Cluster Compounds

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$\{[CuSn_5Sb_3]^{2-}\}_2$: A Dimer of Inhomogeneous Superatoms

Robert J. Wilson, Lies Broeckaert, Fabian Spitzer, Florian Weigend, and Stefanie Dehnen**

Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 75th birthday

Abstract: *Reaction of the binary Zintl anion* $(Sn_2Sb_2)^{2-}$ *with the β-diketiminato complex* $[LCu(NCMe)]$ *(L = nacnac =* $[(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH]^-$*) in ethylenediamine or DMF affords the ternary cluster dimer* $\{[CuSn_5Sb_3]^{2-}\}_2$ *(**1**) as its* $[K(crypt\text{-}222)]^+$ *salt. The chemical formulation of **1** is supported by energy-dispersive X-ray spectroscopy (EDX) and quantum chemical calculations. Each monomeric part of the dimer represents a trimetallic "*$[CuSn_5Sb_3]^{2-}$*" cluster, with an architecture in between a tricapped trigonal prism and a capped square antiprism. As shown by quantum chemical investigations, the presence of Sb atoms and, in particular, of Cu atoms in the cluster skeleton makes the monomeric unit behave like an inhomogeneous superatom, which clearly prefers to dimerize, thereby producing a relatively short, yet virtually non-bonding Cu···Cu distance.*

The formation, characterization, and modelling of all-metal clusters has been a field of great attraction and demand for spectroscopists and theorists over the past three decades, as such clusters represent excellent examples of superatom systems.[1] Isolation and characterization of such clusters in bulk remains a challenge for synthetic chemists. Progress towards this end has been helped by the realization of a versatile synthetic route to heterometallic and intermetalloid cluster anions by reaction of Zintl anions with suitable transition-metal complexes.[2] The most commonly used Zintl ion precursors in these reactions are the homoatomic cluster anions, Tt_9^{4-} (Tt = Ge, Sn, Pb), and Pn_7^{3-} (Pn = P, As, Sb).[3] Our group has investigated the space between these precursors by reacting the tetrahedral, binary group 14/15 Zintl ions, $(Tt_2Bi_2)^{2-}$ (Tt = Sn, Pb), with organometallic transition-metal and lanthanide complexes. This has proved to be an efficient strategy of accessing intermetalloid clusters with different structures, due to alterations in charge and electron count that are intermediate between those of the homoatomic examples including Group 14 or Group 15 elements.[4]

Most of our studies in the meantime have addressed elemental combinations including bismuth atoms, namely Sn/Bi or Pb/Bi. While the Pb/Bi combination is advantageous with respect to solubility and yields, as it represents a *pseudo*-homoatomic situation, it encounters the problem of very high sensitivity to ambient conditions including daylight. The structure of $[K(crypt\text{-}222)]_2(Sn_2Sb_2)\cdot en$ (**A**; en = 1,2-diaminoethane), containing the lighter homologue, was previously published, but its chemistry was never explored.[5] After having optimized the synthesis of **A** towards reasonable yields,[6] and upon noting that it is well soluble in en and dimethylformamide (DMF), we are currently studying its reactivity. As a first result, we report reactions of this precursor salt towards the β-diketiminato Cu^I source $[LCu(NCMe)]$ (**B**; L = nacnac = $[(N(C_6H_3{}^iPr_2\text{-}2,6)C(Me))_2CH]^-$).

Organometallic compounds of Cu^I react with homoatomic Group 14 or 15 Zintl ions to form endohedral intermetalloid clusters and coordination compounds. The most investigated of these complexes is mesitylcopper(I) (CuMes), which reacts with Tt_9^{4-} (Tt = Sn, Pb) in DMF to form the endohedral intermetalloid clusters, $[Cu@Tt_9]^{3-}$.[7] The same precursor, when reacted in en with the Group 15 Zintl ions Pn_7^{3-} (Pn = P, As), is again liberated of its ligands to yield a dimeric copper bridged structure, $[Cu_2(Pn_7)_2]^{4-}$.[8] In liquid ammonia, CuMes may also coordinate and stabilize the small and highly charged Group 14 Zintl ions, Si_4^{4-}, $(Si_{4-x}Ge_x)^{4-}$, and Ge_4^{4-}, affording the clusters, $[MesCu\text{-}Tt_4\text{-}CuMes]^{4-}$ (Tt = Si, Ge).[9] The copper(I) complex $[CuCl(PR_3)]$ (R = Cy, ^iPr) reacts with Ge_9^{4-} in DMF and NH_3 to afford $[Cu(\eta^4\text{-}Ge_9)(PR_3)]^{3-}$, in NH_3 additionally $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$.[10]

