Nanoparticles

Heterocyclic Bismuth(III) Dithiocarbamato Complexes as Single-Source Precursors for the Synthesis of Anisotropic Bi₂S₃ Nanoparticles

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Abstract: New complexes *catena*-(μ_2 -nitrato-*O*,*O*')bis(piperidinedithiocarbamato)bismuth(III) (**1**) and tetrakis(μ -nitrato)tetrakis[bis(tetrahydroquinolinedithiocarbamato)bismuth(III)] (**2**) were synthesised and characterised by elemental analysis, FTIR spectroscopy and thermogravimetric analysis. The single-crystal X-ray structures of **1** and **2** were determined. The coordination numbers of the Bi^{III} ion are 8 for **1** and ≥ 6 for **2** when the experimental electron density for the nominal 6s² lone pair of electrons is included. Both complexes were used as single-source precursors for the synthesis of dodecylamine-, hexadecylamine-, oleylamine and tri-*n*-octylphosphine oxide-capped Bi_2S_3 nanoparticles at different temperatures. UV/Vis spectra showed a blueshift in the absorbance band edge characteristic of a quantum size effect. High-quality, crystalline, long and short Bi_2S_3 nanorods were obtained depending on the thermolysis temperature, which was varied from 190 to 270 °C. A general trend of increasing particle breadth with increasing reaction temperature and increasing length of the carbon chain of the amine (capping agent) was observed. Powder XRD patterns revealed the orthorhombic crystal structure of Bi_2S_3 .

Introduction

Semiconductor materials of type V–VI have recently attracted attention due to their photoconductive, photosensitive, thermoelectric and fluorescence properties.^[1–5] Among these materials, bismuth sulfide (Bi_2S_3), owing to its high figure of merit (ZT value) with a large absorption coefficient and high energy conversion efficiency, is widely used as a thermoelectric-cooling material. It has a direct energy bandgap between 1.3 and 1.7 eV and finds applications in photovoltaic converters^[6] and photodiode arrays.^[7]

The morphology, size and phase of nanostructured materials are influenced by reaction parameters such as passivating groups, monomer concentration, thermolysis temperature and

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precursor type. Many approaches have been proposed for fabricating one-dimensional Bi₂S₃ nanostructures, including microwave irradiation,^[8] the polyol method,^[9] solvo(hydro)thermal routes,^[10–12] and molecular-precursor routes.^[7, 13–16] As a simple, easily controlled, low-cost and effective heating method, thermal decomposition of single-source precursors (SSPs) in coordinating solvents has been widely used in the synthesis of high-quality nanomaterials.^[17]

Trindade et al. reported the synthesis of Bi₂S₃ nanoparticulates from bismuth dithiocarbamato complexes by chemical vapour deposition or by thermal decomposition in an organic solvent at 400 °C.^[7,14] The coordinating solvent used in the hotinjection route had a strong influence on the final properties and morphology of the Bi₂S₃ particles. Shen et al. used bismuth tris(diethyldithiocarbamate) as SSP to prepare Bi₂S₃ nanotubes by pyrolysis at 530 °C.^[13] Xie et al. synthesised Bi₂S₃ nanorods using the same bismuth complex and observed that varying the temperature from 115 to 170 °C did not alter the phase of the products.^[15] Garje and co-workers synthesised Bi₂S₃ nanorods with a small aspect ratio by the thermal decomposition of bismuth(III) dialkyldithiophosphate complexes in ethylene glycol at 197 °C.^[16b]

The mechanism of the preferential growth of Bi_2S_3 nanorods with variation of reaction parameters has been studied in some detail. Many studies have concluded that the type of solvent used, for example, ethylene glycol, diethylene glycol or thioglycolic acid, favoured the formation of Bi_2S_3 nanorods.^[8, 11, 12, 16] Stavila et al. reported the decomposition of bismuth(III) thiourea and thiosemicarbazide complexes in differ-

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ent solvents at 120 °C. The addition of a small amount of dodecanethiol or octadecanethiol resulted in the formation of Bi₂S₃ nanorods up to several nanometres in length, with better

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crystallinity.[18] Recently, we have reported the use of heterocyclic dithiocarbamates as SSPs for the preparation of nanocrystalline materials.^[19-25] These dithiocarbamate complexes containing bulky alkyl groups have been particularly effective in producing high-quality CdS, ZnS and PbS nanomaterials.^[19,21,22] Herein we describe the synthesis of Bi_2S_3 nanorods at different temperatures and with different capping agents from newly synthesised complexes catena-(µ2-nitrato-O,O')bis(piperidinedithiocarbamato)bismuth(III) (1) and the tetranuclear cluster tetrakis(μ nitrato)tetrakis[bis(tetrahydroquinolinedithiocarbamato)bismuth(III)] (2). The single-crystal X-ray structures of both complexes are also reported. Compared with former methods and SSPs, the present technique is more convenient, environmental friendly and scalable.

