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$[Cu@Sn_9]^{3-}$ and $[Cu@Pb_9]^{3-}$: Intermetalloid Clusters with Endohedral Cu Atoms in Spherical Environments

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Since the notification of the resemblance between homoatomic Zintl anions and the class of fullerenes,[1] the discovery of several new polyhedra as well as endohedrally filled cages of the heavier Group 14 elements has been reported. Besides the most common nine-atom clusters $[E_9]^{n-}$ (E = Si–Pb; $n = 3$, 4), a ten-atom *closo*-cluster $[Pb_{10}]^{2-}$ was synthesized and structurally characterized.[2] Larger clusters appear as endohedrally filled cages, and several of those have been studied by single-crystal X-ray structure determination, such as $[Ni_3@Ge_{18}]^{4-}$, $[Pd_2@Ge_{18}]^{4-}$, $[Ni@Pb_{10}]^{2-}$, $[M@Pb_{12}]^{2-}$ (M = Ni, Pd, Pt), $[Ni_2@Sn_{17}]^{4-}$, $[Pt_2@Sn_{17}]^{4-}$, and $[Pd_2@Sn_{18}]^{4-}$.[3,4] They represent impressive examples of so-called *intermetalloid* clusters.[5] The stability and structure of other clusters, such as the binary ions $[M@Sn_{12}]^{-}$ for a series of transition metals (M), have been anticipated by gas-phase experiments and theoretical calculations.[6] The results led to the idea that—in contrast to fullerenes—larger polyhedral cages might exist for the heavier homologues of Group 14 elements only with endohedral atoms. Clusters with less than ten atoms are less capable of encapsulating a transition-metal atom.[7,8]

Recently, we reported on reactions of $[Ge_9]^{4-}$ with PPh_3AuCl, which led to the isolation of $[Au_3Ge_{18}]^{5-}$[5c] and the huge cluster $[Au_3Ge_{45}]^{9-}$.[5d] We have now investigated the related reaction of $[E_9]^{4-}$ (E = Sn and Pb) homologues with mesitylcopper and here we report on the structural and spectroscopic characterization of the first representatives of clusters containing endohedral Cu atoms in an almost perfectly spherical environment of nine tin or lead atoms; two clusters which were not foreseen by gas-phase experiments.[7d]

The compounds $[K([2.2.2]crypt)]_3[Cu@E_9](dmf)_2$ (E = Sn (**1**) and Pb (**2**)) crystallize in the monoclinic space group $P2_1/c$ with two dimethylformamide (dmf) solvate molecules per formula unit.[9] The unit cell parameters of the Pb compound are about 0.07 Å longer than those of the isomorphic Sn compound. According to the number of well-ordered $[K([2.2.2]crypt)]^{+}$ units, the cluster anions $[Cu@Sn_9]^{3-}$ (**1a**) and $[Cu@Pb_9]^{3-}$ (**2a**) have a threefold negative charge and nine Sn and Pb atoms, respectively, encapsulate a Cu atom. In both cases nine crystallographically independent E atoms of the anions build a distorted tricapped trigonal prism with approximate C_{2v} symmetry (Figure 1). The mean interatomic distances (e) within the prism basal planes E1 to E3 and E4 to E6 are 3.097(5) and 3.224(5) Å, respectively, and the contacts to the capping atoms (c) are 3.052(5) and 3.163(5) Å for **1a** and **2a**, respectively. The homoatomic distances are typical for delocalized cluster bonds, and are about 0.1 Å longer than in the empty clusters.[4,10–12] The prism heights (h) E2 to E5 and E1 to E4 of **1a** are 2% and 5% longer than the shortest height E3 to E6 (3.757(5) Å), whereas in **2a** the corresponding distances are elongated by 2% and 6% with respect to the Pb3–Pb6 distance of 3.873(5) Å. Therefore the basal planes E1 to E3 and E4 to E6 are tilted

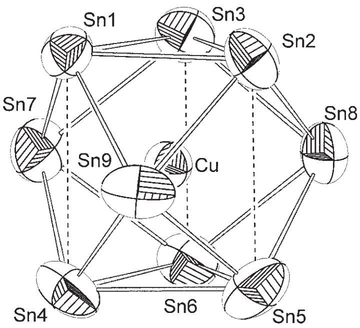

Figure 1. Structure of the $[Cu@Sn_9]^{3-}$ ion (**1a**). Atoms are shown with a 90% occupation probability.