The complex $[LCu(NCMe)]$ (**B**) has recently been demonstrated to stabilize intact Pn_4 moieties (Pn = P, As).[11] Owing to the fact that $(Sn_2Sb_2)^{2-}$ is isoelectronic and isostructural with Pn_4, we presumed that formation of a coordination complex was a plausible outcome of a reaction between **A** and **B**. Alternatively, under the basic conditions in which most Zintl-ion chemistry is carried out, **B** could serve as a clean source of Cu^I by elimination of the monoanionic β-diketiminato ligand, L. Because of this versatility, **B** was determined to be an excellent test case for the reactivity of **A**.

These reactions have afforded the first ligand-free ternary Zintl cluster of the elemental combination M/Sn/Sb,

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$\{[CuSn_5Sb_3]^{2-}\}_2$ in the salt $[K(crypt\text{-}222)]_4[CuSn_5Sb_3]_2{\cdot}n\,solv$ (**1**·*n* solv; *n* solv = 3 en, 2 tol).[12] Herein we report on the synthesis, characterization, and properties of **1**, which was explored by means of experimental and theoretical studies, namely X-ray diffraction, energy-dispersive X-ray (EDX) spectroscopy, electrospray ionization (ESI) mass spectrometry, and quantum chemical calculations using density functional theory (DFT) methods.

The synthesis of **1** can be accomplished by direct reaction of equimolar quantities of **A** with **B** in en or in DMF (for details, see the Supporting Information). The yields of the two reactions vary significantly: **1**·3 en crystallizes in only trace yields from en, while **1**·2 tol is formed in a measurable yield from DMF (ca. 10% crystalline) along with a black/brown amorphous solid.

Compound **1**·3 en crystallizes from en in the monoclinic space group $P2_1/c$, and **1**·2 tol crystallizes from DMF in the triclinic space group $P\bar{1}$, with $^1/_2$ and 1 equivalent of the anion in the asymmetric units, respectively.[13] In both structures, the anion is located on a crystallographic inversion center and may be viewed as two ternary, 9-atomic "$[CuSn_5Sb_3]^{2-}$" cluster subunits being linked by a total of four Sn–Cu contacts (Figure 1). The elemental composition of compound **1** was confirmed by means of EDX analyses (Table S3).

As Sn and Sb atoms are indistinguishable in single-crystal X-ray diffraction, we performed DFT calculations and first-order perturbation theory calculations (with the difference in nuclear charges as perturbation parameter) within the program system TURBOMOLE (for calculation details see the Supporting Information).[15] The assignment of atoms shown in Figure 1 accords with the lowest energy assignment of the two atom types (25 kJ mol^{-1} lower in energy than the second best isomer; Figure S20 in the Supporting information).

