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RESEARCH ARTICLE

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Synthesis and Single Crystal X-ray Characterization of [Sn$_5$Bi$_3$]$^{3-}$

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On the occasion of the 80th birthday of Prof. Dr. Martin Jansen.

The extraction of the solid state materials "$MSnBi_x$" ($M/x=$Cs/1, Na/3) in liquid ammonia in the presence of different chelating agents yielded the novel Zintl anion [Sn$_5$Bi$_3$]$^{3-}$. The anion could be crystallized and characterized via single crystal X-ray diffraction in [Cs@[18]crown-6]$_3$[Sn$_5$Bi$_3$]·7NH$_3$, [K@[18]crown-6]$_{1.5}$[Cs@[18]crown-6][Cs@([18]crown-6)$_2$]$_{0.5}$[Sn$_5$Bi$_3$]·3.98NH$_3$, [Na@DB[18]crown-6]$_2$[Na(NH$_3$)$_6$][Sn$_5$Bi$_3$]·14NH$_3$ and [Cs@[2.2.2]crypt]$_6$[Sn$_5$Bi$_3$]$_2$·9.53NH$_3$. The [Sn$_5$Bi$_3$]$^{3-}$ anion is further investigated by mass spectrometry and DFT calculations to confirm its composition and elucidate its electronic structure.

Introduction

The first observation of heavy main group polyanions was reported in 1891.[1] Joannis found that a blue electride solution of sodium in liquid ammonia were able to dissolve elemental lead or antimony, undergoing a color change. Systematic characterizations were done by Zintl from the 1930s on mainly by means of potentiometric titrations and conductivity measurements.[2–4] For group 14 elements the formula [T_9]$^{4-}$ ($T=$ Sn, Pb) was deduced and this composition could be verified for the first time via single crystal X-ray diffraction for the [Sn$_9$]$^{4-}$ anion in the compound Na$_4$(en)$_7$[Sn$_9$] by Kummer and Diehl in 1970.[5] But this measurement also disproved Zintls expectation of the [Sn$_9$]$^{4-}$ anion being a [Sn]$^{4-}$ anion surrounded by eight tin atoms in a cube like manner. Instead, the geometry of the anion was found to lie somewhere in between a monocapped square antiprism (C_{4v}-symmetry) and a tricapped trigonal prism (D_{3h}-symmetry).[6] Through the years many homoatomic and heteroatomic structures could be characterized. Furthermore polymerization as well as the functionalization of such clusters with various organic and metalorganic fragments was achieved.[7–11] Some prominent examples are [^{t}Bu–Ge$_9$–Ge$_9$–^{t}Bu]$^{4-}$,[12] [Sn$_9$–R]$^{3-}$ ($R=$CH≡CH–Ph, ^{t}Bu, CH≡CH$_2$),[13] [NHC^{Dipp}M–Sn$_9$]$^{3-}$ (M=Cu, Ag, Au),[14] [Sn$_7$Bi$_2$]$^{2-}$,[15] [Ge$_4$Bi$_{14}$]$^{4-}$,[16] [CrPb$_9$(CO)$_3$]$^{4-}$,[17] [Cu@T_9]$^{3-}$ ($T=$Sn, Pb),[18] [Si$_{9-x}$Ge$_x$]$^{3-}$,[19] [T_9ZnR]$^{3-}$ ($T=$Ge–Pb; $R=$Mes, ^{i}Pr),[20]

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[Pb$_9$CdCdPb$_9$]$^{6-}$,[21] [T_9Tl]$^{3-}$ ($T=$Ge, Sn), [Ni@Sn$_9$]$^{4-}$, [Ni@Sn$_9$Tl]$^{3-}$,[22] [(Ni–Ni–Ni)@(Ge$_9$)$_2$]$^{4-}$,[23] [Ge$_9$–TR_3]$^{3-}$, [R_3T–Ge$_9$–TR_3]$^{2-}$, [R_3T–Ge$_9$–Ge$_9$–TR_3]$^{4-}$ ($T=$Ge, Sn; $R=$Me, Ph),[24] [(Sn$_6$Ge$_2$Bi)$_2$]$^{4-}$.[25]