Results and Discussion

Characterisation of the ligand and the complexes

The bismuth dithiocarbamato complexes used in this work are easily synthesised with cost-effective starting materials and reaction protocols; they are stable to air and moisture. The ligands and the complexes were obtained in good yields, and microanalysis confirmed their purity. The complexes are yellow microcrystalline powders soluble in most organic solvents. IR spectroscopic analysis revealed a very broad band around 3324–3367 cm⁻¹ in the spectra of the ligands due to v(O-H) of water (Supporting Information, Figures S1 and S2). This band was absent in the spectra of the complexes. Both the ligands and complexes showed bands in the 1466–1485 cm⁻¹ region, corresponding to v(C=N) and v(C-N). The v(C=S) band was observed in the 999-975 cm⁻¹ region in the spectra of the ligands. The upward shift of this band in the complexes compared to the free ligand, together with a strong band (or very close bands) attributed to v(C-S) was indicative of a bidentate or slightly anisobidentate dithiocarbamate ligand.

The TGA plots of both complexes showed a two-step decomposition pattern. The first step with weight losses of 57.5 and 65.0% (calcd: 55.6 and 63.5%) at 248.4 and 221.6 $^\circ C$ for complexes 1 and 2, respectively (Figure 1), corresponds to the loss of the organic moiety and sulfur atom. The second decomposition step at 436.9 and 436.4 °C corresponds to the loss of more sulfur atoms with mass losses of 7.5 and 6.0% (calcd: 7.3 and 5.8%). The final residues of 35.0 and 29.0% were close to the calculated values of 37.1 and 30.7% for Bi₂S₃ from complexes 1 and 2, respectively.

Single-crystal X-ray structures

Thermal ellipsoid plots of the crystal structures of 1 and 2 are shown in Figures 2, 3 and 4. Crystal data, data collection and structure refinement details for compounds 1 and 2 are summarised in Table 1, and selected bond lengths and angles are

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Figure 1. TGA plots of 1 and 2.



Figure 2. Thermal ellipsoid plot (50% probability surfaces) of the ASU of the single-crystal X-ray structure of 1, determined at 100 K. Labels for all non-H atoms are shown.



Figure 3. Illustration of the 1D coordination polymer formed by 1 and the interaction between adjacent inversion-related chains in the lattice. Selected atoms are rendered as spheres and labelled (others are depicted as cylinders); the Bi-S3 interaction distance is 3.310(2) Å. Atom symmetry operator codes: i) 1-x, -y, 1-z; ii) 1-x, 1-y, 1-z.

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Figure 4. Partially labelled thermal ellipsoid plot (35% probability surfaces) and cylinder model of the X-ray structure of **2**. Labels are shown for selected atoms belonging to the symmetry-unique portion of the molecule. The inset depicts the possible orientations of the stereochemically active $6s^2$ lone pairs on two of the symmetry-related Bi^{III} ions Bi1. The difference electron-density map of **2** confirming the lone pair orientations is given in the Supporting Information (Figure S4).

listed in Tables 2 and 3. Both compounds crystallise in the monoclinic crystal system (space group $P2_1/c$).

The low-temperature X-ray structure of **1** is novel^[26] and reveals that the complex forms a 1D coordination polymer in the crystalline solid state. The asymmetric unit (ASU) shown in Figure 2, which is also the polymer repeat unit, comprises a bismuth(III) ion, the two chelating dithiocarbamate ions, and the bridging nitrate ion. The mean Bi–S coordination bond length is 2.71(8) Å (Table 2) and compares favourably with the mean distance of 2.75(10) Å for the eight known X-ray structures of Bi^{III} coordinated to dithiocarbamate ions of a similar structure.^[27] The Bi–O bond lengths average 2.79(7) Å and are longer than those reported for the monodentate nitrato li-

