphere using standard glovebox techniques. *Synthesis of [K(2,2,2-crypt)]$_4$[(Sn$_6$Ge$_2$Bi)$_2$]·1.5en. Method A:* 3 ml of ethylenediamine were added to 0.1 mmol (0.113 g) of a precursor with nominal composition "$K_4Ge_4Sn_4Bi$" and stirred for 10 minutes at room temperature resulting in a dark red-brown solution. *Method B:* 3 ml of ethylenediamine were added to 0.1 mmol (0.102 g) of a precursor with nominal composition "$K_4Ge_{4.5}Sn_{4.5}$" and stirred for 10 minutes at room temperature resulting in a dark red solution. Two- to three-fold excess of triphenylbismuth (0.3 mmol, 0.105 g) was then added into the reaction and continued stirring for 30 minutes to an hour at room temperature, upon which the reaction turns brownish-green. The reaction is then sonicated or gently heated (75 °C) for 3 days. *Methods A and B:* the resulting solutions were centrifuged for 15 minutes and filtered *via* a glass fiber pipette. Aliquots of this solution were used for crystallization by layering with a solution of 2,2,2-crypt (0.293 mmol, 0.11 g) dissolved in 8 ml of toluene. Purple blocks crystallized after a few weeks (30%).
§ *Crystallographic data for [K(2,2,2-crypt)]$_4$[(Sn$_6$Ge$_2$Bi)$_2$]·1.5en:* $P2_1/c$, $a = 15.8044(7)$, $b = 27.0221(11)$, $c = 28.4067(12)$ Å, $\beta = 94.993(1)°$, $V = 12085.6(9)$ Å^3, $T = 100(2)$ K, $Z = 4$, 43 601 reflections collected, 15 352 independent reflections, $R_1 = 0.0598$ (9171 observed data) and w$R_2 = 0.1630$ (all data). CCDC 865273.

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