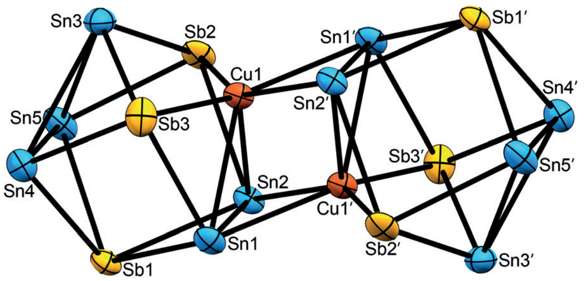

Figure 1. Structure of the ternary intermetalloid anion in **1**, shown for the example of **1**·3 en, with thermal ellipsoids set at 50%. Note that the X-ray experiment yields a statistical distribution of Sn and Sb atoms in the ratio that was determined by EDX analysis. The assignment shown is in accord with the result of the DFT calculations (see text). The structures of both **1**·3 en and **1**·2 tol including cations are in the Supporting Information (Figures S1–S2). The structural parameters for the anions in both structures are similar (Table S2). Interatomic distances for **1**·3en [Å]: Cu1⋯Cu1′ 2.563(3), Cu1-Sn(1,2) 2.855(2), 2.860(2), Cu1′-Sn(1,2) 2.789(2), 2.753(2), Cu1-Sn3 2.961(2), Cu1-Sb(2,3) 2.619(2), 2.641(2), Sn1-Sn2 3.028(1), Sn3-Sn(4,5) 3.101(1), 3.102(1), Sn4-Sn5 3.006(1), Sn(1,2)-Sb1 2.980(1), 2.991(1), Sn(4,5)-Sb1 2.942(1), 2.945(1), Sn(1,2)-Sb(3,2) 2.866(1), 2.889(1), Sb(2,3)-Sn3 2.888(1), 2.882(1), Sn(4,5)-Sb(3,2) 2.919(1), 2.907(1).[14]

According to comprehensive quantum chemical studies (see below), we do not consider the Cu⋯Cu contact in **1** (2.56(2) Å av.) to be a true bond, despite being shorter than the sum of atomic radii (Cu atomic radius: 1.35 Å)[16] and the CCDC average (2.72(19) Å).[17] This is not necessarily exceptional, as the atomic radii are taken from metal structures, arrangements with significantly higher coordination numbers, and the CCDC average also includes structures with higher coordination numbers. The distance is in fact 0.11 Å longer than that of a related Group 15 cluster, $[Cu_2(As_7)_2]^{4-}$ (2.445(2) Å),[8] in which the Cu atoms are not part of the cluster skeleton.

All the Cu–Sn and Cu–Sb distances are significantly larger than typical Cu–Sn or Cu–Sb single bonds (c.f. 2.60(2) Å in $[(Me_3P)_3CuSnCl_3]$[18] and 2.554(9) Å in $[ClCu(SbPh_3)_3]$[19]), and the Cu–Sn contacts are also longer than those in the endohedral complex $[Cu@Sn_9]^{3-}$ (2.6103(7)–2.7004(7) Å).[7] Hence, the bonds that link the two subunits have to be considered as being relatively weak, which already indicates multicenter bonding in agreement with our quantum chemical analyses. Still, the Cu–Sb contacts are shorter than those in $[(o\text{-}(^iPr_2P)C_6H_4)_3SbCu_3(\mu_2\text{-}Cl)_3]$ (2.80(7) Å av.), in which an Sb atom is bonded to a Cu_3 unit in a delocalized manner.[20] In addition, the anion in **1** also contains an even longer contact between Sn3 and Cu1 (2.94(5) Å av.)—longer than the sum of the atomic radii (2.8 Å)[16]—which may not be fully neglected as Cu1 is notably shifted out of a central position above the Sb3-Sn1-Sn2-Sb2 face towards a central position above the slightly folded pentagonal face Sb3-Sn1-Sn2-Sb2-Sn3.

The Sn–Sn bond lengths are 3.06(5) Å on average, which is a little longer than the average distance within the simple 9-atom cage $Sn_9{}^{4-}$ in $[Na(crypt\text{-}222)]_4(Sn_9)$ (2.928(6)–3.308(5) Å; mean value 3.02(12) Å),[21] but within a smaller range.

The Sn–Sb bond lengths (2.92(4) Å av.) do not deviate significantly from the values of the only two Sn/Sb Zintl ions, $(Sn_2Sb_2)^{2-}$ and $[Sn_2Sb_5(ZnPh)_2]^{3-}$, which have average Sn–Sb bond lengths of 2.874(15) and 2.90(6) Å respectively.[5] The only other compound containing an Sn–Sb bond, $[(Me_3Sn)_2Sb]_2$, has an average Sn–Sb bond length of 2.797(6) Å,[22] shorter than that in **1**, as would be expected for an electron-precise compound.

