Alternate precursors for the synthesis of binary Sb_2E_3 and Bi_2E_3 (E = S, Se, Te) nanoparticles by hot injection method

Monika Rusek, Georg Bendt, Christoph Wölper, and Stephan Schulz*

Dedication ((optional))

Abstract: Intermolecular-stabilized $\text{Sb}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **1** and $\text{Bi}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **2** readily react with $(\text{Me}_3\text{Si})_2\text{S}$ and $(\text{Et}_3\text{Si})_2\text{E}$ (E = Se, Te) at moderate temperatures with elimination of the corresponding silyl ether and subsequent formation of the corresponding group 15 chalcogenides Sb_2E_3 and Bi_2E_3 (hot injection method), which were characterized by XRD, SEM and EDX. In addition, the solid state structure of **1** was determined by single crystal X-ray diffraction.

Introduction

Binary antimony chalcogenides such as Sb_2S_3 , Sb_2Se_3 as well as ternary phases $\text{Sb}_2(\text{S/Se})_3$ show promising technical applications in sensitized solar cells (SSCs),^[1] battery materials,^[2] photovoltaics,^[3] and phase change memory devices.^[4] In addition, Sb_2Te_3 , Bi_2Se_3 , Bi_2Te_3 and their multinary solid solutions such as $(\text{Sb}_x\text{Bi}_{1-x})_2\text{Te}_3$ or $(\text{Sb}_x\text{Bi}_{1-x})_2(\text{Te}_y\text{Se}_{1-y})_3$ have a long standing history as thermoelectric (TE) materials,^[5] which allow the interchange of thermal energy and electricity for the utilization of waste heat and for cooling. Nanostructuring of a thermoelectric material was theoretically and experimentally shown to be a promising process to enhance the figure of merit ZT due to reduction of the thermal conductivity in the range of up to 50% for Bi_2Te_3 -based nanograined bulk materials.^[6] Moreover, Sb_2Te_3 , Bi_2Se_3 , Bi_2Te_3 and their alloys are currently intensely studied since they represent prototypical three-dimensional topological insulators (TIs). Topological insulators, which have been theoretically predicted before experimentally confirmed,^[7] are materials with a bulk insulating gap, but exhibiting quantum-Hall like behavior in zero magnetic fields.^[8] While topological states in most solid state materials are fragile and difficult to realize without extremely low temperature or high orders of magnetic fields in most materials systems, two- and three-dimensional topological insulators (TI) can overcome these physical boundaries and exhibit protected surface states and topological behavior potentially up to the room temperature regime. The Zhang group showed that binary chalcogenide materials Sb_2Te_3 , Bi_2Te_3 and Bi_2Se_3 , for which a strong spin-orbit coupling is observed, as well as ternary $(\text{Bi}_{1-x}\text{Sb}_x)_2\text{Te}_3$ materials are 3D TI with a simple surface state consisting of a single Dirac cone.^[9] Due to these interesting physical properties, the

synthesis of binary and multinary V-VI nanoparticles and thin films is currently of high interest.

Bottom-up chemistry approaches are currently investigated in detail for the synthesis of tailor-made TE materials.^[10] Liquid-phase approaches such as solvothermal routes, polyol processes, glucose-assisted reduction route and others for the synthesis of nanostructured metal chalcogenides are of particular interest and have frequently been reviewed.^[11] In addition, thin films as well as super lattices of such materials were deposited by gas phase processes including metal organic chemical vapor deposition (MOCVD)^[12] and atomic layer deposition (ALD) processes.^[13] Metal organic precursors are of particular interest since they allow very often the synthesis of the corresponding materials under kinetically controlled reaction conditions at low temperatures due to rather weak metal-carbon bonds. However, the very weak metal-carbon bonds of the heaviest metals of each group can result in unwanted decomposition reactions. For instance, the synthesis of Bi-containing materials such as Bi_2Te_3 is often accompanied by the formation of elemental Bi or Bi-rich phases.