Table 2. Selected bond lengths [Å] and angles [°] for 1.						
Bi(1)—S(1)	2.6480(14)	S(1)-Bi(1)-S(2)	66.25(5)			
Bi(1)—S(2)	2.7937(16)	S(1)-Bi(1)-S(3)	78.32(5)			
Bi(1)—S(3)	2.7980(14)	S(1)-Bi(1)-O(1)	137.69(9)			
Bi(1)—S(4)	2.6169(14)	S(2)-Bi(1)-S(3)	134.65(4)			
Bi(1)–O(1)	2.723(4)	S(4)-Bi(1)-S(1)	94.64(5)			
S(1)–C(1)	1.744(5)	S(4)-Bi(1)-S(2)	88.27(5)			
S(2)–C(1)	1.727(5)	S(4)-Bi(1)-S(3)	66.63(4)			
S(3)—C(7)	1.736(5)	S(4)-Bi(1)-O(1)	72.54(8)			

Table 3. Selected bond lengths [Å] and angles [°] for 2.						
Bi(1)—S(1)	2.7734(14)	Bi(1)-O(1)	2.694(5)			
Bi(1)—S(3)	2.6343(15)	Bi(2)—S(5)	2.7313(14)			
Bi(1)—S(4)	2.7745(16)	Bi(2)—S(7)	2.6174(16)			
Bi(1)—S(2)	2.6456(14)	Bi(2)—S(6)	2.6026(15)			
Bi(1)-O(4)	2.725(4)	Bi(2)—S(8)	2.8105(15)			
S(1)-Bi(1)-S(4)	137.35(5)	O(1)-Bi(1)-S(1)	112.28(11)			
S(3)-Bi(1)-S(1)	86.28(4)	O(1)-Bi(1)-S(4)	83.23(12)			
S(3)-Bi(1)-S(4)	66.27(5)	S(5)-Bi(2)-O(4)	81.50(9)			
S(3)-Bi(1)-S(2)	95.02(6)	S(7)-Bi(2)-O(4)	170.49(9)			
S(3)-Bi(1)-O(4)	76.40(9)	O(4)-Bi(1)-S(1)	69.31(9)			
S(2)-Bi(1)-O(4)	134.67(9)	O(4)-Bi(1)-S(4)	128.64(9)			
S(2)-Bi(1)-O(1)	71.53(11)	Bi(1)-O(4)-Bi(2)	150.95(15)			

gands (η^1 -NO₃⁻), for example, bis(nitrato)(methanol){*N*-phenyl-*N'*-[1-(pyrazin-2-yl)ethylidene]carbamohydrazonothioato}bismuth(III), which are distinctly non-bridging (Bi–O, 2.45(6) Å).^[28] Bidentate coordination of nitrate ions (η^2 -NO₃⁻) tends to be the most common binding mode in Bi^{III} complexes (presumably the large ionic radius of Bi³⁺ facilitates increased donor atom density at the metal centre), whereas monodentate polymeric or multinuclear nitrato-bridged species are infrequently observed. More specifically, only three crystallographically characterised examples of complexes with linking μ_2 -nitrato-*O*,*O'* ligands, Bi–O(NO)O'–Bi, are known: the room-temperature structure of 1,^[26] catena-{(μ_2 -nitrato-*O*,*O'*)-bis[(η^5 -cyclopentadienyl)dicarbonyliron(II)]bismuth(III)}^[29] and the Bi^{III}–Nd^{III} heterome-

Table 1. Crystal system, selected data collection parameters, and X-ray structure refinement details for 1 and 2.				
Chemical formula	$C_{12}H_{20}BiN_{3}O_{3}S_{4}$	$2(C_{40}H_{40}Bi_2N_6O_6S_8)$		
M _r	591.53	2750.44		
Crystal system, space group	monoclinic, P2 ₁ /c	monoclinic, P2 ₁ /c		
7 [K]	100	296		
a, b, c [Å]	13.712 (7), 6.172 (3), 22.415 (11)	14.1529 (16), 12.8531 (15), 26.270 (3)		
β[°]	102.351 (7)	90.773 (2)		
V [Å ³]	1853.0 (16)	4778.3 (9)		
Z	4	2		
radiation	Μο _{κα}	Μο _{κα}		
μ [mm ⁻¹]	9.98	7.76		
crystal size [mm]	0.35×0.2×0.15	0.4×0.16×0.12		
T _{min} , T _{max}	0.421, 0.746	0.226, 0.746		
no. of measured, independent, and observed $[l > 2\sigma(l)]$ reflections	67 445, 5396, 5276	114395, 12667, 9423		
R _{int}	0.040	0.044		
$(\sin \theta / \lambda)_{max} [Å^{-1}]$	0.717	0.697		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.033, 0.073, 1.15	0.035, 0.096, 1.09		
no. of reflections, parameters	5396, 208	12667, 560		
$\Delta ho_{max} \Delta ho_{min} [e\AA^{-3}]$	3.10, -2.81	1.69, -1.24		