Several compounds exist in which a single metal atom is coordinated by two homoatomic Zintl ions including the Group 14 examples, $_\infty[HgGe_9]^{2-}$,[23] $[Cu(\eta^4\text{-}Ge_9)(\eta^1\text{-}Ge_9)]^{7-}$,[10] and $[In(Ge_9)_2]^{5-}$,[24] and the Group 15 examples, $[M(Pn_7)_2]^{4-}$ (M = Zn, Cd, In; Pn = P, As),[8,25] and $[Fe(HP_7)_2]^{2-}$.[26] In $[Ag(Sn_9\text{–}Sn_9)]^{5-}$,[27] the Sn_9 cages are additionally connected upon oxidative coupling. There are also known compounds in which diatomic and triatomic transition metal units are stabilized by Zintl ion coordination, such as $[Au_3(Ge_9)_2]^{5-}$ and $[Cd_2(Pb_9)_2]^{6-}$,[28] for Group 14, and $[M_2As_{14}]^{4-}$ (M = Pd, Au),[29] $[Cu_2(Pn_7)_2]^{4-}$ (Pn = P, As),[8] $[M_2(HP_7)_2]^{2-}$ (Ag, Au),[30] and $[Sb_3Au_3Sb_3]^{3-}$,[31] as examples for Group 15. In the case of **1**, however, there is virtually no Cu–Cu bond. Thus it should not be seen as a Cu_2 dumbbell stabilized between two clusters, but rather as two Cu-containing 9-atom cages connected via Cu–Sn interactions, as outlined below.

To understand the bonding situation in the anion in **1**, further quantum chemical investigations were carried out. It is instructive to first view the hypothetical half of the cluster, "$[CuSn_5Sb_3]^{2-}$". If the Cu atom contributes one electron, each Sn four electrons, and each Sb five electrons, the total valence electron count is $1+(5\times4)+(3\times5)+2=38$ electrons. This is two valence electrons less than the established and stable Tt_9^{4-} (Tt = Si…Pb) *nido* cluster, despite "$[CuSn_5Sb_3]^{2-}$" having the same number of skeletal electrons (22) as Tt_9^{4-}. This complicates a consideration according to the Wade–Mingos rules.[32]

For a more comprehensive view of the bonding in the anion in **1**, one may therefore consider the cluster orbitals of the hypothetical monomer from which it is composed, in the sense of the superatom model,[1] exemplified here by Sn_9^{4-}.[33] This takes into account all valence electrons, yielding the "magic" shell-closing number of 40 electrons for Sn_9^{4-}, which is only matched in a fourfold charged "$[CuSn_5Sb_3]^{4-}$" monomer.

In Sn_9^{4-}, the valence electrons occupy energetically well separated shells of cluster orbitals. The shells 1S (−12.3 eV), 1P (−10.7 eV to −10.4 eV), 1D (−8.2 to −7.7 eV), 2S (−4.9 eV), and 1F2P (−4.3 to −3.0 eV) are occupied; the unoccupied higher shells are separated from those by the HOMO–LUMO gap of 2.1 eV. At the left hand side of Figure 2, the highest occupied shells, 2S and 1F2P, are shown for a tricapped trigonal prismatic topology; for Sn_9^{4-}, this D_{3h}-symmetric isomer is only slightly higher in energy than the C_{4v}-symmetric global minimum (+2.4 kJ mol^{-1}; respective orbital data for the C_{4v} isomer are given in the Supporting Information, Figure S22), and more closely related to the structure of the cluster half in **1**.