We are generally interested in the development of alternative metal organic precursors for the synthesis of nanostructured group 15 chalcogenide materials using wet-chemical and gas-phase based processes and recently reported on the solution-based synthesis of highly stoichiometric, crystalline Sb_2E_3 (E = S, Se, Te)^[14] and Bi_2Te_3 nanoparticles by thermal decomposition of suitable - often metal organic - *single source precursors*.^[15] Unfortunately, the weak Bi-N bonds in the starting trisamidobismuthines $\text{Bi}(\text{NR}_2)_3$ often yielded Bi-rich materials such as BiTe and Bi_4Te_3 , respectively.^[15] Moreover, gas-phase processes including MOCVD^[16] and ALD processes^[17] were successfully applied for thin film deposition of the desired materials. However, the low vapor pressure of SbCl_3 and BiCl_3 , which were applied together with $(\text{Et}_3\text{Si})_2\text{Te}$ for the ALD deposition of Sb_2Te_3 and Bi_2Te_3 thin films, is a major drawback. We therefore prompted our attention to liquid group 15 precursors with a reasonable vapor pressure and high reactivity. Since intermolecular base-stabilization is known to suppress the formation of - often solid - dimeric or polymeric molecules, which typically show low vapor pressures, we turned our attention to aminoalkoxides as possible ligands.

We herein report on the synthesis of $\text{Sb}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **1** and $\text{Bi}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **2** including the solid state structure of **1** and their promising potential to serve as reactive precursors for the synthesis of binary group 15 chalcogenide nanoparticles Sb_2E_3 and Bi_2E_3 (E = S, Se, Te) in solution by reaction with $(\text{R}_3\text{Si})_2\text{E}$ (E = S, Se, Te; R = Me, Et) at moderate temperatures.

Results and Discussion

[a] S. Schulz,* M. Rusek, G. Bendt, C. Wölper
Faculty of Chemistry, University of Duisburg-Essen (Campus Essen)
Universitätsstraße 7, 45141 Essen
E-mail: stephan.schulz@uni-due.de

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$\text{Sb}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **1** and $\text{Bi}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **2** were synthesized according to a modified route by reaction of MCl_3 ($\text{M} = \text{Sb, Bi}$) with three equivalents of freshly prepared $\text{M'OCH}_2\text{CH}_2\text{NMe}_2$ ($\text{M}' = \text{Li, K}$).^[18]

Scheme 1. Synthesis of **1** and **2**.

The ^1H and ^{13}C NMR data of **1** correspond to values reported previously^[19] and are also similar to those observed for **2**. **1** is a colorless liquid which starts to decompose at 300 °C, while **2** is a light yellow solid, which starts to decompose at 256 °C according to a DSC study (Fig. 1).

Figure 1. DSC study of **1** and **2** (the asterisk indicates the melting point of bismuth at 271 °C).

Single crystals of **1** were grown on the diffractometer using an IR-laser-assisted technique in a closed quartz glass capillary under an inert argon atmosphere. The IR-laser allowed a very controlled and focused heating of the sample, which is frozen in

a nitrogen steam, hence resulting in optimized growth conditions, in which the sample re-crystallizes without decomposition.^[20] Figure 2 shows the crystal structure of **1**.

Figure 2. Solid state structure of **1** and reduced structure showing the coordination sphere of the central Sb atom; H-atoms have been omitted for clarity and displacement ellipsoids are drawn at the 50% probability levels. Selected bond lengths [Å] and angles [°]: Sb1-O1 2.009(2), Sb1-O2 2.000(2), Sb1-O3 2.024(2), Sb1-N1 2.664(3), Sb1-N2 2.909(3), Sb1-N3 2.888(3); O1-Sb1-O2 89.73(9), O1-Sb1-O3 85.99(9), O2-Sb1-O3 88.05(9), O1-Sb1-N1 73.13(8), O2-Sb1-N2 70.17(8), O3-Sb1-N3 71.37(11), N1-Sb1-N2 116.08(7), N1-Sb1-N3 116.07(10), N2-Sb1-N3 115.61(7).