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by 3.4° (**1a**) and 4.0°(**2a**).[13] Compared to empty $[E_9]^{3-}$ clusters with approximate C_{2v} symmetry, the mean prism heights are elongated by 17% for **1a** and 15% for **2a**.[11] The average h/e ratios of 1.239 for **1a** and 1.234 for **2a** are larger than in other known E_9 cluster compounds with a similar skeleton,[11,12] and the capping atoms in **1a** and **2a** are located closer to the center of gravity of the corresponding rectangular planes.

As a result of this distortion the E_9 polyhedra possess an almost spherical shape, and the Cu–E contacts are in the very narrow range of 2.611(7) to 2.700(7) Å for **1a** and 2.71(1) to 2.802(11) Å for **2a**, with slightly longer contacts to the capping atoms. This is also expressed by the offset of the Cu atoms to the centers of the E_9 cages, which is as short as 0.02 Å in both clusters.[14] The "sphere radii" for **1a** and **2a** are given by the mean Cu–E distances of 2.645 and 2.759 Å, respectively. In the case of an error-free arrangement of nine atoms on the surface of a sphere with equalized interatomic distances of 1, the radius can be geometrically calculated by using $r=1/2\sqrt{3}$,[15,16] leading to ideal interatomic distances of 3.054 and 3.186 Å for **1a** and **2a**, respectively. These values are very close to the average measured E–E contacts in the clusters ignoring the prism heights (**1a**: 3.067 Å and **2a**: 3.183 Å). Thus. the ideal, geometrically determined nine-atom polyhedron is best described as an elongated tricapped trigonal prism with $h/e=\sqrt{5/3}=1.29$ and hence very close to the values found for the $[Cu@E_9]^{3-}$ clusters.

The highly symmetric cluster shape suggests a spherical coordination environment for the Cu atom, which accounts for a d^{10} configuration for the Cu atom (Cu^+) and consequently a charge of 4− for the E_9 skeleton. Magnetic measurements showed that the crystals of **1** are diamagnetic and confirmed the proposed charge distribution. Indeed, the cluster shape is very different from that of a 22-electron *nido*-cluster expected according to Wade's rules. However, the uncertainty of the assignment of the number of electrons to homoatomic nine-atom cages based on their shapes has previously been pointed out.[17]

Since crystals of **1** could be obtained in higher yields than those of **2**, further investigations were carried out only for **1**. The ^{119}Sn NMR spectrum of **1** in acetonitrile at room temperature displays a single resonance at $\delta=-1440$ ppm (see the Supporting Information), which indicates that all Sn atoms are time-averaged in solution. The chemical shift is in the range of related cluster compounds and high-field shifted relative to the empty cluster $[Sn_9]^{4-}$ ($\delta=-1230$ ppm).[4,17,18] The ^{119}Sn NMR signal appears as a 1:1:1:1 quartet with a coupling constant of $J(^{119}Sn–^{63/65}Cu)=286$ Hz due to the interstitial Cu atom (69% ^{63}Cu and 31% ^{65}Cu with $\gamma(^{63}Cu)/\gamma(^{65}Cu)=0.934$), although the quadrupolar momentum of the $I=3/2$ nuclei usually quenches coupling because of very short relaxation times.[19,20] In our measurement the coupling was observed because the Cu atom is surrounded by a highly symmetrical Sn_9 cluster, whose atoms are not distinguishable on the spectral NMR time scale. Each resonance signal is accompanied by two satellites with $J(^{119}Sn–^{117}Sn)=85$ Hz arising from Sn–Sn coupling due to homoatomic contacts. For comparison, the Pt-filled cluster $[Pt_2@Sn_{17}]^{4-}$ shows a $^{119}Sn–^{117}Sn$ coupling of 170 Hz.[4]