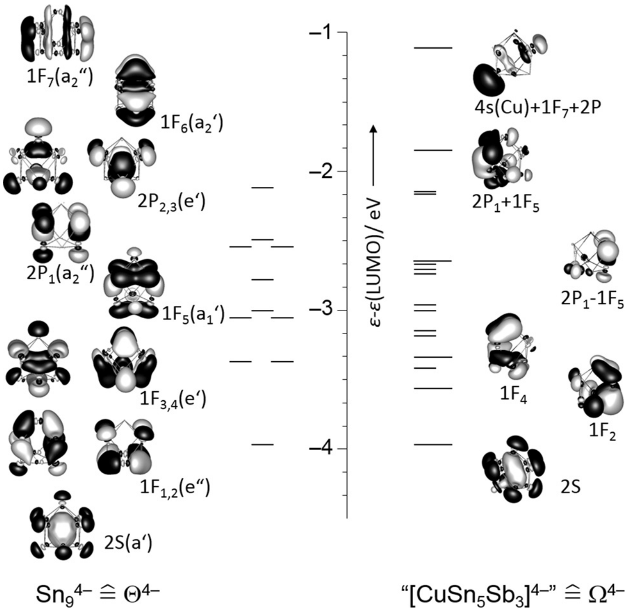

Figure 2. Highest occupied cluster MOs, that is, superatom orbital shells, of Sn_9^{4-} (denoted as Θ^{4-} in the text, left) and hypothetical "$[CuSn_5Sb_3]^{4-}$" (denoted as Ω^{4-} in the text, right). Amplitude contours are drawn at 0.03 a.u. Energies are given as differences to the LUMO energies, which are −0.90 eV for Sn_9^{4-} and −1.35 eV for "$[CuSn_5Sb_3]^{4-}$". For Sn_9^{4-}, all MOs of the 1F2P shell ('1F$_1$'…'1F$_7$', '2P$_1$'…'2P$_3$') and the 2S shell are plotted. For "$[CuSn_5Sb_3]^{4-}$", this is done only for MOs with an evident relationship to those of Sn_9^{4-}, which is indicated by the labeling. The respective MOs are marked in the energy-level scheme by longer bars. Both clusters were fixed to have the same tricapped trigonal-prismatic structures.

The electronic situation in the superatom Tt_9^{4-} is similar to that in a noble-gas atom. Consequently, the electronic situation in Tt_9^{3-} resembles a halide atom, and thus it has a tendency to dimerize. Also in Tt_9^{2-} (isoelectronic to the hypothetical "$[CuSn_5Sb_3]^{2-}$"), the deficit of two electrons can be released by sharing them with bonding partners, as is typical for the atomic analogues, the chalcogens. However, in contrast to dioxygen, a doubly bonded dimer is unknown. Instead polymeric chains (known for E = Ge; reminiscent of long-chain sulfur, selenium, or tellurium modifications) or oligomers, such as $[Ge{=}Ge{=}Ge_9]^{6-}$ and $[Ge{=}Ge_9{=}Ge_9{=}Ge_9]^{8-}$ that contain two (non-classical) bonds between adjacent cluster units (similar to the situation in ozone), are formed.[34]

The hypothetical, reduced cluster half, "$[CuSn_5Sb_3]^{4-}$" (denoted as heteroatomic superatom Ω^{4-}) differs from Sn_9^{4-} (denoted as homoatomic superatom Θ^{4-}) mainly in the distribution of the nuclear charges, apart from the fact that Cu is one period above Sn and Sb. Nevertheless, only the oxidized dimer $(\Omega^{2-})_2$, consisting of two "$[CuSn_5Sb_3]^{2-}$" units, is found experimentally, but thus far not the fourfold negatively charged monomer, Ω^{4-}.

Direct comparison of stabilities of the dimer $(\Theta^{2-})_2$ or $(\Omega^{2-})_2$, respectively, versus that of two monomeric units Θ^{4-} or Ω^{4-}, respectively, is not trivial for the homoatomic (Θ) or the heteroatomic (Ω) case because of the charge imbalance. The following reactions comparing real and hypothetical systems are considered instead to gain insight into the energetic reasons for the aforementioned observations (or lack thereof) [Eq. (1)–(5); reaction energies in kJ mol^{-1} for optimized structures with two-component[15k,m] density functional theory[15h] using polarized triple zeta valence basis sets[15l] and effective core potentials[15g] (for Sn and Sb), compensation of charges with the conductor-like screening model,[15f] COSMO]:

$$Sn_9^{4-} + 3\,Sb + Cu \rightarrow [CuSn_5Sb_3]^{4-} + 4\,Sn \qquad |+102 \tag{1}$$

$$Sn_9^{2-} + 3\,Sb + Cu \rightarrow [CuSn_5Sb_3]^{2-} + 4\,Sn \qquad |+8 \tag{2}$$

$$2\,[CuSn_5Sb_3]^{2-} \rightarrow \{[CuSn_5Sb_3]^{2-}\}_2 \qquad |-97 \tag{3}$$

$$2\,Sn_9^{2-} \rightarrow (Sn_9^{2-})_2 \qquad |-14 \tag{4}$$

$$(Sn_9^{2-})_2 + 6\,Sb + 2\,Cu \rightarrow \{[CuSn_5Sb_3]^{2-}\}_2 + 8\,Sn \qquad |-68 \tag{5}$$

According to the given reaction energies, for Θ^{4-}/Ω^{4-}, the homoatomic species is clearly preferred over the heteroatomic one [102 kJ mol^{-1}, Eq. (1)], whereas for Θ^{2-}/Ω^{2-}, they are of similar energy [8 kJ mol^{-1}, Eq. (2)]. For Θ^{2-}/Ω^{2-}, dimerization is favorable in both cases, but with much higher energy gain for the heteroatomic system Ω^{2-} [−97 kJ mol^{-1}, Eq. (3)] than for the homoatomic system Θ^{2-} [−14 kJ mol^{-1}, Eq. (4)]. This yields a clear preference of the heteroatomic dimer $(\Omega^{2-})_2$ over the homoatomic one $(\Theta^{2-})_2$ [−68 kJ mol^{-1}, Eq. (5)].