The coordination number of the Sb atom can be considered as 3+3. Its inner coordination sphere is built by three O atoms, leading to the common trigonal-pyramidal coordination sphere. Opposing to the O atoms, three N atoms form the outer coordination sphere, finally resulting in the formation of a distorted octahedron. The Sb1–N1 bond length (2.664(3) Å) is significantly shorter than the other Sb–N bond lengths (2.909(3), 2.888(3) Å). The conformation (C1–O1–Sb1–O3 177.5(3)°) of this ligand is optimal for facilitating a short distance between the Sb atom and the amino group (N1) of the ligand. The other two ligands show less suitable conformations (C21–O2–Sb1–O1 137.1(3)° and C31–O3–Sb1–O2 149.2(3)°), leading to longer Sb–N distances. The structure of **1** agrees with those reported for organoantimony(III) compounds with three (C,N)-chelating ligands, for which either distorted octahedral or distorted trigonal antiprismatic coordination modes have been reported.^[21] The

dative N→Sb bonds in these compounds are typically elongated compared to those observed in **1** and typically range from 2.85 to 3.2 Å, most likely resulting from the decreased Lewis acidity of the Sb atom due to the C-substituents compared to O-substituents in **1**. However, the significantly shorter Sb1-N1 bond lengths (2.664(3) Å) points to a stronger Sb-N interaction compared to the Sb1-N2 (2.909(3) Å) and Sb1-N3 (2.888(3) Å) interactions, which agree with those reported for hypervalent organoantimony compounds with a pendant N-donor arm.^[21] The O atoms of these ligands are involved in non-classical hydrogen bonding (C4-H4C...O2' 2.50 Å, 159.9°; C23-H23C...O3' 2.61 Å, 153.7°), which might explain the non-optimal conformation.^[22] The S-analogue Sb(SCH₂CH₂NMe₂)₃,^[19] in which the Sb atom adopts a distorted octahedral coordination geometry, shows no hydrogen bonding and all three ligands have C-S-Sb-S torsion angles larger than 170°. Consequently, nearly equal Sb-S (2.8443(18), 2.8481(18), 2.838(2) Å), which are longer than the Sb-O bond lengths in **1** due to the different covalent radii of O and S, and Sb-N bond lengths were observed [2.8443(18), 2.8481(18), 2.838(2) Å].

The Sb-O bond lengths of **1** (2.000(2) - 2.024(2) Å) agree with the sum of the covalent radii (2.03 Å),^[23] but they are slightly elongated compared to values as experimentally observed for monomeric trisalkoxystibines Sb(OR)₃ such as Sb(O-2,6-Me₂C₆H₃)₃ (1.967(2)-1.976(2) Å),^[24] and Sb(O-2,6-Ph₂C₆H₃)₃ (1.975(2) Å),^[25] as well as to those calculated for monomeric Sb(OMe)₃ (1.958 Å).^[26] In addition, the weakly bonded dimer [Sb(Oi-Pr)₃]₂ (1.935(2)-1.976(2) Å), in which the Sb atom adopts a pseudo trigonal bipyramidal configuration, also shows shorter Sb-O bond lengths,^[26] whereas Sb(OMe)₃ (1.986(6)-2.102(8) Å), which forms a three-dimensional networks via Sb ... O-Sb bridges in the solid state, hence resulting in a distorted octahedral coordination sphere at the Sb atoms, shows comparable Sb-O bond lengths.^[27]

Compared to the sum of the covalent radii (2.11 Å^[23]), the Sb-N bonds in **1** are significantly elongated, clearly reflecting the dative character of the N→Sb bonding interaction. The homoleptic bismuth trisulfide Bi(SCH₂CH₂NH₂)₃ also adopts a monomeric structure, but the central Bi atom adopts a distorted pentagonal pyramidal environment formed by one apical sulfur site, two cis-equatorial sulfur sites and three equatorial nitrogen sites, indicating the presence of a stereochemically active electron lone pair in apical position.^[28] In contrast, the amino-functionalized bismuth alkoxide Bi[OC(CH₂NMe₂)₃]₃ shows a six-coordinate bismuth atom with a *fac, fac*-BiO₃N₃ coordination sphere.^[29] Moreover, the structures of several other main group metal complexes containing the aminoalkoxide ligand have been reported, including that of Ga(OCH₂CH₂NMe₂)₃.^[30] Unfortunately, the poor quality of the crystals only allowed for the description of the atom connectivity, showing the formation of a monomeric tris(alkoxide), which was somewhat surprising since based on mass spectroscopy studies, the compound was previously described to adopt a dimeric, oxygen-bridged structure^[31] as was also observed for the corresponding indium trisalkoxide In(OCH₂CH₂NMe₂)₃.^[32] In contrast, the Pb(II) complex {Pb₃[OCH₂CH₂NMe₂]₃}₂ shows a trimeric unit with bridging oxide-groups.^[33]