The substitution of one or two vertices of the nine-atom polyanions by atoms of group 13/15 or even by a metal organic fragment led to heteroatomic clusters in which the original geometry of the clusters is in general maintained. Burns and Corbett characterized the [TlSn$_8$]$^{3-}$ anion which crystallized in superposition with the ten-atom cluster [TlSn$_9$]$^{3-}$.[26] [TlSn$_8$]$^{3-}$ could be obtained by dissolution of the mixed precursor phase KTlSn in ethylenediamine and its geometry approximates a (pseudo) tricapped trigonal prism with the thallium atom in a capping position. The reaction between [Ge$_9$]$^{4-}$ and [Fe-(cot)(CO)$_3$] (cot=cyclooctatriene) resulted in the formation of the unusually built [Ge$_8$Fe(CO)$_3$]$^{3-}$.[27] The Fe(CO)$_3$ fragment forms one of the vertices in the basal quadrangular face and is –based on the isolobal relationship to a germanium vertex– supposed to contribute electrons to the delocalized cluster bonding.

Another example of a heterometallic cluster was characterized by Dehnen et al. in 2017. In the compound described by them the Zintl anion [Ge$_4$Bi$_{14}$]$^{4-}$ showed a structurally complex cluster in which two Bi$_7$ units are connected via a Ge$_4$ chain.[16]

In the field of tinbismuthides the [Sn$_7$Bi$_2$]$^{2-}$ anion was reported by Dehnen et al. in 2009 as a side product of the reaction between [Sn$_2$Bi$_2$]$^{2-}$ and ZnPh$_2$.[15] Quantum chemical calculations predict the two bismuth atoms lying on opposite vertices of the basal plane. Subsequently, the eight atomic Zintl anion [Sn$_4$Bi$_4$]$^{2-}$ was synthesized and characterized by single crystal X-ray diffraction and theoretical calculations. In this case the [Sn$_7$Bi$_2$]$^{2-}$ anion was as well a side product like in the previous studies.[28]

An all-metal carbonate analogue [SnBi$_3$]$^{5-}$ was reported 2017 by Fässler et al. in liquid ammonia. Theoretical studies confirmed Sn–Bi bond lengths between a single and double bond despite the high negative charge.[29]

The only known *hypho* Zintl cluster [Sn$_3$Bi$_3$]$^{5-}$ could be isolated in 2016 from liquid ammonia solutions.[30]

In contrast to the growing number of tinbismuthides, rather little is known about lighter analogue tinantimonides. For a long time the only known anions were $[Sn_2Sb_2]^{2-}$, $[Sn_3Sb_4]^{6-}$ and the functionalized species $[Sn_2Sb_5(ZnPh)_2]^{3-}$. All three were synthesized by the extraction of the solid-state phase K_8SnSb_4.[31] Adding to this list is the rare eight-vertex *arachno* Zintl cluster $[Sn_5Sb_3]^{3-}$, which was characterized in 2020 by the Dehnen group. Until now only few deltahedral Zintl ions could be synthesized from solution with eight vertices and being from the *arachno* type. As antimony and tin only differ by one electron, the unambiguous determination of the respective elements by single crystal X-ray structure analysis is very difficult. Therefore, these materials need additional methods like quantum chemical calculations. The structure determined by X-ray diffraction was found to be the global minimum in the computationally investigated eight-atomic series $[Sn_xSb_{8-x}]^{2-x}$ ($x = 0$–8).[32] This cluster is also present in the dimer $\{[CuSn_5Sb_3]^{2-}\}_2$, where the free vertex of $[Sn_5Sb_3]^{3-}$ is occupied by a copper atom. Quantum chemical investigations supported the trend of dimerization of the respective monomeric unit, which was observed in the experiments. This is caused by the additional inhomogeneity in the cluster unit.[33]

During our studies on tinbismuthides in liquid ammonia we encountered the analogue anion $[Sn_5Bi_3]^{3-}$, which crystallized readily with different counterions and chelating agents. The structures found were also examined with DFT and ELF calculations.

