A Step in Between: $[\text{Sn}_3\text{Bi}_3]^5^-$ and Its Structural Relationship to $[\text{Sn}_3\text{Bi}_5]^3^-$ and $[\text{Sn}_4\text{Bi}_4]^4^-$

Ute Friedrich and Nikolaus Korber[a]

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Supporting Information

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1 Compound [Rb@[2.2.2]crypt][Sn₃Bi₅] · 8.87 NH₃ (1)

1.1 Synthesis of 1

The starting material 'RbSnBi' was synthesized from stochiometric amounts of the elements in glass ampoules at 723 K. Heating and cooling was done with a 50 K/h rate. [2.2.2]crypt was used without further purification. 'RbSnBi' (165 mg, 0.2 mmol) and [2.2.2]crypt (113 mg, 0.3 mmol) were weighed into a baked-out Schlenk tube inside a glovebox. Afterwards about 10 ml of dry ammonia were condensed on the solids. The latter dissolved instantaneously forming a red-brown reaction solution. Parts of the starting material remained undissolved on the bottom of the Schlenk tube. The Schlenk tube was stored at 236 K. After about six weeks black, block-shaped crystals were formed in about 10% crystalline yield.

1.2 Crystal structure of 1

| Sum formula                  | C₅₄H₁₃₄Bi₅N₁₄O₁₈Rb₃Sn₃       | Temperature          | 123(1) K          |
|------------------------------|-------------------------------|----------------------|-------------------|
| M_r                          | 2937.95 g·mol⁻¹               | F(000)               | 2766.0            |
| Crystal form                 | block                         | Measured reflections | 71547             |
| Crystal size                 | 0.2x0.1x0.1 mm                | Independent reflections | 18665           |
| Crystal colour               | black                         | 2Θ-range             | 6.78°–52.63°      |
| Crystal system               | triclinic                     | Completeness         | 99.77%            |
| Space group                  | P1 (Nr.2)                     | hkl-range            | 16≤h≤16, 20≤k≤20, 30≤l≤30 |
|                             |                               | Absorption correction | multiscan        |
|                             |                               | Rint                 | 0.034             |
|                             |                               | Tmin, Tmax           | 0.606, 1.000      |
|                             |                               | R1, wR2 (all reflections) | 0.038, 0.081   |
|                             |                               | R1, wR2 (I ≥ 2σ(I)) | 0.031, 0.077     |
|                             |                               | S                    | 1.018             |
|                             |                               | Parameters/Restraints | 925/0             |
|                             |                               | Δρ_min               | -2.43 e·Å⁻³      |
|                             |                               | Δρ_max               | 3.25 e·Å⁻³       |
| Radiation                   | MoKα, λ = 0.71073 Å           |                      |                   |
| Device                      | SuperNova (Mo)                |                      |                   |

The [Sn₃Bi₅]³⁻ anion is disordered over two positions, as depicted in Figure S 1. All atoms of the lower occupied anionic part had to be treated with an EADP-Constraint. Due to the short distance Sn2A–N8 of 2.058(12) Å, N8 has the same site occupation factor of 0.87 as the higher occupied anionic part. Furthermore, the ammonia molecule N11 is disordered over two positions with a 0.81:0.19 ratio.
Figure S 1 – Rotational disorder of the $[\text{Sn}_3\text{Bi}_5]^3^-$ anion, depicted as full and open bonds; left: top-view, right: side-view; the anion is disordered with a 0.87:0.13 ratio; tin atoms light grey, bismuth atoms dark grey; anisotropic displacement ellipsoids at 50% probability level.

Figure S 2 – Asymmetric unit of 1; disorder shown as full and open bonds; H-atoms not depicted; anisotropic displacement ellipsoids at 50% probability level.
Compound $[\text{Rb}@[2.2.2]\text{crypt}]_3[\text{Sn}_3\text{Bi}_5] \cdot 8.87\text{NH}_3 \ (1)$

**Figure S 3** – Cell content of 1; disorder and H-atoms not shown; Rb, O, N and C atoms depicted isotropic; anisotropic displacement ellipsoids at 50% probability level
1.3 Quantumchemical calculations of \([Sn_3Bi_5]^{3-}\)

Quantumchemical calculations of \([Sn_3Bi_5]^{3-}\) were done with the program package \textsc{TURBOMOLE} [1] on DFT-level. Basis sets were of def2-TZVPP [2–8] quality and the B3LYP-functional [9–14] was used. For a better description of relativistic effects effective core potentials [15] were used (Sn: ecp-28-mdf, Bi: ecp-60-mdf). The COSMO model [16, 17] was applied to consider counterion effects. Therefore \(\epsilon = 16.9\) and unoptimized radii were chosen. All other default options of the program were accepted. Geometry optimization was done without symmetry restrictions (\(C_1\)). For the localization of the molecular orbitals the method of Boys with a number of 30000 sweeps was chosen.