Synthesis of Sb₂E₃ and Bi₂E₃

The nanoparticles were synthesized at moderate temperatures (Sb₂E₃ 140 - 180 °C, Bi₂E₃ 120 - 140 °C) by reaction of M'(OC₂H₄NMe₂)₃ (M' = Li, K) with (Me₃Si)₂S, (Et₃Si)₂Se and (Et₃Si)₂Te, respectively, in diisopropylbenzene (DIPB) under inert gas conditions in a glovebox (*hot injection* method). The resulting materials were isolated by centrifugation and purified by several washing steps with methanol (3x) and *n*-hexane (1x). Temperature-dependent *in situ* ¹H NMR studies of the reaction of **1** with (Me₃Si)₂S (Fig. S1) and **2** with (Et₃Si)₂Te (Fig. S2), respectively, clearly demonstrate that both reactions proceeded with immediate formation - even at ambient temperature - of the expected silyl ethers Me₃SiOC₂H₄NMe₂ and Et₃SiOC₂H₄NMe₂.

The black solids obtained from the six different thermolysis reactions are crystalline Sb₂E₃ and Bi₂E₃ (E = S, Se, Te) materials as was shown by XRD (Fig. 3, Fig. S3-S6). All Bragg reflections with a significant intensity can be indexed based on the structures of orthorhombic Sb₂S₃, Sb₂Se₃ and Bi₂S₃ as well as rhombohedral Sb₂Te₃, Bi₂Se₃ and Bi₂Te₃. There are no signs for the formation of elemental antimony or elemental bismuth as was previously observed for thermal decomposition reactions of *single source precursors*^[14b,15] as well as elemental chalcogens or the corresponding oxides (Sb₂O₃, Bi₂O₃, ...). No significant texture effects were observed for the Sb₂E₃ and Bi₂E₃ materials. The crystallographic density of the materials was calculated by Rietveld refinement (table 1). The calculated lattice parameters are in a very good agreement with the ICSD database files for the pure orthorhombic M₂E₃ phases. Based on the PXRD studies, the formation of phase-pure materials can be concluded.

Table 1. Lattice parameters, density and crystallite size of as-synthesized Sb₂E₃ and Bi₂E₃ phases as determined by the Rietveld refinement.

Phases	Lattice parameters			Density ρ (g/cm ³)	Crystallite size D (nm)
	a (Å)	b (Å)	c (Å)		
Sb ₂ S ₃ (<i>Pnma</i>)	11.308(5)	3.836(3)	11.227(2)	4.99	64.9(2)
Sb ₂ Se ₃ (<i>Pnma</i>)	11.632(6)	3.977(2)	11.777(7)	5.86	121.9(5)
Sb ₂ Te ₃ (<i>R3-mH</i>)	4.267(1)		30.524(6)	6.48	46.9(9)
Bi ₂ S ₃ (<i>Pnma</i>)	11.300(3)	3.981(7)	11.155(1)	6.80	54.5(1)
Bi ₂ Se ₃ (<i>R3-mH</i>)	4.140(1)		28.693(6)	7.66	28.3(9)
Bi ₂ Te ₃ (<i>R3-mH</i>)	4.379(3)		30.520(9)	7.87	33.5(4)

Figure 3. PXRDs of Sb_2Te_3 and Bi_2Se_3 nanoparticles as obtained by reaction of **1** and **2** with $(\text{Et}_3\text{Si})_2\text{E}$ ($\text{E} = \text{Se}, \text{Te}$) at 170°C in DIPB and reference (red: ICSD 192780 (Sb_2Te_3) and ICSD 72545 (Bi_2Se_3)); XRDs of the remaining four materials are given in the electronic supplement (Fig. S3-S6).

FT-IR investigations of all materials (Sb_2E_3 and Bi_2E_3) reveal the absence of any organic molecules (Fig. S9-S14). Absorption bands due to CH-stretching vibrations were not observed in the typical region between 2800 and 3000 cm^{-1} , which clearly proves that the washing agent methanol does not bind to the nanoparticle surface. In addition, the IR-spectra do not show any absorbance bands in the region above 3000 cm^{-1} , which is typical for stretching vibrations of aromatic CH moieties, proving that solvent molecules (DIPB) are also completely removed from the nanoparticle surface.