Results and Discussion

The above mentioned novel anion $[Sn_5Bi_3]^{3-}$ could be obtained in four different crystal structures, in general by the extraction of the solid state material with the nominal composition "$MSnBi_x$"($M/x = $ Cs/1, Na/3) in the presence of [18]crown-6, DB[18]crown-6 or [2.2.2]crypt in liquid ammonia. The compounds found are $[Cs@[18]crown-6]_3[Sn_5Bi_3]\cdot 7NH_3$ (**1**), $[K@[18]crown-6]_{1.5}[Cs@[18]crown-6][Cs@([18]crown-6)_2]_{0.5}[Sn_5Bi_3]\cdot 3.98NH_3$ (**2**), $[Na@DB[18]crown-6]_2[Na(NH_3)_6][Sn_5Bi_3]\cdot 14NH_3$ (**3**) and $[Cs@[2.2.2]crypt]_6[Sn_5Bi_3]_2\cdot 9.53NH_3$ (**4**). (The complete single crystal X-ray diffraction analysis can be found in the Supporting Information.)

The anion present in all compounds is depicted in Figure 1 and consists of five tin and three bismuth atoms. The overall charge of −3 was deduced from the number of counterions present in each crystal structure. It is not possible to assign these charges to specific atoms, but as the bismuth atoms are all three bonded and are therefore formally neutral, the negative charges must be divided among the five tin atoms.

The $[Sn_5Bi_3]^{3-}$ anion deviates from the $[Sn_9]^{4-}$ ion (C_{4v}) by removing one vertex of the capped quadrangular face –leaving a buckled 5-atomic face– and substituting the capping and the two adjacent basal atoms by bismuth. The symmetry of the anion is thereby reduced to C_s. The great difference in electron density between tin and bismuth atoms allows the substitution pattern of the cluster directly to be identified from X-ray data and affirms the results presented by Dehnen et al. for the $[Sn_5Sb_3]^{3-}$ cluster. According to the Wade rules, the $[Sn_5Bi_3]^{3-}$ anion has a total of $(5\times4)+(3\times5)+3=38$ valence electrons. Subtracting $(8\times2)=16$ electrons for the lone pair on each atom, 11 skeleton electron pairs remain. Considering the eight vertices, the anion represents, like its analogue $[Sn_5Sb_3]^{3-}$, an *arachno*-cluster ($n+3$).[32]

In **1** the anion is surrounded by three $[Cs@[18]crown-6]^+$ complexes. One Cs^+ cation lies in front of the open face and has contacts to Bi2 and Bi3 with 3.964(2) Å and 4.128(2) Å. Due to the long interatomic distances of at least 5.2 Å interactions with Bi1, Sn1 and Sn2 can be excluded. The two remaining $[Cs@[18]crown-6]^+$ complexes cap the quadrangular basal plane and the triangular face Sn2–Sn4–Bi2. Cs–Sn/Bi distances vary between 4.034(2) Å and 4.379(2) Å.

The $[Sn_5Bi_3]^{3-}$ anion in **2** is disordered over two positions with a ratio of 0.52:0.48. The disorder can in general be described as a 70°-rotation of the anion around an imaginary axis to the Cs^+-cation in front of the pentagonal open face. The Cs–Bi distances for both components range from 3.783(1) Å to 4.103(2) Å. The disorder of the anion corresponds to the positional disorder of the crown ether that chelates the cesium cation. The ratio is here found to be 0.54:0.46.

Also disordered over two positions is the $[Sn_5Bi_3]^{3-}$ ion in **3**, but in difference to **2** the symmetry element to convert the components into each other is a mirror plane through the anion. The ratio is 0.55:0.45. Contacts to sodium cations are not present, as two of the three sodium cations are chelated by DB[18]crown-6 molecules and their coordination spheres are saturated by two ammonia molecules each. The third sodium cation forms a distorted hexammine-complex.