At room temperature, compound **1** displays one sharp ^{63}Cu NMR resonance signal at $\delta=-330$ ppm (Figure 2). The high-resolution satellite pattern permits the rare determination of the $^{63}Cu–^{119}Sn$ coupling constant of $J(^{119}Sn–^{63}Cu)=280$ Hz, which is in good agreement with the ^{119}Sn NMR spectrum. The signal's pattern arises from different isotopomers $[Cu@^{117/119}Sn_xSn_{(9-x)}]^{3-}$ (with $x=0, 1,.., 4$), since only 16% of Sn atoms have spin $I=1/2$ and couple with the Cu atom (8.58% ^{119}Sn and 7.61% ^{117}Sn with $\gamma(^{119}Sn)/\gamma(^{117}Sn)=1.047$). The intensity distribution of the observed seven peaks is consistent with a Sn_9 cluster core (Figure 2). The observed resonance frequency is in the range of other Cu^I compounds.[20,21] Therefore the Cu atom in **1** is assumed to have the formal oxidation state +1. Generally the major challenge of ^{63}Cu NMR studies in solution is the enhanced line width, which seriously affects the sensitivity of the measurement. Since ^{63}Cu is a $I=3/2$ nucleus, a small electric field gradient is necessary for sharp signals. Therefore, the observed line width is highly dependent on the symmetry of the surrounding atoms. A discrete signal can thus only be obtained of Cu atoms in an environment of at least cubic symmetry.[19,20,22] In our investigation, the copper atom occupies the center of a spherical Sn_9 cluster, as anticipated already from the single resonance in the ^{119}Sn NMR spectrum. Hence the line width is as narrow as 17 Hz and considerably smaller than those reported up to now. The ^{119}Sn and ^{63}Cu NMR spectra do not change upon cooling to −40°C.

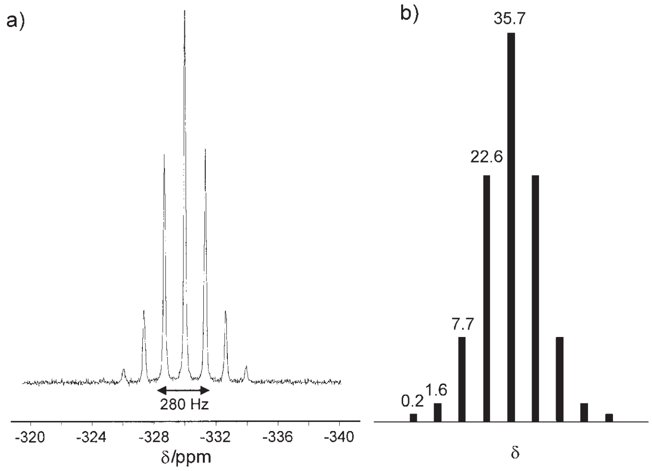

Figure 2. ^{63}Cu NMR spectrum of **1**. a) Measured spectrum in acetonitrile at room temperature, b) simulated spectrum for $[Cu@^{117/119}Sn_xSn_{(9-x)}]^{3-}$ (with $x=0, 1,.., 4$).

DFT calculations have been performed on the $[Cu@Sn_9]^{3-}$ ion and the empty $[Sn_9]^{n-}$ clusters ($n=2, 3, 4$). Structure optimizations at the B3LYP/aug-cc-pVDZ-PP level lead to ground state structures with D_{3h} symmetry for $[Cu@Sn_9]^{3-}$, $[Sn_9]^{2-}$, and $[Sn_9]^{3-}$, and C_{4v} symmetry for $[Sn_9]^{4-}$.[23] The interatomic distances calculated for $[Cu@Sn_9]^{3-}$ are somewhat longer (max. 0.09 Å) than the mean crystallographically observed distances, but the trends are consistent with those found experimentally. (Calculated Sn–Sn distances: $h=3.930$ Å, $e=3.171$ Å, $c=3.129$ Å; calculated Cu–Sn distances: 2.763 Å to capping Sn atoms, 2.686 Å to Sn atoms in basal planes.) Notably, the calculated and observed h/e ratios agree exactly for $[Cu@Sn_9]^{3-}$. Single-point calculations at the B3LYP level using aug-cc-pVTZ-PP basis sets of triple zeta quality were performed on the optimized structures to analyze the electronic structures of the clusters. The calculated HOMO–LUMO gap of $[Cu@Sn_9]^{3-}$ is 2.93 eV. This value lies in between those for D_{3h}-symmetric $[Sn_9]^{2-}$ (1.90 eV) and $[Sn_9]^{3-}$ [2.56 eV (α-HOMO–α-LUMO)] and the one for $[Sn_9]^{4-}$ with an optimized C_{4v}-symmetric structure (3.11 eV). It is also larger than the HOMO–LUMO gap calculated for a D_{3h}-symmetric $[Sn_9]^{4-}$ ion with the structure of the Sn_9 skeleton optimized for $[Cu@Sn_9]^{3-}$ (2.70 eV). A positive natural charge of 0.20 for Cu calculated in $[Cu@Sn_9]^{3-}$ points towards the same Cu oxidation state as in linear $[CuCl_2]^-$ with a natural charge of +0.58 for Cu.