EDX analyses of the resulting nanoparticles show the formation of slightly chalcogen-rich Sb_2E_3 and Bi_2E_3 ($\text{E} = \text{S}, \text{Se}, \text{Te}$) materials (table 2). According to ESEM studies, the six different materials obtained from precursors **1** and **2** are highly non-uniform concerning their size and shape. This is not surprising since no capping agents such as PVP, oleylamine, TOP or TOPO, which are typically used for the size and shape-selective synthesis of these type of materials, have been used. The focus of this study was clearly on the synthesis of phase-pure materials in order to prove the potential capability of **1** and **2** to serve as alternate precursor for Sb_2E_3 and Bi_2E_3 materials rather than on the morphology-selectivity. However, the general morphologies observed herein have been previously reported for these types of materials. The resulting Sb_2S_3 and Sb_2Se_3 materials show the typical nanobundle-type and nanorod-type morphology. This morphology is typical for these materials and results from the crystal structure of these materials, which crystallize in orthogonal space groups. In contrast, hexagonal Sb_2Te_3 nanoplates were obtained as is typical for this material (Fig. 4).^[14,34] Fig. 5 shows ESEM images of the Bi_2E_3 materials. Bi_2S_3 again crystallizes in a rod-like morphology as was observed in previous studies,^[35] while a mixed flower-like/cloud-like morphology was observed for Bi_2Se_3 . These findings do not surprise since Bi_2Se_3 is known to crystallize in various morphologies including nanobelts, nanotubes and cloud-like nanostructures.^[36] The Bi_2Te_3 nanoparticles adopts a knob-like morphology, although flower-like morphologies have also been mentioned.^[37] In contrast, hexagonal plate-like particles or pseudo-cubic particles as have been previously reported for Bi_2Te_3 nanoparticles were not observed in this study.^[15]

Table 2. EDX results of the Sb_2E_3 and Bi_2E_3 nanoparticles.

compound	Sb/Bi [at%]	E [at%]
Sb_2S_3	39.89(96)	60.11(24)
Sb_2Se_3	39.38(64)	60.62(56)
Sb_2Te_3	39.87(76)	60.13(68)
Bi_2S_3	39.74(98)	60.58(10)
Bi_2Se_3	38.81(56)	61.19(19)
Bi_2Te_3	39.29(62)	60.71(31)

Figure 4. ESEM photographs of Sb_2S_3 (A), Sb_2Se_3 (B) and Sb_2Te_3 (C) nanowires and nanoplates as-obtained from the reactions of **1** and $(\text{Me}_3\text{Si})_2\text{S}$ and $(\text{Et}_3\text{Si})_2\text{E}$ ($\text{E} = \text{Se}, \text{Te}$) in DIPB at 170°C .

Figure 5. ESEM photographs of Bi_2S_3 (A), Bi_2Se_3 (B) and Bi_2Te_3 (C) nanoparticles as-obtained from the reactions of **2** and $(\text{Me}_3\text{Si})_2\text{S}$ and $(\text{Et}_3\text{Si})_2\text{E}$ ($\text{E} = \text{Se}, \text{Te}$) in DIPB at 170°C .

Sb_2E_3 and Bi_2E_3 nanoparticles have been synthesized in the past typically by hydrothermal reactions,^[38] microwave irradiation,^[39] sonochemical methods,^[40] mechanochemical approaches^[41] as well as in biomolecule-assisted approaches.^[42] These reactions often require temperatures higher than 160°C or the presence of an additional reducing agent.^[40] In contrast, our approach uses a specific chemical reaction, whose energetic driving force is the formation of the silyl ether containing a stable Si-O bond. In remarkable contrast to bismuth triamide $\text{Bi}(\text{NMe}_2)_3$, which was recently reported to react with $\text{Te}(\text{SiEt}_3)_2$ at low temperature with formation of Bi_2Te_3 nanoparticles,^[15] the novel precursors **1** and **2** described herein are thermally more stable. $\text{Bi}(\text{NMe}_2)_3$ decomposes below 150°C with formation of elemental Bi, often leading to the formation of Bi-rich materials such as BiTe or Bi_4Te_3 , whereas **1** and **2** are stable up to 250°C (**2**) and almost 300°C (**1**), respectively (Fig. 1). Consequently,

the formation of pnictogen-rich materials, a particular problem in the synthesis of Bi_2Te_3 , due to decomposition of the pnictogen precursor is avoided using **1** and **2**. Furthermore, the new precursors are not sensitive regarding light irradiation and can be stored over a long time without any decomposition under Ar-atmosphere. Moreover, the required reaction temperatures (140 - 180 °C) are high enough to obtain crystalline nanoparticles without further heating treatment. We recently reported on the thermal decomposition of tailor-made *single-source precursors* $(\text{Et}_2\text{Sb})_2\text{S}$ at low temperatures. The resulting Sb_2S_3 materials required reaction temperatures of at least 140 °C in order to get crystalline.^[14b]