Structure **4** contains two symmetry independent $[Sn_5Bi_3]^{3-}$ anions (A and B), each disordered over two positions. For A a ratio of 0.83:0.17 and for B of 0.68:0.32 is found. The use of [2.2.2]crypt prohibits cation-anion interactions and thus causes the high degree of disorder in this structure which cannot be described by means of a simple symmetry element. Bond lengths in $[Sn_5Bi_3]^{3-}$ for structures **1–4** are $d(\text{Sn–Sn}) = 2.929(6)$ Å $-$ 3.301(5) Å, $d(\text{Sn–Bi}) = 2.876(6)$ Å $-$ 3.018(7) Å and $d(\text{Bi–Bi}) = 2.984(4)$ Å $-$ 3.029(1) Å. Due to 3*centre*-bonding contributions the tin bonds are slightly elongated in contrast to the other bonds. The highest values are calculated especially for Sn1/2–Sn5. The geometries of the anion in the different crystal structures were compared based on the diagonal ratio $d = d_1/d_2$ of the quadrangular basal plane, the distance between Sn1 and Sn2, the height h, measured from Bi1 to the basal plane as well as the angle α between the two planes Sn1–Bi1–Sn2 and
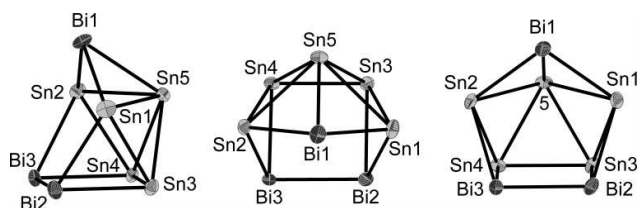
Figure 1. $[Sn_5Bi_3]^{3-}$ anion from different perspectives.

Sn1–Bi2–Bi3–Sn2 (Table 1). Despite the substitution with bismuth atoms the basal plane deviates only very slightly from the quadratic shape. The Sn1–Sn2 distance and the height h differ by 0.12 Å at most and thus are rather independent from the packing conditions, while for the angle α such a dependency is very likely. In **1** only Bi1 and Bi2 have contact to the coordinating Cs^+ cation, thus the angle is widened significantly in contrast to structure **2** in which cation-anion interactions to all bismuth atoms exist. Also, in **3** and **4**, with no direct cation-anion interactions, diverging angles are calculated, which can only be attributed to the specific surroundings in the crystals.

DFT-calculations of the localized molecular orbitals show the presence of 3*centre*-bonds in the tin triangles Sn1–Sn3–Sn5 and Sn2–Sn4–Sn5 (Figure 2, see more Details in the Supporting Information), which supports the structure interpretation of the anion. Among the orbitals representing 2*centre*-bonds different kinds can be distinguished. The orbital on the Sn3–Sn4-axis,

Table 1. Geometry of the $[Sn_5Bi_3]^{3-}$ –anion compared based on different parameters.

	1	**2***	**3***	**4***
d	1.02	1.06/1.00	1.04/1.02	1.01/1.01
Sn1-Sn2 [Å]	4.648	4.587/4.654	4.668/4.690	4.570/4.666
h [Å]	4.206	4.245/4.205	4.153/4.122	4.200/4.152
α [°]	40.31	34.83/32.00	47.34/48.68	41.19/39.33

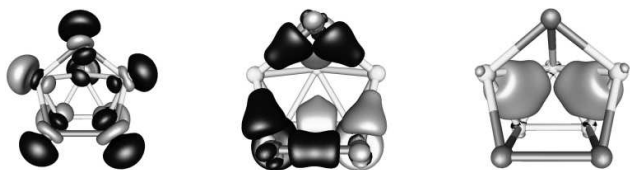[*] Disordered structures contain two cluster units.

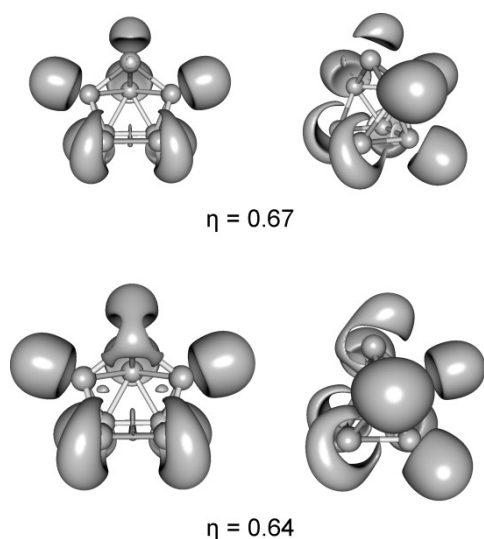**Figure 2.** Localized molecular orbitals of $[Sn_5Bi_3]^{3-}$.

