

Cite this: *Chem. Commun.*, 2012, **48**, 10544–10546

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COMMUNICATION

Synthesis of heteroatomic Zintl anions in liquid ammonia – the new highly charged $[\text{Sn}_4\text{Bi}_4]^{4-}$ and fully ordered $[\text{Sn}_2\text{Bi}_2]^{2-}$ †Ute Friedrich,^a Maria Neumeier,^b Carina Koch^b and Nikolaus Korber*^a

Received 17th February 2012, Accepted 5th September 2012

DOI: 10.1039/c2cc35380f

The new Zintl anion $[\text{Sn}_4\text{Bi}_4]^{4-}$, synthesized by dissolving CsSnBi in liquid ammonia, forms a monocapped nortricyclane-like cage. Its electron localization function (ELF) analysis shows evidence for 3-centre bonding. The analogous reaction with KSnBi results in a crystallographically fully ordered tetrahedral $[\text{Sn}_2\text{Bi}_2]^{2-}$ ion.

Since the discovery by Joannis in 1891^{1,2} and the development of Eduard Zintl's well known potentiometric analysis,^{3–5} the chemistry of main group metal polyanions, often called Zintl anions, has flourished, greatly facilitated by the introduction of cryptands as alkali metal cation ligands by J. Corbett.^{6,7} Next to the better known homoatomic Zintl anions, heteroatomic polyanions have also been investigated by the same methods. Reported molecular species include $[\text{Sb}_2\text{Ge}_7]^{2-}$, $[(\text{SbGe}_8)(\text{Ge}_8\text{Sb})]^{4-}$,⁸ $[\text{In}_4\text{Bi}_5]^{3-}$, $[\text{InBi}_3]^{2-}$, $[\text{GaBi}_3]^{2-}$,⁹ $[\text{TlSn}_8]^{3-}$ and $[\text{TlSn}_9]^{3-}$.¹⁰ The tetrahedral cages $[\text{Te}_2]^{2-}$,¹¹ $[\text{Pb}_2\text{Sb}_2]^{2-}$ ¹² or $[\text{Sn}_2\text{Bi}_2]^{2-}$,¹³ which have the same number of valence electrons as the phosphorus molecule P_4 , have also been among the early examples. The isostructural anion $[\text{Sn}_2\text{Sb}_2]^{2-}$ was obtained by Dehnen *et al.* in 2009.¹⁴ In 2011 the same group reported the structural characterisation of $[\text{Sn}_7\text{Bi}_2]^{2-}$ as one product of the reaction between $[\text{K}(\text{2.2.2crypt})]_2[\text{Sn}_2\text{Bi}_2]\text{-en}$ and ZnPh_2 .¹⁵ Unfortunately, all of the crystal structures of tin–bismuth anions reported to date show severe disorder, which does not allow the Sn and Bi positions to be distinguished.

In this communication we report the preparation of $[\text{K}(\text{18crown-6})]_2[\text{Sn}_2\text{Bi}_2]\text{-2NH}_3$ (**1**) and $[\text{Cs}(\text{18crown-6})]_4[\text{Sn}_4\text{Bi}_4]\text{-12NH}_3$ (**2**), in which fully ordered anions could be characterised. The starting materials of nominal compositions KSnBi and CsSnBi , respectively, were prepared at the comparatively low temperature of 723 K using glass ampoules. Each solid state material was dissolved in liquid ammonia together with an equimolar amount of [18]crown-6. After storage at 237 K, reddish-brown crystals of **1** (Table 1) and black crystals of **2** (Table 1) could be isolated from solution. Both crystalline

compounds reveal the usual pronounced thermal instability of ammoniates.

The anion $[\text{Sn}_2\text{Bi}_2]^{2-}$ of compound **1** is anchored in the crystal structure by contact with two K^+ cations, as depicted in Fig. 1. Disorder of the anion, which has been reported for $[\text{K}(\text{2.2.2crypt})]_2[\text{Sn}_2\text{Bi}_2]\text{-en}^{13}$ or $[\text{K}(\text{18crown-6})]_2[\text{Sn}_2\text{Bi}_2]^{16}$ is prevented by the use of [18]crown-6 as a sequestering agent on the one hand and by the low temperatures during the crystallisation process on the other. Goicoechea and Sevov demonstrated that the use of [18]crown-6 as a sequestering agent can successfully prevent disorder during the investigation of the Zintl ion Si_9^{2-} .¹⁷ This anion, which is fully ordered in $[\text{K}(\text{18crown-6})]_2\text{Si}_9\text{-py}$, shows great disorder in its cryptate compound $[\text{K}(\text{2.2.2crypt})]_2\text{Si}_9$.