The new precursors **1** and **2** are currently investigated in ALD processes together with $\text{E}(\text{SiEt}_3)_2$ (E = Se, Te), since their specific chemical and physical properties, a combination of high thermal stability coexisting with high chemical reactivity and reasonable vapor pressure, which are essential prerequisites for suitable ALD precursors, render them very promising for these processes.

Conclusions

Crystalline binary antimony (Sb_2E_3) and bismuth chalcogenides (Bi_2E_3) nanoparticles were obtained by reaction of the new intermolecular-stabilized precursors $\text{Sb}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **1**, whose solid state structure was determined by single crystal X-ray diffraction, and $\text{Bi}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **2** with $(\text{Me}_3\text{Si})_2\text{S}$ and $(\text{Et}_3\text{Si})_2\text{E}$ (E = Se, Te) at moderate temperatures. The inhomogeneous size and morphology of the nanoparticles was shown by SEM, while EDX and XRD revealed an almost perfect stoichiometric chemical composition of the crystalline nanomaterials, which do not contain any organic substances on the surface as was proven by IR spectroscopy. In addition, The formation of phase-pure Bi_2Te_3 without any additional elemental Bi or Bi-rich phases clearly proves our concept to use thermally more stable but chemically very reactive precursors containing a pendant donor side-arm function.

Experimental Section

Materials. Solvents were carefully dried over Na/K alloy and degassed prior to use. $(\text{Me}_3\text{Si})_2\text{S}$ and $(\text{Et}_3\text{Si})_2\text{E}$ (E = Se, Te) were prepared according to literature methods.^[43] All synthetic steps were performed in a glovebox under Ar atmosphere or using standard Schlenk techniques under Ar atmosphere.

$\text{Sb}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **1** was synthesized according to a modified literature method.^[44] $\text{Me}_2\text{NC}_2\text{H}_4\text{OH}$ was stored over molecular sieves for several days and degassed prior to use. 15.26 g (171.19 mmol) of the amino alcohol were dissolved in 100 mL of *n*-hexane, cooled down to 0 °C and then reacted with a 2.5 M *n*-butyllithium solution in *n*-hexane (68.48 mL, 171.19 mmol), resulting in gas evolution which was finished within 30 min. The resulting Li salt was isolated by filtration and used without further purification.

A solution of 8.19 g (35.90 mmol) of SbCl_3 in 80 mL of Et_2O was added dropwise at ambient temperature to a solution of 10.24 g (107.71 mmol)

$\text{LiOC}_2\text{H}_4\text{NMe}_2$ in 70 mL Et_2O within 60 min. The resulting light yellow suspension was stirred overnight. After removal of the solvent in vacuum, the resulting residue was distilled in vacuum at 180 °C, yielding **1** as colorless liquid (91 % yield, 10.23 g, 32.78 mmol). $\text{C}_{12}\text{H}_{30}\text{N}_3\text{O}_3\text{Sb}$ (386.15 g/mol): calcd. C 37.33, H 7.83, N 10.88; found C 37.05, H 6.93, N 11.20. - IR ν [cm^{-1}] = 2942, 2853, 2819, 2768, 1615, 1583, 1527, 1455, 1406, 1370, 1351, 1332, 1255, 1189, 1157, 1084, 1040, 951, 875, 840, 796. - $^1\text{H-NMR}$ (300 MHz, C_6D_6 , 298 K): δ [ppm] = 2.09 (s, 18H, $\text{OCH}_2\text{CH}_2\text{NMe}_2$), 2.39 (t, $^3J_{\text{HH}} = 4.8$ Hz, 6H, $\text{OCH}_2\text{CH}_2\text{NMe}_2$), 4.23 (t, $^3J_{\text{HH}} = 5.0$ Hz, 6H, $\text{OCH}_2\text{CH}_2\text{NMe}_2$). - $^{13}\text{C-NMR}$ (73 MHz, C_6D_6 , 298 K): δ [ppm] = 44.5 ($\text{OCH}_2\text{CH}_2\text{NMe}_2$), 61.7 ($\text{OCH}_2\text{CH}_2\text{NMe}_2$), 62.6 ($\text{OCH}_2\text{CH}_2\text{NMe}_2$).