Calculations of the electron localization function (ELF) were performed with the program \textsc{DGRID} [18] and based on HF-calculations (same parameters as for DFT calculations). For representations of the localized molecular orbitals the program \textsc{gOpenMol} [19] and of the ELF the program \textsc{Molekel} [20] was used.

\[
\begin{array}{cccc}
\text{d}_{\text{exp}} / \text{Å} & \text{d}_{\text{opt}} / \text{Å} & \text{d}_{\text{exp}} / \text{Å} & \text{d}_{\text{opt}} / \text{Å} \\
\text{Sn1–Sn2} & 3.096 & 3.151 & \text{Sn3–Bi1} & 2.969 & 2.993 \\
\text{Sn1–Sn3} & 3.145 & 3.284 & \text{Sn3–Bi4} & 2.924 & 2.952 \\
\text{Sn2–Sn3} & 3.120 & 3.150 & \text{Bi1–Bi2} & 2.968 & 2.995 \\
\text{Sn1–Bi1} & 2.985 & 2.994 & \text{Bi2–Bi5} & 2.897 & 2.943 \\
\text{Sn1–Bi3} & 2.920 & 2.950 & \text{Bi3–Bi5} & 3.018 & 3.053 \\
\text{Sn2–Bi3} & 3.018 & 3.069 & \text{Bi4–Bi5} & 3.006 & 3.053 \\
\text{Sn2–Bi4} & 2.998 & 3.071 & & & \\
\end{array}
\]

\textbf{Table S 2} – Experimental and geometry optimized distances in \([Sn_3Bi_5]^{3-}\)
1 Compound $[\text{Rb}@[2.2.2]\text{crypt}]_3[\text{Sn}_3\text{Bi}_5] \cdot 8.87\text{NH}_3$ (1)

Figure S 4 – Valence orbitals of $[\text{Sn}_3\text{Bi}_5]^{3-}$; tin atoms yellow, bismuth atoms green
Compound \([\text{Rb} @(2.2.2) \text{crypt}]_3 \text{[Sn}_3 \text{Bi}_5] \cdot 8.87 \text{NH}_3\) (1)

|       | HF          | DFT        |
|-------|-------------|------------|
|       | Mulliken   | NPA        | Paboon | Mulliken  | NPA        | Paboon |
| Bi1   | −0.39173   | −0.44847   | −0.3430 | −0.36572  | −0.40288   | −0.2714 |
| Bi2   | −0.76735   | −0.75356   | −0.9445 | −0.71733  | −0.69899   | −0.7601 |
| Bi3   | −0.47947   | −0.52898   | −0.4057 | −0.47467  | −0.51213   | −0.4145 |
| Bi4   | −0.47981   | −0.52928   | −0.4060 | −0.47532  | −0.51228   | −0.4150 |
| Bi5   | −0.12529   | −0.09375   | −0.1620 | −0.16385  | −0.13020   | −0.0998 |
| Sn1   | −0.25067   | −0.23289   | −0.2702 | −0.26640  | −0.26060   | −0.3529 |
| Sn2   | −0.25587   | −0.18109   | −0.1988 | −0.27167  | −0.22221   | −0.3338 |
| Sn3   | −0.24982   | −0.23199   | −0.2697 | −0.26503  | −0.26071   | −0.3526 |

Table S 3 – Different population analysis for \([\text{Sn}_3 \text{Bi}_5]^{3−}\)

The lowest negative charge is located on Bi5, which is formally neutral and only involved in homoatomic bonds. As it is expected, for the two-bonded Bi2 the highest charge is found. In general the negative charge within the tin-triangle is distributed almost equally.