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tallic coordination polymer {[(NO₃)Nd(H₂O)₄(μ_3 -cydta)Bi-(μ -ONO₂)]-2.5 H₂O}_n, where cydta is *trans*-cyclohexylene-1,2-diaminetetraacetate.^[30]

The intrachelate S-Bi-S bond angles of 1 average 66.4(2)°, consistent with the mean of 65(2)° for related structures in the literature.^[27] The coordination group of each BiS₄ unit is completed by one O atom of a nitrate ion (Bi-O1 2.723(4) Å). However, the coordination geometry around Bi^{III} in **1** is distinctly irregular, and defies typical classification. Each nitrate ion functions as a bridging ligand in the 1D chain by virtue of coordination of its second oxygen atom to the adjacent Bi^{III} ion in the lattice (Figure 3). The extended structure may thus be described as a 1D coordination polymer comprising alternating BiS₄ repeat units and bridging nitrate ions. Interestingly, the inversion-related 1D polymer chain interacts significantly with its counterpart through weaker (longer) Bi---S interactions (3.31 Å). Note that the sum of the van der Waals radii^[31] of Bi (2.54 Å) and S (1.89 Å) far exceeds the Bi-S interaction distance in 1, consistent with the interaction being effectively a dative covalent bond. This results in the formation of columns comprising symmetry-related pairs of 1D chains whose axes run parallel to one another but in opposite directions. The obtuse O1ⁱ-Bi-O3ⁱⁱ bond angle of 125.2° (Figure 3) suggests, furthermore, that the Bi^{III} valence lone pair (6s²) may be stereochemically active in 1, as in soft scorpionate^[32] and tetraphenylimidodiphosphinate^[33] chelates of Bi^{III}, and is most likely positioned midway between the two nitrate ion O donors (projecting approximately out of the plane of Figure 3 towards the reader). This electron-density projection is in fact clearly supported by the difference Fourier map for 1 shown in the Supporting Information (Figure S3). It is common to count the lone pair as occupying one coordination site at the metal centre for Bi^{III} coordination compounds.^[34] Applying this principle here suggests that the Bi^{III} ions of 1 are in fact eight-coordinate. Interestingly, there are some well-characterised Bi^{III} coordination complexes in the literature with geometries that clearly indicate the presence of the stereochemically active 6s² lone pair of Bi^{III}; however, its contribution to the irregular coordination geometry around the metal ion is apparently not always recognised.^[35] A sound theoretical basis (s-p mixing of metal-cation and oxide-ligand atomic orbitals) exists to account for the variable appearance of the lone pair in Sb₂O₃ and other 6s² metal oxides (e.g., PbO),^[36] but has seemingly not yet been extended to a molecular orbital treatment of lone-pair effects in large coordination complexes of Bi^{III} with complex ligands such as those described in this work.

Complex **2** is a centrosymmetric tetranuclear Bi^{III} cluster with bridging nitrate groups (μ_1 , η^1 -NO₃⁻, Figure 4). Because the geometry about the centre of gravity of the cluster is opened out by the bridging nitrate ions, no acutely short Bi-··S intramolecular interactions are evident. The shortest of these, Bi1···S1ⁱ (3.650(1) Å, symmetry code i: -x, -y, -z), is probably too long to be considered even a weak dative covalent bond, despite the contact distance lying within the sum of the van der Waals radii of the bonded elements. Consistent with **1**, the obtuse O1-Bi1-O4 bond angle of 133.7(1)° probably signals the presence of the stereochemically active nominally 6s² lone pair

of the Bi^{III} ion, which evidently projects in a direction that roughly bisects the O1-Bi1-O4 bond angle (inset to Figure 4). If the $6s^2$ lone pair is treated as occupying one coordination site, each symmetry-unique Bi^{III} ion labelled Bi1 in **2** should be regarded as seven-coordinate with the remaining coordination sites occupied by the four sulfur atoms of the bidentate 3,4-di-hydroisoquinoline-2(1*H*)-carbodithioate ions and the two nitrate ion oxygen atoms O1 and O4.