$\text{Bi}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **2**: 584 mg (1.85 mmol) of BiCl_3 were suspended in 10 mL THF and cooled down to -78 °C. The suspension was treated dropwise with a suspension out of 707 mg (5.56 mmol) $\text{KOC}_2\text{H}_4\text{NMe}_2$ in 10 mL of THF and stirred overnight, yielding a light yellow suspension, which was refluxed for additional 2 h at 75 °C. After cooling down to ambient temperature, the solvent was evaporated under reduced pressure and the resulting solid residue was suspended in 15 mL of CHCl_3 , filtered through celite and then extracted twice with the same solvent amount. After evaporation of the solvent, 414 mg (0.87 mmol, 47 %) of a light yellow smeary solid were obtained. $\text{C}_{12}\text{H}_{30}\text{N}_3\text{O}_3\text{Bi}$ (473.37 g/mol): calcd. C 30.45, H 6.39, N 8.88; found C 29.87, H 6.38, N 7.98. - IR ν [cm^{-1}] = 2973, 2941, 2843, 2812, 2769, 2684, 1462, 1403, 1371, 1349, 1321, 1273, 1186, 1157, 1075, 1039, 1017, 985, 948, 874, 774. - $^1\text{H-NMR}$ (300 MHz, C_6D_6 , 298 K): δ [ppm] = 2.21 (s, 18H, $\text{OCH}_2\text{CH}_2\text{NMe}_2$), 2.45 (t, $^3J_{\text{HH}} = 5.0$ Hz, 12H, $\text{OCH}_2\text{CH}_2\text{NMe}_2$), 4.65 (bs, 6H, $\text{OCH}_2\text{CH}_2\text{NMe}_2$). - $^{13}\text{C-NMR}$ (73 MHz, C_6D_6 , 298 K): δ [ppm] = 45.4 ($\text{OCH}_2\text{CH}_2\text{NMe}_2$), 60.5 ($\text{OCH}_2\text{CH}_2\text{NMe}_2$), 64.8 ($\text{OCH}_2\text{CH}_2\text{NMe}_2$).

Single crystal X-ray diffraction. Crystallographic data of **1** were collected on a Bruker D8 Kappa APEX2 diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å) at 100(1) K: $M = 386.14$, colourless crystal, (0.300 × 0.300 × 0.300 mm); monoclinic, space group Cc; $a = 16.6823(10)$ Å, $b = 9.7657(6)$ Å, $c = 12.0241(7)$ Å; $\alpha = 90^\circ$, $\beta = 115.3210(10)^\circ$, $\gamma = 90^\circ$, $V = 1770.70(18)$ Å³; $Z = 4$; $\mu = 1.566$ mm⁻¹; $\rho_{\text{calc}} = 1.448$ g · cm⁻³; 26872 reflexes ($\theta_{\text{max}} = 30.569^\circ$), 2701 unique ($R_{\text{int}} = 0.0381$); 180 parameters; Flack-Parameter $x = 0.10(2)$; largest max./min in the final difference Fourier synthesis 0.865 e · Å⁻³ / -0.864 e · Å⁻³; max./min. transmission $0.39/0.75$; $R_1 = 0.0178$ ($I > 2\sigma(I)$), $wR_2 = 0.0447$ (all data). The solid-state structure of **1** is shown in Figure 1. The structure was solved by Direct Methods (SHELXS-97)^[45] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-2014).^[46,47] Absorption correction was performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. The crystal was a three component non-merohedral twin. The refinement was done using detwinning HKLF4 data. The crystal of **1** was grown at a temperature of 235 K by an *in-situ* zone melting process inside a quartz capillary using focused infrared-laser-radiation.^[48] The experimental setup does only allow for ω scans with χ set to 0°. Any other orientation would have partially removed the capillary from the cooling steam and thus led to a melting of the crystals. This limits the completeness to 65% to 90% depending on the crystal system.