Using the terminology of tensor surface harmonic theory, we classified the molecular orbitals of $[E_9]^{n-}$ into S, P, D, and F orbitals having shapes and nodal patterns similar to the corresponding atomic orbitals.[24] In D_{3h} point symmetry the s, p, and d orbitals of the endohedral Cu atom and the S, P, D orbitals of the tricapped trigonal prismatic E_9 cluster transform under the a_1' (s, d_{z^2}), a_2'' (p_z), e' (p_x, p_y, $d_{x^2-y^2}$, d_{xy}) and e'' (d_{xz}, d_{yz}) irreducible representations, the F orbitals have a_1', a_2', a_2'', e', and e'' symmetry. An analysis of the molecular orbitals of $[Cu@Sn_9]^{3-}$ shows that the main interactions between the central Cu atom and the E_9 cage involve Cu-d, -s, and -p orbital contributions (Figure 3).

Even though mass spectrometric investigations show the absence of $CuSn_9$ clusters,[7d] the present study proves that Cu ions can be trapped in homoatomic cages even in macroscopic quantities. The surrounding Sn and Pb atoms build a nine-atom cage whose structure is optimized towards a perfect sphere. In contrast to the closely related $Cu@C_{60}$, which has been characterized by mass spectrometry and EPR spectroscopy as $[Cu^{2+}@C_{60}{}^{2-}]$,[25] **1a** can be formulated as $[Cu^{+}@Sn_9{}^{4-}]$. The rapid exchange of the Sn atoms on the NMR time scale in solution creates an ideal spherical environment around the Cu atom and allows the examination of ^{63}Cu NMR spectra of these complexes.

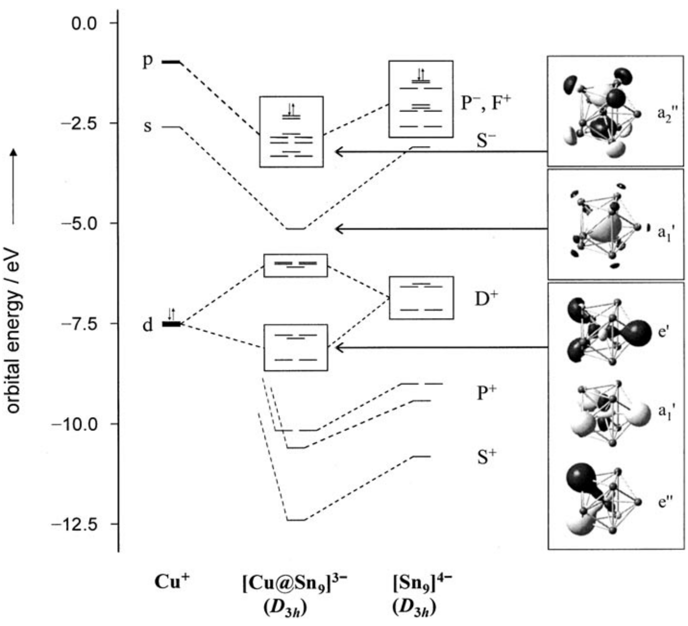

Figure 3. Molecular orbital interaction diagram of $[Cu@Sn_9]^{3-}$ in fragments of Cu^+ and D_{3h}-$[Sn_9]^{4-}$. Important contributions are indicated by dashed lines, and relevant molecular orbitals of $[Cu@Sn_9]^{3-}$ are shown on the right.

Experimental Section and Methods

General: All manipulations and reactions were performed under an argon atmosphere with standard Schlenk techniques or in an argon-filled glove box. K_4Sn_9 and K_4Pb_9 were prepared by fusion of stoichiometric amounts of the elements in stainless steel tubes at 550 °C and 400 °C, respectively. Dimethylformamide (Merck) was distilled over calcium hydride and used immediately after collection. Toluene and tetrahydrofuran were dried in a solvent purification system (MBraun). [2.2.2]crypt (Merck) was dried in vacuo for eight hours. Mesitylcopper was prepared according to reference [26].