The absence of disorder allowed the bond lengths within this anion to be determined for the first time (Table 2). As expected, the largest distance of 3.0316(6) Å in the tetrahedral anion can be found between the two bismuth atoms, whereas the two tin atoms are closest to each other with a distance of 2.8700(8) Å. The bond lengths between bismuth and tin atoms range from 2.9815(10) Å to 2.9923(8) Å. The total average bond length for the tetrahedron is calculated to be 2.9749 Å, which is in accordance with the value of 2.957 Å found by Critchlow and Corbett¹³ and 2.949 Å reported by Dehnen and co-workers¹⁶ for the disordered anions.

The electron spray mass spectrum of a fresh solution of KSnBi in ethylenediamine–dimethylformamide shows no signal for the $[\text{Sn}_2\text{Bi}_2]^-$ fragment. Instead, mainly nine-atom species $\text{Sn}_{9-x}\text{Bi}_x^-$ ($x = 0\text{--}3$) are present in solution, which seem to be the more stable cages. The ^{119}Sn NMR spectrum of the crude reaction mixture shows a singlet at -1746 ppm ($J(^{119}\text{Sn}\text{--}^{117}\text{Sn}) = 1532$ Hz), which can be assigned to $[\text{Sn}_2\text{Bi}_2]^{2-}$. The upfield shift with respect to the values of -1575 ppm ($J(^{119}\text{Sn}\text{--}^{117}\text{Sn}) = 1638$ Hz)¹⁸ found by Wilson *et al.* and of -1650 ppm¹⁵ reported by Lips and Dehnen is due to the presence of [18]crown-6 in solution. Studies on the influence of cryptands on the chemical shift show an increasing upfield shift with an increasing amount of sequestering agent.¹⁹ In addition, nine-atom species such as Sn_9^{4-} (-1267 ppm) and Sn_6Bi_3^- (-1244 ppm) could be identified (for more details see ESI†).

The use of caesium as the alkali metal in the solid precursor material resulted in the formation of **2** upon dissolution in liquid ammonia. The central structural unit of **2** is a novel eight-atom tin–bismuth species (Fig. 2 and 3). The triangular

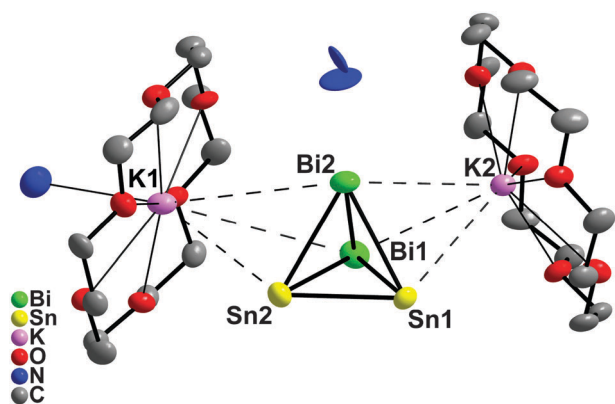
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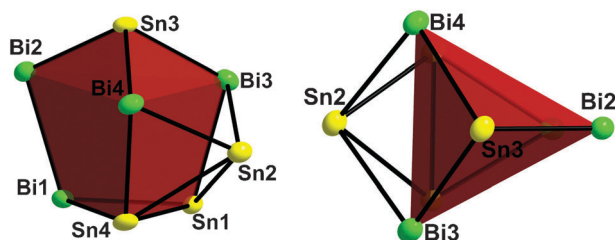
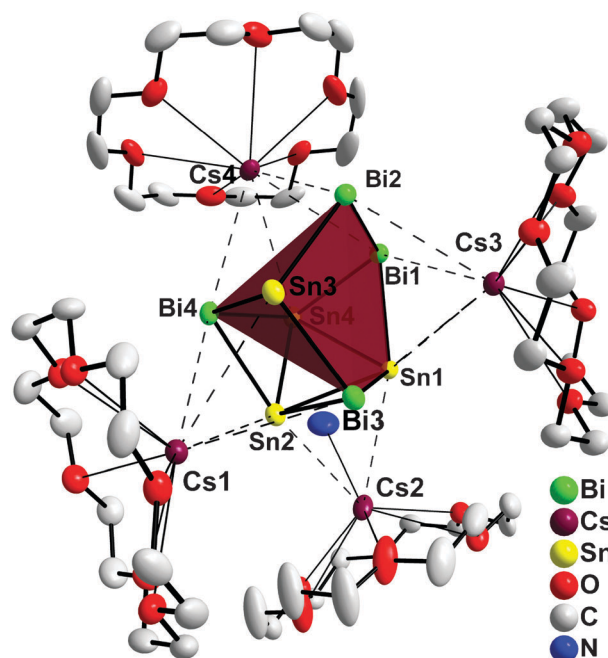
Table 1 Crystallographic data of **1** and **2**