The crystallographic data (without structure factors) were deposited as „supplementary publication no. CCDC-1476697“ at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).

Synthesis of M_2E_3 nanoparticles

Sb₂S₃/Sb₂Se₃/Sb₂Te₃: 100 mg (0.26 mmol) of **1** was dissolved in 5 mL of DIPB at 140 °C, 160 °C and 180 °C, respectively, and the corresponding silylchalcogenide (R₃Si)₂E (69.32 mg (0.39 mmol) (Me₃Si)₂S; 120.23 mg (0.39 mmol) (Et₃Si)₂Se; 149.61 mg (0.39 mmol) (Et₃Si)₂Te) was injected into this hot solution (hot injection method), whereupon the solutions immediately turned black. The suspensions were heated to the desired temperature for 6 h and the resulting solid materials were isolated by centrifugation and purified by several washing steps with methanol (3x) and *n*-hexane (1x).

Bi₂S₃/Bi₂Se₃/Bi₂Te₃: 100 mg (0.21 mmol) of **2** were dissolved in 5 mL of DIPB at 120 °C, 140 °C and 160 °C, respectively, and the corresponding silylchalcogenide (56.21 mg (0.32 mmol) (Me₃Si)₂S; 97.49 mg (0.32 mmol) (Et₃Si)₂Se; 112.81 mg (0.32 mmol) (Et₃Si)₂Te) were injected, resulting in an immediate darkening of the clear solutions. The suspensions were heated to the desired temperature for 5 hours and the resulting black solids were isolated by centrifugation and several washing steps with methanol (3x) and *n*-hexane (1x).

Thermal Analysis. Netzsch Phox 200 machine was used for the DSC studies, which were performed with a heating rate of 2 °C per minute.

SEM and EDX Analysis. SEM studies were carried out on an ESEM Quanta 400 FEG and a Jeol JSM 6510 equipped with an energy dispersive X-ray spectroscopy (EDX) device (Bruker Quantax 400).

X-ray Analysis. PXRD patterns were obtained using a Bruker D8 Advance powder diffractometer with Cu K α radiation (λ : 1.5418 Å, 40 kV and 40 mA) using a silicon single crystal as sample holder to minimize scattering. For better homogenization, the dried powder samples were re-dispersed in ethanol on the silicon surface and then investigated in the range from 10 to 90° 2 θ with a step size of 0.01° 2 θ with a counting time of 0.6 s. Rietveld refinement was performed with the program package TOPAS 5.0 (Bruker) to determine the lattice parameters and average crystallite size by use of the Scherrer equation^[49] with the program package TOPAS 5.0 (Bruker). The background was modelled using Chebyshev polynomials. The structure models of Sb₂S₃ (#171853), Sb₂Se₃ (#85676), Sb₂Te₃ (#192780), Bi₂S₃ (#30775), Bi₂Se₃ (#72545) and Bi₂Te₃ (#74348) from the ICSD database were used. For each Rietveld refinement, the instrumental correction as determined with a standard powder sample from NIST (National Institute of Standards and Technology) as standard reference material (SRM 660b; a(LaB6) = 4.15689 Å) was taken into account.

Supporting Information. A cif file of **1** and temperature-dependent ¹H-NMR studies on the reactions of **1** and (Me₃Si)₂S as well as **2** and (Et₃Si)₂Te in toluene-d₈; XRDs and Rietveld refinements of Sb₂E₃ and Bi₂E₃ as well as FT-IR spectra of Sb₂E₃ and Bi₂E₃ are given in the electronic supplement.

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Keywords: nanoparticle • hot injection • chalcogenide • antimony • bismuth

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Entry for the Table of Contents

FULL PAPER

Binary antimony (Sb_2E_3) and bismuth chalcogenide (Bi_2E_3) nanoparticles were obtained by reaction of the intermolecular-stabilized stibine $\text{Sb}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **1** and bismuthine $\text{Bi}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_3$ **2** with $(\text{R}_3\text{Si})_2\text{E}$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$; $\text{R} = \text{Me}, \text{Et}$) at moderate reaction temperatures. The reactions were studied by *in situ* ^1H NMR spectroscopy, while the materials were characterized by EDX, XRD, IR and SEM.

Monika Rusek, Georg Bendt, Christoph Wölper, and Stephan Schulz*

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