![Figure S 5](https://example.com/figureS5.png)

Figure S 5 – Localized molecular orbitals of \([\text{Sn}_3 \text{Bi}_5]^{3−}\); tin atoms yellow, bismuth atoms green; left: orbital for a 3centre bond, middle: orbitals for 2centre bonds, right: orbitals representing lone pairs

The localized molecular orbitals show one orbital in the tin triangle representing a 3centre bond (Figure S 5 left). Conical orbitals for heteropolar 2centre bonds can be found on each Sn–Bi axis. Orbitals for homoatomic bismuth 2centre bonds show an almost cylindrical shape (Figure S 5 middle). One orbital representing a lone pair (Figure S 5 right) can be found on each atom, Bi2 has according to its formal charge two orbitals.
Figure S 6 – Electron localization function of $[\text{Sn}_3\text{Bi}_5]^{3-}$ for different orientations of the anion and different isosurface values $\eta$; tin atoms yellow, bismuth atoms green and numbered without element symbol.
2 Compound Rb₆[Sn₃Bi₃][Sn₄]₁/₄ • 6.75 NH₃ (2)

2.1 Synthesis of 2

The starting materials 'RbSn₂' and 'Rb₃Bi₂' were synthesized from stochiometric amounts of the elements in glass ampoules at 723 K. Heating and cooling was done with a 50 K/h rate. [2.2.2]crypt was used without further purification. 'RbSn₂' (323 mg, 1 mmol), 'Rb₃Bi₂' (674 mg, 1 mmol) and [2.2.2]crypt (80 mg, 0.2 mmol) were weighed into a baked-out Schlenk tube. Afterwards about 10 ml of dry ammonia were condensed on the mixture. The latter dissolved instantaneously forming a red-brown reaction solution. Parts of the starting materials remained undissolved on the bottom of the Schlenk tube. The Schlenk tube was stored at 236 K. After approximately eight weeks black, hexagonal rods formed on the bottom of the vessel in 10%-20% yield.

2.2 Crystal structure of 2

| Sum formula         | Bi₃N₀.₇₅Rb₆Sn₄          | Temperature | 123(1) K       |
|---------------------|-------------------------|-------------|----------------|
| M_r                 | 1709.09 g·mol⁻¹         | F(000)      | 2873.0         |
| Crystal form        | hexag. pillar           | Measured reflections | 10309         |
| Crystal size        | 0.3×0.1×0.1 mm          | Independent reflections | 1927         |
| Crystal colour      | black                   | 2θ-range    | 7.39°–48.71°   |
| Crystal system      | trigonal                | Completeness | 99.75%         |
| Space group         | P3c1 (Nr. 165)          | hkl-range   | −17 ≤ h ≤ 18  |
| ρ                   | 3.478 g·cm⁻³            | −18 ≤ k ≤ 12 |
| µ                   | 28.011 mm⁻¹             | −16 ≤ l ≤ 18 |
| a                   | 15.5790(4) Å            | H-atoms     | —              |
| b                   | 15.5790(4) Å            | R_int       | 0.062          |
| c                   | 15.5289(6) Å            | Absorption correction | analytical |
| α                   | 90°                     | T_min, T_max | 0.073, 0.160   |
| β                   | 90°                     | R1, wR2 (all reflections) | 0.062, 0.108 |
| γ                   | 120°                    | R1, wR2 (I ≥ 2σ(I)) | 0.040, 0.105 |
| V                   | 3264.0(2) Å³           | S           | 0.942          |
| Z                   | 4                       | Parameters/Restraints | 74/0         |
| Radiation           | MoKα, λ = 0.71073 Å    | Δρ_min      | −1.66 e·Å⁻³    |
| Device              | SuperNova (Mo)          | Δρ_max      | 6.74 e·Å⁻³     |

Table S 4 – Details on single crystal X-ray structure determination

The atoms Sn1, Bi1, Rb1 and Rb2 of the asymmetric unit are fully occupied and form a framework with channel-like cavities. Bonded to these rubidium cations are the ammonia molecules N(1)H₃ and N(2)H₃, both also fully occupied and partly depicted in Figure S 7 left. Within the channels [Sn₄]¹⁻ anions (built of Sn2 and Sn3), Rb3 and N(3)H₃ are disordered, with the site occupation factors given in Table S 5.
2 Compound Rb$_6$[Sn$_3$Bi$_3$][Sn$_4$]$_{1/4}$·6.75NH$_3$ (2)

| atom / compound | s.o.f. |
|-----------------|--------|
| Sn2             | 0.50   |
| Sn3             | 0.25   |
| Rb3             | 0.75   |
| N3              | 0.66   |