The low stability of the heteroatomic monomer Ω^{4-} is in line with its electronic structure, shown for “$[CuSn_5Sb_3]^{4-}$” (with the structure parameters calculated for D_{3h}–symmetric Sn_9^{4-}) at the right hand side of Figure 2. The HOMO is destabilized owing to its significant contributions from the Cu(4s) orbital, which is much higher in energy than the Sn(5s) orbitals. Occupation of this MO is thus unfavorable; if it is unoccupied, as in Ω^{2-}, the homo- and heteroatomic species are of similar stability [see Eq. (2)], and tend to form dimers/oligomers/polymers.

The energy gain for dimerization is much higher for the inhomogeneous, heteroatomic system Ω^{2-} than for that of the homogeneous, homoatomic one Θ^{2-}, as the LUMO of “$[CuSn_5Sb_3]^{2-}$” is dominated by Cu(4s) and is thus able to act as an acceptor orbital. Consequently, localization procedures yield two three-center localized molecular orbitals (LMOs, Figure S23), Cu1-Sn1′-Sn2′ and Cu1′-Sn1-Sn2, which may be interpreted as three-center bonds. Contributions to these mainly arise from the Sn(5p) orbitals and the Cu(4s) orbital. For the LMOs obtained by a Pipek-Mezey procedure,[15e] one gets 0.65 electrons from each Sn(5p) orbital, 0.35 electrons from Cu(4s) and 0.15 electrons from Cu(4p), according to a Mulliken population analysis;[35] respective numbers for Boys’ LMOs[15b] are similar, 0.54, 0.35, and 0.18 electrons, respectively. This is not seen for $(\Theta^{2-})_2$, which is also reflected by the respective differences of electron densities of the dimers $(\Theta^{2-})_2$ or $(\Omega^{2-})_2$ with that of the corresponding monomers Θ^{2-} or Ω^{2-} (Figure 3).

From the upper part of Figure 3 it is clear that upon dimerization of the heteroatomic system, the density is moved towards the region between Cu1, Sn1′ and Sn2′ (and in the same way for the symmetry equivalent atoms Cu1′, Sn1 and Sn2), which is characteristic for a covalent bond and reflected by a Mulliken overlap population[35] of 4×0.31; 1.24 electrons, whereas the overlap between the two Cu atoms is close to zero.

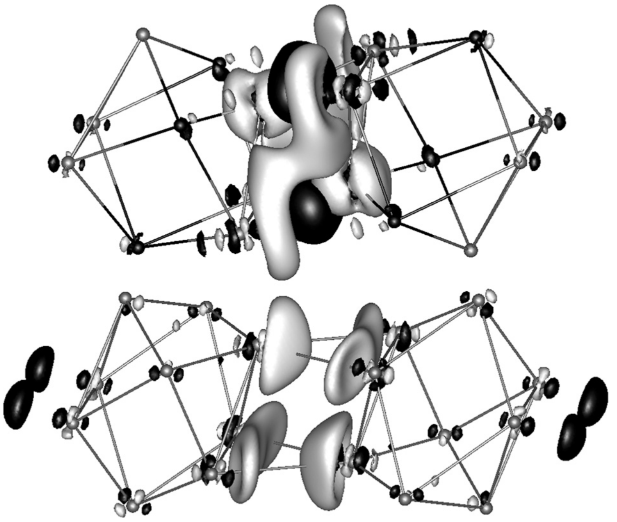

Figure 3. Difference of electron densities of dimer and monomers for the real $\{[CuSn_5Sb_3]^{2-}\}_2=(\Omega^{2-})_2$ (top) and hypothetic “$(Sn_9{}^{2-})_2$” $=(\Theta^{2-})_2$ (bottom), shown in the same orientation of the cluster anion as in Figure 1. Amplitude contours are drawn at 0.0016 a.u. For black areas, electron density in the dimer is higher than in the monomers, for light areas it is lower.