| | Compound 1 | Compound 2 |
|------------------------------------|---|--|
| Formula | C ₂₄ H ₅₄ Bi ₂ K ₂ N ₂ O ₁₂ Sn ₂ | C ₄₈ H ₁₃₂ Bi ₄ Cs ₄ N ₁₂ O ₂₄ Sn ₄ |
| Formula weight/g mol ⁻¹ | 1296.23 | 3103.98 |
| Crystal system | Orthorhombic | Triclinic |
| Space group, Z | P2 ₁ 2 ₁ 2 ₁ , 4 | P1̄, 2 |
| a/Å | 10.4079(7) | 15.5211(2) |
| b/Å | 14.4988(10) | 16.7664(2) |
| c/Å | 27.679(2) | 21.7756(2) |
| α/° | 90 | 72.442(1) |
| β/° | 90 | 87.793(1) |
| γ/° | 90 | 62.570(1) |
| V/Å ³ | 4176.8(5) | 4761.4(1) |
| Radiation, λ | Mo-Kα, 0.71073 | Mo-Kα, 0.71073 |
| T/K | 123(1) | 123(1) |
| μ/mm ⁻¹ | 9.831 | 9.964 |
| R _{int} | 0.0958 | 0.0783 |
| R ₁ (all data) | 0.0445 | 0.0612 |
| wR ₂ (all data) | 0.0887 | 0.0931 |
| S | 0.944 | 1.047 |

**Fig. 1** Coordination of [Sn₂Bi₂]²⁻ by [K([18]crown-6)]⁺ in **1**. Anisotropic displacement ellipsoids at the 50% probability level, hydrogen atoms neglected.**Table 2** Bond lengths of [Sn₂Bi₂]²⁻ in **1**

| Atoms | d/Å | Atoms | d/Å |
|---------|------------|---------|-----------|
| Bi1–Bi2 | 3.0316(6) | Bi2–Sn2 | 2.9857(9) |
| Bi1–Sn1 | 2.9923(8) | Bi2–Sn1 | 2.9880(8) |
| Bi1–Sn2 | 2.9815(10) | Sn1–Sn2 | 2.8700(8) |

base of the nortricyclane-like cage consists of two tin atoms and one bismuth atom, three bismuth atoms connect the base to the apical tin atom. The single resulting symmetrical quadrangular face (Sn1–Sn4–Bi4–Bi3) is capped by a tin atom, in such a way that an approximate mirror plane bisecting the anion is observed. The height *h* of the cage, as defined by Von Schnering and Hönl,²⁰ is calculated to be 4.2230 Å, the

**Fig. 2** Structure of [Sn₄Bi₄]⁴⁻. Left: side-view. Right: top-view.**Fig. 3** Interactions between [Sn₄Bi₄]⁴⁻ and [Cs([18]crown-6)]⁺ counteranions in **2**. Anisotropic displacement ellipsoids pictured at the 50% probability level, hydrogen atoms neglected.

angles are $\gamma(\text{Sn3–Bi2–Bi1}) = 97.614(12)^\circ$, $\delta(\text{Sn3–Bi3–Sn1}) = 103.007(14)^\circ$ and $\varepsilon(\text{Sn3–Bi4–Sn4}) = 103.414(14)^\circ$. The isostructural clusters [E₇Tl]²⁻ (E = P, As) were characterised by Goicoechea *et al.* in 2011.²¹ These were synthesized by a metathesis reaction between ethylenediamine solutions of K₃E₇ (E = P, As) and TlCl. A well resolved crystal structure of [TlAs₇]²⁻ was obtained exclusively by use of [18]crown-6 as a sequestering agent.

Considering the nortricyclane cage of **2**, its distribution of tin and bismuth atoms is in accordance with the minimum structure previously calculated by Dehnen *et al.*,²² which demonstrates the predictive power of quantum chemical calculations even for these heavy atom clusters. However, a closed-shell Sn₃Bi₄ cage of this configuration would have an overall charge of –6 (one formal charge per threefold-bonded tin atom, one formal charge per twofold-bonded bismuth atom),

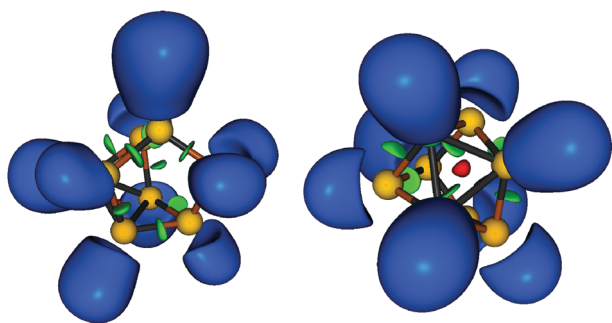


Fig. 4 ELF representation of $[\text{Sn}_4\text{Bi}_4]^{4-}$, $\eta = 0.66$; monosynaptic valence basins, blue; monosynaptic core basins, yellow; disynaptic valence basins, green; trisynaptic valence basins, red.