Table S 5 – Overview of disordered atoms

Figure S 7 – left: network with channel-like cavities along the crystallographic c-axis formed by cation-anion-interactions (cations white, anions grey), bonded ammonia molecules depicted partly; right: disordered [Sn$_4$]$_4^-$ anions along the channel midths, surrounded by N(3)H$_3$ and Rb3 (depicted partly)
2 Compound Rb$_6$[Sn$_3$Bi$_3$][Sn$_4$]$_{1/4}$·6.75NH$_3$ (2)

Figure S 8 – left: contacts of the [Sn$_3$Bi$_3$]$^{5-}$ anion to a total of 14 Rb$^+$ cations, Rb2 above and below the anion, contacts to disordered Rb3 depicted as broken bonds; middle: axial concatenation of two anions by Rb2; right: lateral conjunction of two anions by Rb1; coordination of disordered N3 depicted as broken bond.

Figure S 9 – left: content of the channel upright to the channel axis with different arrangements of the compounds, hourglass-like disorder of the [Sn$_4$]$^{4-}$ anions with contacts to Rb$^+$ cations and coordination of latter by ammonia molecules; right: projection along the c-axis.
2.3 Quantumchemical calculations of [Sn₃Bi₃]⁵⁻

For the quantumchemical calculations of [Sn₃Bi₃]⁵⁻ the same parameters as for [Sn₃Bi₃]³⁻ were used with exception of the functional that in this case was PBE-0 [9, 10, 21–23].

| Bond                  | \( d_{\text{exp}} / \text{Å} \) | \( d_{\text{DFT opt}} / \text{Å} \) | \( d_{\text{HF opt}} / \text{Å} \) | \( d_{\text{exp}} / \text{Å} \) | \( d_{\text{DFT opt}} / \text{Å} \) | \( d_{\text{HF opt}} / \text{Å} \) |
|-----------------------|-----------------|-----------------|-----------------|----------------|----------------|----------------|
| Sn₁–Sn₁'              | 3.124           | 3.162           | 3.210           | Sn₁'–Bi₁       | 2.998          | 2.964          | 2.983          |
| Sn₁–Sn₁''             | 3.124           | 3.162           | 3.210           | Sn₁''–Bi₁'     | 2.981          | 2.964          | 2.983          |
| Sn₁'–Sn₁''            | 3.124           | 3.162           | 3.210           | Sn₁''–Bi₁      | 2.981          | 2.964          | 2.983          |
| Sn₁–Bi₁               | 2.998           | 2.965           | 2.983           | Sn₁–Bi₁'       | 2.998          | 2.964          | 2.983          |
| Sn₁–Bi₁'              | 2.981           | 2.964           | 2.984           |                 |                |                |                |

Table S 6 – Experimental and optimized bond lengths in [Sn₃Bi₃]⁵⁻

The angle \( \alpha \) between a plane through the tin triangle and a plane through each triangle Sn–Sn–Bi was found to be 138.95(3)° in the crystal structure. For the optimized structure the values are 137.82° for \( \alpha_{\text{DFT}} \) and 138.37° for \( \alpha_{\text{HF}} \). For the chosen methods the geometry of the anion remains rather stable in comparison to the experimental values, although no Bi–Bi bonds are present and the stabilizing counterions are neglected in the calculations.

To examine the charge distribution within the anion, different population analysis are compared in Table S 7. It can be found that about 80% of the charge is distributed equally among the bismuth atoms, compared to formally 60% as deviated from the sum formula.

In Figure S 11 the molecular orbitals of the [Sn₃Bi₃]⁵⁻ anion are depicted. The energy values are given for DFT and HF calculations. Figure S 10 shows the localized molecular orbitals of the [Sn₃Bi₃]⁵⁻ anion. Two orbitals that represent lone pairs are located on each bismuth atom and one orbital is located on each tin atom. On every Sn–Bi bond an orbital for a 2centre bond is found. According to the electronegativity difference these orbitals expand in the direction of the bismuth atoms. Within the tin triangle an orbital for a 3centre bond is located. In accordance with the localized molecular orbitals are the results of the electron localization function (ELF) that is given in Figure S 12.