η = 0.67

η = 0.64

Figure 3. Electron localization function of $[Sn_5Bi_3]^{3-}$.

which would be expected to have a cylindrical shape, shows a clear expansion into the Sn3–Sn4–Sn5 triangle. This effect might indicate some delocalization of the electrons within the tin backbone, as the other orbitals are not affected or the effect is much less pronounced. Furthermore, the orbitals of the heteroatomic bonds show a conical expansion in the direction of the bismuth atoms that is a little bit more pronounced for the orbitals in the open pentagonal face and can be explained by the electronegativity difference of the elements. The slightly asymmetric form of the lone pair orbital at Bi1 hints at a special electronic situation in this region that is also found in calculations of the electron localization function (ELF) but is not completely understood yet.

The ELF is depicted for different isosurface values in Figure 3 (see more Details in the Supporting Information). The monosynaptic basins at the tin atoms are populated with $2.29e^-$–$2.35e^-$ ($σ^2 = 1.31$–1.32), while for the more electronegative Bi2 and Bi3 a value of $3.40e^-$ ($σ^2 = 2.00$) is found.

Unexpectedly, for Bi1 two monosynaptic basins with populations of $3.65e^-$ ($σ^2 = 2.14$) and $0.96e^-$ ($σ^2 = 0.75$) are present. The attractor of the basin with lower population is located in front of the open pentagonal face of the anion and its isosurface fuses at $η = 0.64$ with the one of the other monosynaptic basins at Bi1 and the two adjacent disynaptic basins, which are populated with $1.63e^-$ ($σ^2 = 1.13$) each. In return, for the additional monosynaptic basin the attractor between Bi1 and Sn5 is missing. The disynaptic basins between Sn3–Bi2 and Sn4–Bi3 contain $1.25e^-$ ($σ^2 = 0.93$) and are therefore slightly depopulated in contrast to the basins between Sn1–Bi2 and Sn2–Bi3 with $1.54e^-$ ($σ^2 = 1.07$) each. The homoatomic basins have $1.49e^-$ ($σ^2 = 1.03$) for bismuth and $1.93e^-$ ($σ^2 = 1.28$) for tin. The trisynaptic basins are both populated with $1.55e^-$ ($σ^2 = 1.10$). In contrast to the localized molecular orbitals, the delocalization indices of the ELF do not indicate an increased delocalization of the electrons in the tin framework compared to other tinbismuthide clusters.

ESI-MS characterizations were done in a mixture of ethylenediamine and DMF (the spectra can be found in the Supporting Information). We surveyed solutions of MSnBi ($M =$ Li–Cs), whereupon the best results could be obtained for a solution of RbSnBi/[18]crown-6. Problematically, most of the time the signal of the $[Sn_5Bi_3]^-$ anion at $m/z = 1220.43$ is of very low intensity and can additionally be overlaid by two different fragments. On the one hand there is the signal of $[Sn_{10}]^-$ at $m/z = 1187.02$ that, if very strong, can lead to an overlap. On the other hand, there is a signal at about $m/z = 1226$, which could not be identified yet, but seems to emanate from a carbon-containing fragment. Remarkably, for all solid-state starting materials used for ESI-MS characterization in general the same anions are formed in solution, independent from the chosen counterion and the chelating agent. The use of CsSnBi as precursor phase has in our studies led solely to the crystallization of eight-atomic species, namely $[Sn_5Bi_3]^{3-}$ and $[Sn_4Bi_4]^{4-}$,[33] while for the potassium analogue only the $[Sn_2Bi_2]^{2-}$ anion was found up to now.[34] This indicates a trend, as for the intermediate sized Rb^+ counterion four-, six- and

eight-atomic species ($[Sn_2Bi_2]^{2-}$, $[Sn_3Bi_3]^{5-}$ and $[Sn_3Bi_5]^{3-}$) crystallized.[34]