Table 3 Bond lengths of $[\text{Sn}_4\text{Bi}_4]^{4-}$ in **2**

| Atoms | $d/\text{\AA}$ | Atoms | $d/\text{\AA}$ |
|---------|----------------|---------|----------------|
| Bi1–Sn1 | 2.9594(5) | Bi4–Sn4 | 2.9495(5) |
| Bi1–Sn4 | 2.9717(5) | Bi4–Sn3 | 2.9826(5) |
| Bi1–Bi2 | 3.0307(3) | Bi4–Sn2 | 2.9886(5) |
| Bi2–Sn3 | 2.8647(5) | Sn1–Sn2 | 3.0932(6) |
| Bi3–Sn1 | 2.9542(5) | Sn1–Sn4 | 3.1363(6) |
| Bi3–Sn3 | 2.9799(5) | Sn2–Sn4 | 3.0515(7) |
| Bi3–Sn2 | 3.0173(5) | | |

which is an unusually high charge for ions observed in solution. The formal coordination of the $[\text{Sn}_3\text{Bi}_4]^{6-}$ ion by a Sn^{2+} cation reduces the charge, but leads to a cluster in which the four remaining negative charges cannot be assigned to four specific atoms any more. The electron distribution closest to a traditional Lewis formula would have one formal charge at Sn3 and Bi2 each and the remaining two charges indeterminately distributed between Sn1, Sn2 and Sn4. Electron localization function calculations (ELF)^{23–27} on $[\text{Sn}_4\text{Bi}_4]^{4-}$ support this view of the chemical bonding in the cage anion. Disynaptic basins can be found between the bismuth and tin atoms as well as between Bi1 and Bi2. Each basin is populated by 1.42 to 1.73 electrons. One trisynaptic basin is located in the middle of the triangular face Sn1–Sn2–Sn4 with a population of 1.52 electrons (Fig. 4). This basin complies with a 3-centre-bond and explains the elongated tin–tin bonds for this face that are observed in the crystal structure (Table 3). Each monosynaptic valence basin is populated by 2.10 to 2.27 electrons for all tin atoms and Bi2. For Bi1, Bi3 and Bi4 a population of 2.82 to 3.01 electrons can be found. The higher electron density in the valence basins of bismuth atoms is in accordance with results of Eisenstein *et al.*²⁸ Their theoretical calculations on $[\text{Sn}_2\text{Bi}_2]^{2-}$ proved that more charge is located on bismuth atoms ($-0.58e$) than on tin atoms ($-0.42e$).

The electron spray mass spectrum of a fresh solution of CsSnBi in ethylenediamine–dimethylformamide shows neither the $[\text{Sn}_2\text{Bi}_2]^-$ nor the $[\text{Sn}_4\text{Bi}_4]^-$ fragment. Again different nine-atom clusters are dominant in the spectrum, as was found for KSnBi.

The highly unstable solution of CsSnBi can be stabilized by the addition of small amounts of [18]crown-6. In this case the ESI mass spectrum reveals the formation of smaller fragments such as the $[\text{Sn}_2\text{Bi}_2]^-$ anion. ¹¹⁹Sn NMR experiments on the crude reaction mixture confirm the presence of $[\text{Sn}_2\text{Bi}_2]^{2-}$ and several nine atom species. The singlet at -1699 ppm with a coupling constant of $J(^{119}\text{Sn}-^{117}\text{Sn}) = 1525$ Hz (47 ppm upfield shift with respect to the KSnBi sample) is assigned to $[\text{Sn}_2\text{Bi}_2]^{2-}$. Further signals at -1185 ppm and -1162 ppm are attributed to Sn_9^{4-} and Sn_6Bi_3^- . Thus, $[\text{Sn}_4\text{Bi}_4]^{4-}$ clearly exists in the solid compound **2**, but its existence in solution has remained elusive up to now.

The preparation and structural analysis of **2** show that it is possible to obtain new Sn–Bi clusters by dissolving ternary alkali metal–tin–bismuth solid state materials in liquid ammonia. The crystallisation at low temperatures and the use of crown ethers as sequestering agents contribute to the prevention of disorder in the anions. An unusual bonding situation is encountered in $[\text{Sn}_4\text{Bi}_4]^{4-}$, which is currently the subject of further investigation.

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