For the homoatomic system (lower part of Figure 3) a different picture is revealed: in this case, the electron density is mainly moved from the central to the outer regions of the molecule, which is reminiscent of the charge transfer when approximating two negatively charged, polarizable spheres. Nevertheless, a small positive Mulliken overlap of 0.10 electrons is found for the respective contacts, in line with the slightly exothermic dimerization.

The impact of the heteroatomic nature of the anion in **1** (versus an effect based only on structural differences) becomes even more obvious if performing calculations of the heteroatomic dimerization reaction, while maintaining the structural parameters of the homoatomic “reactants”. The according reaction energy is $-132\,kJ\,mol^{-1}$, which is indeed much closer to the value obtained for the relaxed heteroatomic system [$-97\,kJ\,mol^{-1}$, Eq. (3)] than to that obtained for the homoatomic, but isostructural system [$-14\,kJ\,mol^{-1}$, Eq. (4)].

Finally, “$[CuSn_5Sb_3]^{3-}$”, that is, Ω^{3-} could be considered as the heteroatomic analogue of the Θ^{3-} moiety in “$(Sn_9{}^{3-})_2$” (which, in contrast to its lighter homologue $(Ge_9{}^{3-})_2$, has only been detected upon stabilization by an Ag^+ atom in $[Ag(Sn_9\text{-}Sn_9)]^{5-}$). The dimerization energy of two Ω^{3-} units [calculated as reaction energy analogous to Eq. (3)] amounts to $-106\,kJ\,mol^{-1}$; two Θ^{3-} units give $-38\,kJ\,mol^{-1}$ [calculated as reaction energy analogous to Eq. (4)]. In this case, the higher value for the heteroatomic $(\Omega^{3-})_2$ does not reflect its stability, but rather the instability of the Ω^{3-} monomer, for which the energetically unfavorable highest MO (see Figure 2) has to be (singly) occupied. Consequently, the exchange reaction linking homo- and heteroatomic dimers [the analogue to the reaction given in Eq. (5)] is endothermic ($+51\,kJ\,mol^{-1}$).

Overall, the 1F2P shell of the ternary superatom $\Omega^{4-/2-}$ is energetically split by its inhomogeneity in a way that is unfavorable for the monomer, and thus a fourfold negatively charged dimer $(\Omega^{2-})_2$ is formed instead.

Note, for the mixed-metallic Sn/Sb system, endohedral clusters, such as “$[Cu@Sn_7Sb_2]^{-}$” or “$[Cu@Sn_6Sb_3]$”, being isoelectronic with $[Cu@Sn_9]^{3-}$, can be probably ruled out as alternative crystalline products of the reactions under the given reaction conditions; although both of the (empty) binary 9-atom cages are known from single-crystal structures or mass spectrometry, the endohedral clusters are not expected to form stable crystals with $[K(crypt\text{-}222)]^+$ owing to their low or missing anionic charge.

In summary we synthesized and isolated the first ligand-free ternary Zintl cluster of the elemental combination Cu/Sn/Sb as its salt $[K(crypt\text{-}222)]_4[CuSn_5Sb_3]_2\cdot n\,solv$ ($\mathbf{1}\cdot n\,solv$; $n\,solv = 3\,en, 2\,tol$). Its elemental composition was confirmed by EDX analyses and unambiguous assignment of Sn and Sb atomic positions was carried out by DFT calculations, which showed a $25\,kJ\,mol^{-1}$ energy gap between the primary and secondary isomer. It was noted that $\{[CuSn_5Sb_3]^{2-}\}_2$ may be viewed as a dimer of inhomogeneous superatoms, and further computational analysis was performed to compare these superatoms to their well-established homoatomic cousins.

Our results show that the hypothetical monomers, "$[CuSn_5Sb_3]^{4-}$" and "$[CuSn_5Sb_3]^{2-}$", are energetically unfavorable compared with their isoelectronic, homoatomic counterparts, Sn_9^{4-} and Sn_9^{2-}, respectively. However, formation of the heteroatomic dimer, $\{[CuSn_5Sb_3]^{2-}\}_2$, under formation of two Cu-Sn-Sn three-center bonds is favored over the hypothetical homoatomic case, "$(Sn_9^{2-})_2$", in agreement with the experimental findings.

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