Synthesis of 1 and 2: K_4E_9 (0.15 mmol), mesitylcopper (0.15 mmol), and [2.2.2]crypt (0.27 mmol) were dissolved in dimethylformamide (2 mL) and stirred for two hours. The intense dark red to brown solution was separated from the residue by filtration and carefully layered with toluene (1 mL). Compound **1** crystallized after two weeks at −25 °C in the form of dark red prisms, in contrast dark brown and cubic shaped crystals of **2** were obtained after three months (yield: **1**: 50 %; **2**: 10 %).

Characterization: EDX analyses of the crystals carried out on a JEOL-SEM 5900 LV spectrometer confirm the K, Cu, and E (**1**: E = Sn, **2**: E = Pb) composition of the X-ray structure elucidation. Elemental analysis calcd (%) for **1**: C 28.5, H 4.8, N 4.4, Cu 2.5, Sn 42.3, K 4.6; found: C 27.9, H 4.6, N 4.1, Cu 2.6, Sn 40.3, K 4.5. The magnetic investigations were performed on a Quantum Design SQUID magnetometer MPMS-XL7.

NMR spectra of 0.05 mol L^{-1} solutions of single crystals of **1** in acetonitrile were recorded on a Bruker AMX400. The observed frequencies were ^{119}Sn (149.211 MHz) and ^{63}Cu (106.096 MHz). ^{119}Sn was referenced to Me_4Sn in C_6D_6 (0 ppm) and ^{63}Cu to $[Cu(CH_3CN)_4]ClO_4$ in CH_3CN (0 ppm) as external standards. Block searches of 500 ppm windows were used to explore the ^{119}Sn NMR shifts. A total of 2487 scans were accumulated for the ^{119}Sn NMR spectrum, 1876 scans for the ^{63}Cu NMR spectrum.

Single crystals of **1** and **2** were fixed on glass capillaries. The data were collected on an Oxford Diffraction Xcalibur3 diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å).[9a] The structures were solved by direct methods (SHELXS-97[9b]) and refined by full-matrix least-squares calculations on $\Sigma\omega(F_o^2-F_c^2)^2$ (SHELXL-97[9c]). All non hydrogen atoms were refined with anisotropic displacement parameters, all hydrogen atoms were placed in calculated positions and refined by using a riding model.

DFT calculations have been performed by using the GAUSSIAN 03 package of programs (Revision D.01).[27] Natural charges were calculated by using Version 3.1 of the NBO program[28] as implemented in GAUSSIAN 03. The self-consistent isodensity polarizable continuum model (SCI-PCM)[29] was used in all calculations to account for solvation effects (dielectric constant ε_r(dmf) = 36.71). GaussView was used to visualize molecular orbitals.[30] Structure optimizations were first carried out at the B3LYP/cc-pVDZ-PP level of theory, that is Becke's hybrid three-parameter exchange functional[31] with the Lee–Yang–Parr correlation functional[32] (UB3LYP for open shell $[Sn_9]^{3-}$) with small-core relativistic pseudopotential correlation consistent valence double zeta plus polarization basis sets.[33] Further optimizations were performed with B3LYP using aug-cc-pVDZ-PP (augmented correlation consistent polarized valence double zeta) basis sets[33] that include diffuse functions. Harmonic vibrational frequencies were calculated numerically for the optimized structures to verify the nature of the stationary point on the potential energy surface. Single-point calculations (Natural charge, HOMO–LUMO gaps, MOs, MO eigenvalues) on the optimized (B3LYP/aug-cc-pVDZ-PP) structures were performed at the B3LYP level using aug-cc-pVTZ-PP basis sets of triple zeta quality.[33] Calculations for $[CuCl_2]^-$ were carried out correspondingly, using cc-pVDZ, aug-cc-pVDZ (optimization) and aug-cc-pVTZ (single point) basis sets for Cl.[34] All basis sets were obtained from the EMSL Basis Set Exchange.[35]

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Keywords: cluster compounds · copper · density functional calculations · NMR spectroscopy · Zintl anions

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[8] There are two earlier reports on a Ni-centered Ge_9 cluster.[3a,36] Both structure determinations of $[Ni@Ge_9]$ are of poor quality and do not allow an unambiguous description of the cluster. According to the authors of reference [3a] "*the structure determination of this compound was somewhat problematic owing to its extremely large unit cell, the presence of two crystallographically different* $[Ni@Ge_9]^{3-}$ *clusters per cell, and the observed disorder in some of the germanium atoms of the clusters*". The $[Ni@Ge_9]$ cluster reported in reference [36] appears to be even more disordered and overlapping with a $[Ni@(Ge_9Ni\text{-}en)]$ cluster in a ratio of 0.265:0.735.