Figure S 13 shows different isomers of the [Sn₃Bi₃]⁵⁻ anion and their corresponding total energies. Isomer A (original anion) is found to be the most stable of all calculated isomers for
2 Compound Rb$_6$[Sn$_3$Bi$_3$][Sn$_4$]$_{1/4}$·6.75NH$_3$ (2)

|        | HF       | NPA      | Paboon   | DFT       | NPA      | Paboon   |
|--------|----------|----------|----------|-----------|----------|----------|
| Bi1    | -1.34134 | -1.40360 | -1.2515  | -1.27757  | -1.33009 | -1.2311  |
| Bi1'   | -1.34036 | -1.40305 | -1.2508  | -1.27651  | -1.32965 | -1.2304  |
| Bi1''  | -1.34110 | -1.40367 | -1.2514  | -1.27678  | -1.33010 | -1.2308  |
| Sn1    | -0.32607 | -0.26357 | -0.4158  | -0.38993  | -0.33708 | -0.4363  |
| Sn1'   | -0.32518 | -0.26285 | -0.4150  | -0.38908  | -0.33625 | -0.4354  |
| Sn1''  | -0.32595 | -0.26326 | -0.4155  | -0.39012  | -0.33684 | -0.4360  |

Table S 7 – Different population analysis for [Sn$_3$Bi$_3$]$^{5-}$

Figure S 10 – Localized molecular orbitals of [Sn$_3$Bi$_3$]$^{5-}$; tin atoms yellow, bismuth atoms green

at least 80kJ·mol$^{-1}$. While isomers D and E are not stable in the observed (experimental) geometry, the geometry optimization of isomer F runs back to the geometry of A.
Figure S 11 – Valence orbitals of [Sn₃Bi₃]⁵⁻; tin atoms yellow, bismuth atoms green
Compound Rb$_6[Sn_3Bi_3][Sn_4]_{1/4} \cdot 6.75 NH_3 (2)

**Figure S 12** – Electron localization function of $[Sn_3Bi_3]^{5-}$ for different orientations of the anion and different isosurface values $\eta$; tin atoms yellow, bismuth atoms green
Figure S 13 – Different possible isomers of \([\text{Sn}_3\text{Bi}_3]^{5-}\); **left column:** distribution of tin (white) and bismuth (grey) atoms in the starting geometries; **right column:** structures after geometry optimization, tin atoms yellow, bismuth atoms green; note that isomer F optimizes to the original configuration as found by single crystal X-ray diffraction.
3 Mass spectrometry analysis

3.1 General

ESI-MS was performed on a TSQ 7000 spectrometer by Thermoquest Finnigan in the negative ion mode. All ions were detected singly charged. The following parameters were chosen:

- spray voltage 3 kV
- capillary voltage 5 V
- tube lens voltage −95 V
- capillary temperature 200°C

The solid state starting materials and the chelating reagents were dissolved in about 2 ml of ethylenediamine and stirred until an intense red-brown colour was observed. Then the mixture was diluted with dimethylformamide. Upon addition of dimethylformamide the solutions start to decompose rapidly. The stability of the solution is further influenced by the alkali metal counterion, decreasing from Li to Cs.
3.2 ESI-MS of "RbSnBi"

Figure S 14 – Mass spectrum of "RbSnBi" – overview
Figure S 15 – Measured signal of the $[\text{Sn}_4\text{Bi}_4]^{-}$ fragment black and simulated blue in 'RbSnBi'
3.3 ESI-MS of "RbSnBi"/[2.2.2]crypt

Figure S 16 – Mass spectrum of "RbSnBi"/[2.2.2]crypt – overview
Figure S 17 – Measured signal of the $[\text{Sn}_4\text{Bi}_4]^{-}$ fragment black and simulated blue in 'Rb-SnBi'/[2.2.2]crypt
Figure S 18 – Measured signal of the \([\text{Sn}_3\text{Bi}_3]\)^− fragment black and simulated blue in "Rb-SnBi'/[2.2.2]crypt"
3 Mass spectrometry analysis

Figure S 19 – Measured signal at $m/z = 1398$ black in ‘RbSnBi’/[2.2.2]crypt and simulated $[\text{Sn}_3\text{Bi}_5]^{-}$ fragment (blue), $[\text{Sn}_{10}\text{Bi}]^{-}$ fragment (rose), both probably overlaid
3.4 ESI-MS of "RbSn$_2$/Rb$_3$Bi$_2"/[2.2.2]crypt

The full spectrum of "RbSn$_2$/Rb$_3$Bi$_2"/[2.2.2]crypt is depicted in Figure 20. Due to the rapid decomposition of the reaction mixture upon addition of dimethylformamide no better data could be obtained. The [Sn$_2$Bi$_2$]$^-$-fragment is the only anion that could clearly be identified in the spectrum.