Conclusions
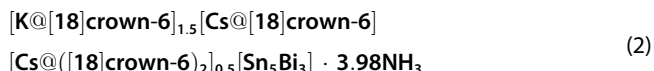
In summary the geometry of the novel *arachno* $[Sn_5Bi_3]^{3-}$ anion was found to formally derive from the $[Sn_9]^{4-}$ anion. It also confirms the buildup postulated for its lighter analogue $[Sn_5Sb_3]^{3-}$. Furthermore, it shows some structural flexibility depending on the packing conditions in the crystal structure. The use of Cs^+ counterions facilitates its crystallization independent from the kind of chelating agent present. Thereby, the capping of the 5-atomic open face by the cation seems to have a positive effect on the stability of the observed compounds. DFT-calculations of the localized molecular orbitals show the presence of 3*centre*-bonds in the tin triangles of the cluster anion. The elucidation of the electronic structure of the $[Sn_5Bi_3]^{3-}$ anion remains the topic of further investigations. The functionalization of the here reported heteroatomic anion for example by transition metal complexes remains a topic for future experiments.

Experimental Section

All manipulations were carried out under an argon atmosphere using standard Schlenk and glovebox techniques. The solid-state materials with the nominal composition CsSnBi and $NaSnBi_3$ were synthesized from stoichiometric amounts of the elements at 975 °C in tantalum containers, which were jacketed in glass ampoules to avoid oxidation. [18]crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and DB[18]crown-**6** (2,3,11,12-Dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene) were dried in vacuum, [18]crown-6 was additionally sublimated prior to use. [2.2.2]crypt (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) and $K_3[Fe(CN)_6]$ were used without further purification. Ammonia was condensed on elemental potassium and dried for at least 24 h.

$$[\mathbf{Cs@[18]crown\text{-}6}]_3[\mathbf{Sn_5Bi_3}] \cdot \mathbf{7NH_3} \quad (1)$$
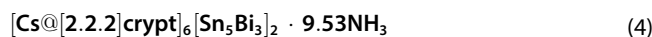
CsSnBi (230 mg, 0.5 mmol) and [18]crown-6 (80 mg, 0.3 mmol) were dissolved in approximately 10 ml of liquid ammonia forming a reddish-brown reaction solution. After several weeks at 236 K crystals of $[Cs@[18]crown\text{-}6]_4[Sn_4Bi_4] \cdot 12NH_3$ could be found in the residuum. About four months later, black block shaped crystals of $[Cs@[18]crown\text{-}6]_3[Sn_5Bi_3] \cdot 7NH_3$ had formed on the wall of the Schlenk tube.

$$[\mathbf{K@[18]crown\text{-}6}]_{1.5}[\mathbf{Cs@[18]crown\text{-}6}]$$
$$[\mathbf{Cs@([18]crown\text{-}6)_2}]_{0.5}[\mathbf{Sn_5Bi_3}] \cdot \mathbf{3.98NH_3} \quad (2)$$

A mixture of CsSnBi (400 mg, 0.87 mmol) and [18]crown-6 (80 mg, 0.3 mmol) was extracted with approximately 10 ml of liquid ammonia, giving a reddish brown reaction solution. After storage at 236 K for about three days, $K_3[Fe(CN)_6]$ (132 mg, 0.4 mmol) was added. After several months, crystals of $[K@[18]crown\text{-}6]_{1.5}[Cs@[18]crown\text{-}6][Cs@([18]crown\text{-}6)_2]_{0.5}[Sn_5Bi_3] \cdot 3.98NH_3$ could be isolated and characterized via single crystal X-ray diffraction.