[9] a) Details of the crystal structure determination of **1**: Crystal size $0.3\times0.2\times0.1$ mm^3; cell parameters at 150 K: $a=17.6901(2)$, $b=14.4382(2)$, $c=35.6145(5)$ Å, $\beta=92.307(1)°$, $V=9089.0(2)$ Å^3; monoclinic, space group $P2_1/c$ (no. 14), $Z=4$, $\rho_{calcd}=1.845$ g cm^{-3}, $\mu=2.856$ mm^{-1}; $\theta_{max}=25.26°$, 70380 measured reflections, 16408 independent reflections, $R_{int}=0.032$; $R_1=0.033$ and $wR_2=0.082$ for $I>2\sigma(I)$, $R_1=0.052$ and $wR_2=0.096$ for all data. Details of the crystal structure determination of **2**: Crystal size $0.3\times0.2\times0.1$ mm3; cell parameters at 150 K: $a=17.7509(2)$, $b=14.4890(1)$, $c=35.7038(3)$ Å, $\beta=92.316(1)°$, $V=9175.3(2)$ Å^3; monoclinic, space group $P2_1/c$ (no. 14), $Z=4$, $\rho_{calcd}=2.404$ g cm^{-3}, $\mu=16.872$ mm^{-1}; $\theta_{max}=23.26°$, 108597 measured reflections, 13142 independent reflections, $R_{int}=0.056$; $R_1=0.029$ and $wR_2=0.069$ for $I>2\sigma(I)$, $R_1=0.045$ and $wR_2=0.081$ for all data. CCDC-668708 (**1**) and CCDC-668709 (**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; b) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Universität Göttingen, **1997**; c) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Universität Göttingen, **1997**.

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[13] The prism heights for **1a** (3.757(5), 3.820(5), and 3.936(5) Å) as well as for **2a** (3.873(5), 3.964(6), and 4.095(5) Å) are considerably larger than twice the covalent radii of the elements (Sn: 2.82 Å and Pb: 2.92 Å), but they are shorter than twice the van der Waals radii (Sn: 4.16 Å, Pb: 4.04 Å).

[14] In comparison, the average distance between the capping atoms and the center of gravity of empty $[E_9]^{3-}$ clusters is 2.800 Å for $E=Sn$ and 2.895 Å for $E=Pb$, and exceeds the distances to prism vertices by 0.384 and 0.357 Å, respectively. Thus, the shapes of the empty clusters diverge remarkably from a spherical species.

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pVDZ-PP basis sets. The structures of $[Cu@Sn_9]^{3-}$ and the empty $[Sn_9]^{n-}$ ($n=2$, 3, 4) anions were first optimized without constraints of symmetry using the atomic positions deduced from the single-crystal X-ray analysis of the $[Cu@Sn_9]^{3-}$ ion as a starting point. Analysis of the vibrational modes of the optimized structures showed no imaginary frequencies. The optimized structures of $[Cu@Sn_9]^{3-}$, $[Sn_9]^{2-}$, and $[Sn_9]^{3-}$ deviate only slightly from D_{3h} symmetry; for $[Sn_9]^{4-}$, the optimized structure is close to C_{4v}. Therefore, further structure optimizations of these anions were carried out in which the symmetry was restricted to D_{3h} or C_{4v}, respectively. This led to ground state structures with D_{3h} symmetry for $[Cu@Sn_9]^{3-}$, $[Sn_9]^{2-}$, and $[Sn_9]^{3-}$, and C_{4v} symmetry for $[Sn_9]^{4-}$. b) For gas phase calculations on $[Sn_9]^{n-}$ see ref. [17] and A. Hirsch, Z. Chen, H. Jiao, *Angew. Chem.* **2001**, *113*, 2916–2920; *Angew. Chem. Int. Ed.* **2001**, *40*, 2834–2838.

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