![Figure S 20 - Mass spectrum of "RbSn$_2$/Rb$_3$Bi$_2"/[2.2.2]crypt – overview](image)
3.5 ESI-MS of "LiSnBi"

Additional ESI-MS characterization was done on a solution of "LiSnBi". The full spectrum of 'LiSnBi' is depicted in Figure S 21.

Figure S 21 – Mass spectrum of "LiSnBi" – overview
Figure S 22 – Measured signal of the [Sn₃Bi₃]⁻ fragment black and simulated blue in 'LiSnBi'
Figure S 23 – Measured signal at $m/z = 1401$ (black) in 'LiSnBi' and simulated $[\text{Sn}_3\text{Bi}_5]^{-}$ fragment (blue), $[\text{Sn}_{10}\text{Bi}]^{-}$ fragment (rose), both probably overlaid and very likely another (unknown) fragment with $m/z \approx 1414$ contributes to the signal.
Figure S 24 – Measured signal of the [LiSn₄Bi₄]⁻ fragment black and simulated blue in "LiSnBi"
4 Characterization of the starting material "RbSnBi"

For characterizations via powder diffraction a small amount of the solid state material with nominal composition 'RbSnBi' was comminuted with approximately the same volume of powdered fused silica in order to reduce absorption effects. The mixture was filled in capillary tubes ($\phi = 0.5 \text{ mm}$) and measured on a "Stadi P" diffractometer of STOE & Cie GmbH with Cu-K$_{\alpha 1}$-radiation.

For all characterized 'RbSnBi' materials, which were synthesized from stoichiometric amounts of the elements at different temperatures (450°C, 975°C or short heating with a Bunsen burner), RbBi$_2$ with slightly diverging cell constants in contrast to the ICSD reference could be found as crystalline phase (see Figure S 25). In some cases it was possible to find additional weak reflections of elemental tin.

Further Raman characterizations (DRX SmartRaman spectrometer of Thermo Scientific, $\lambda = 780 \text{ nm}$, $P = 0 \text{ mW} - 24 \text{ mW}$) hint at the presence of [Sn$_9$$^{4-}$] anions. The quality of the data does not allow to distinguish between "isolated" [Sn$_9$$^{4-}$] anions or the formation of the Rb$_{12}$Sn$_{17}$ phase in which the [Sn$_9$$^{4-}$] and the [Sn$_4$$^{4-}$] anions are present simultaneously.

**Figure S 25** – Powder diffractogram of 'RbSnBi' synthesized at 975°C; blue: experimental; purple: RbBi$_2$ (ICSD-55069)
5 Preparative studies

The phase "RbSnBi" was extracted in liquid ammonia with or without the addition of different chelating agents. If no chelating agent is present in solution, compounds containing the homoatomic $[\text{Sn}_9]^{4-}$ anion crystallize without exception from such solutions. The long known $[\text{Sn}_2\text{Bi}_2]^{2-}$ anion crystallized readily and much faster in contrast to other species, quite independently from the chelating agent (Figure S 26) and also from the chosen solid state material "$M\text{SnBi}"$ ($M = \text{Li-Rb}$). Only the extend of disorder in the anion can be affected by whether the cation is fully shielded (as with [2.2.2]crypt or [18]crown-6 with additional coordinating ammonia molecules) or able to establish direct cation-anion interactions.

![Diagram](image)

**Figure S 26** – Crystallizing anions from solutions of "RbSnBi" in the presence of different chelating agents

The crystallization of six- or eight-membered clusters seems to be influenced by both, the counterion of the solid state material and the chelating agent. It is remarkably that by now we only could crystallize tinbismuthides when a chelating agent was present in solution, although it does not necessarily need to appear in the crystal structure and is not necessary for the formation of tinbismuthides in solution according to ESI-MS. The amount of chelating agent added is found to be rather insignificant.

The system "RbSn$_2$/Rb$_3$Bi$_2" was used to demonstrate that the solid state materials do not need to contain preformed tinbismuthides, as to be expected from powder and Raman data. Systematic characterizations on the influence of the chelating agent are currently running.
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