$$[\mathbf{Na@DB[18]crown\text{-}6}]_2[\mathbf{Na(NH_3)_6}][\mathbf{Sn_5Bi_3}] \cdot \mathbf{14NH_3} \quad (3)$$
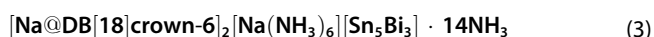
The solid state material $NaSnBi_3$ could not be removed from the tantalum container wall, hence the cap of the ampoule with the adherent phase (ca. 400 mg) was put in the Schlenk tube together with DB[18]crown-6 (20 mg, 0.1 mmol). About 15 ml of dried ammonia were condensed and the Schlenk tube was stored at 236 K. After some days the solid-state starting material dissolved, forming a dark reddish-brown reaction solution. By a micro fissure in the glass the ammonia evaporated slowly, leaving behind a black, oily substance. From this oil black block shaped crystals of $[Na@DB[18]crown\text{-}6]_2[Na(NH_3)_6][Sn_5Bi_3] \cdot 14NH_3$ could be isolated and characterized via single crystal X-ray diffraction.

$$[\mathbf{Cs@[2.2.2]crypt}]_6[\mathbf{Sn_5Bi_3}]_2 \cdot \mathbf{9.53NH_3} \quad (4)$$

A mixture of CsSnBi (184 mg, 0.4 mmol) and [2.2.2]crypt (94 mg, 0.25 mmol) was dissolved in approximately 10 ml of liquid ammonia, giving a reddish brown reaction solution that was stored at 236 K. After several weeks, black crystals of $[Cs@[2.2.2]crypt]_6[Sn_5Bi_3]_2 \cdot 9.53NH_3$ had formed.

Single Crystal X-ray Diffraction

Single crystals were selected under Galden HT 230 and mounted on micro loops (MiTeGen, 100 μm–300 μm). Data were collected at 123(1) K on a SuperNova (Agilent) with MoK_α-radiation (Microfocus) for **1** and **2**, on a SuperNova (Agilent) with CuK_α-radiation (Microfocus) for **3** and on a Gemini R Ultra (Agilent) with CuK_α-radiation (sealed tube) for **4**. Data reduction and integration was done with the CrysAlisPRO software.[35] Structures were solved with olex.solve[36] or SHELX-S and refined on F^2 using SHELX-L.[37]

Crystallographic data for the compound has been deposited in the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2357636 (1) CCDC-2357637 (2), CCDC-2357638 (3) and CCDC-2358391 (4) (Fax: +44-1223-336-033, E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Electrospray Mass Spectrometry (ESI-MS)

The precursor phases and [18]crown-6 were extracted in about 2 ml ethylenediamine and stirred for 2 h to guarantee an adequate dissolution. Afterwards the mixture was diluted with dimethylformamide.

ESI-MS was performed on a TSQ 7000 spectrometer by Thermoquest Finnigan in the negative ion mode with a spray voltage of 3 kV, a capillary voltage of 5 V, a tube lens voltage of −95 V and a capillary temperature of 200 °C. All species were detected singly charged.

Computational Methods

Quantum chemical calculations were performed with the program package TURBOMOLE.[38] Basis sets were of def2-TZVPP quality.[39–41] For a better description of relativistic effects effective core potentials for tin (ecp-28-mdf) and bismuth (ecp-60-mdf) were used.[42] Geometry optimization was done without symmetry restrictions. The COSMO model was applied, the chosen ε of 16.9 corresponds to ammonia.[43] For DFT calculations the B3LYP-functional was used.[44–49] HF calculations were used for calculations of the electron localization function[50–54] which was calculated with the program DGRID.[55]

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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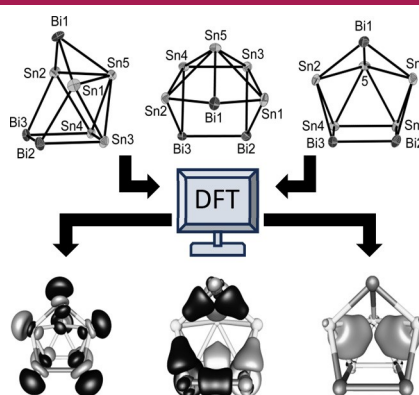
U. Friedrich, F. Schmidt, Prof. Dr. N. Korber*

1 – 6

Synthesis and Single Crystal X-ray Characterization of [Sn$_5$Bi$_3$]$^{3-}$