The coordination geometry around the second symmetryunique Bi^{III} ion, Bi2, is markedly different to that of Bi1. For example, the O1-Bi2-O4ⁱ bond angle is 85.8(1)° and the structural distortion around Bi2 appears to be less severe. Since we cannot be certain of the existence of a stereochemically active 6s² electron pair for Bi2 (as suggested by the more diffuse electron density distribution about Bi2, see Figure S4 of the Supporting Information), the coordination number around Bi2 is best regarded as being definitively six. The Bi-S bond lengths for 2 range from 2.603(1) to 2.810(2) Å (av 2.70(8) Å), in agreement with those of **1** and other similar Bi^{III} chelate complexes in the literature.^[27] The Bi–O bond lengths average 2.74(4) Å, consistent with the bridging nature of the NO3- ions in the structure, as noted for 1. The S-Bi-S bond angles for 2 average $66.3(5)^{\circ}$, are similar to those of **1** and in close agreement with S-Bi-S intrachelate angles observed for related compounds in the CSD. $^{\mbox{\tiny [27,37]}}$ For both 1 and 2, the C–S bond lengths are statistically equivalent, averaging 1.74(1) and 1.72(1) Å, respectively, consistent with the expected resonance-delocalised electronic structure of the dithiocarbamate ions in both compounds.

The crystal packing in **2** is somewhat loose, presumably because of the inherent difficulty of efficiently packing the large tetranuclear cluster. The total solvent-accessible volume per unit cell is 227.5 Å³ (4.8%), and the total electron count within the void space is 19.9 electrons; this equates to two water molecules per unit cell. Due to their disorder, the water molecules occupying the two larger void spaces (2×51.4 Å³; Figure 5) were not discretely modelled during structure refinement. The smaller void spaces (2×25.7 Å³, 4×10.1 Å³, and 4× 8.2 Å³) are vacant.

The reaction between Bi(NO₃)₃·4H₂O and piperidinedithiocarbamate in water followed by recrystallisation from chloroform/ methanol afforded complex 3. A thermal ellipsoid view of the crystal structure of the bis-chloroform solvate of tris(piperidinedithiocarbamato)bismuth(III) (3; space group $P2_1/c$), is shown in the Supporting Information (Figure S5). Crystal data, data collection and structure refinement details for complex 3 (two independent molecules per ASU) are summarised in the Supporting Information (Table S1). The independent bismuth(III) ions are bound to six sulfur donor atoms, each from three chelating dithiocarbamate ligands. The coordination geometry about each Bi^{III} ion reflects an uneven distribution of the three chelate rings due to formation of a dimer comprising the two crystallographically independent molecules in the lattice (Supporting Information, Figure S6). The dimer is stabilised by intramolecular Sb---S interactions with distances of 3.367(1) Å (Bi2...S4) and 3.402(1) Å (Bi1...S8); the B1-S4...Bi2-S8 and S4-Bi1...S8-Bi2 dihedral angles of 45.53(3) and 45.46(3)°, respec-

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Figure 5. Void locations (gold surfaces) in the lattice of complex 2 (unit cell oriented approximately along the *b* axis). The larger voids (51.4 Å) are occupied by a single disordered water molecule; the smaller voids are vacant. The voids were calculated with a probe radius of 1.2 Å. H atoms have been omitted for clarity, Bi^{II} ions are rendered as spheres (arbitrary radii), and all other bonds and atoms are shown as cylinders.

tively, reflect considerable twisting of the Bi₂S₂ core of the dimer. Interestingly, the Bi₂S₂ core of the centrosymmetric dimer observed for the analogous morpholinodithiocarbamate derivative^[38] is planar (Supporting Information, Figure S7). This leaves substantial room in the morpholinodithiocarbamate complex for a stereochemically active, nominally 6s², lone pair, which clearly culminates in a coordination number of eight for this complex. The twisted Bi₂S₂ dimer core of **3**, in contrast, appears to exclude space for the 6s² lone pair, such that the Bi^{III} ions are seven-coordinate. The Bi–S and S-Bi-S bond lengths and angles of **3** average 2.81(12) Å and $63.9(7)^{\circ}$, respectively, which are normal for this class of compounds (as discussed above).

Bi₂S₃ nanoparticles

The thermolysis of precursors in high-boiling point solvents is a well-reported route to high-quality nanoparticles. The size of the nanoparticles depends on the reaction time and temperature, precursor/capping agent ratio and alkyl groups. Longchain amines were found to be suitable surfactants for II–VI semiconductor nanomaterials. In this work we explored the use of long-chain amines, such as hexadecylamine (HDA), dodecylamine (DDA) and oleylamine (OLA), as well as traditional tri-*n*-octylphosphine oxide (TOPO), as capping agents for Bi_2S_3 nanoparticles. Bismuth complexes **1** and **2** were thermolysed in coordinating solvents at temperatures of 190, 230, and 270 °C for 2 h. The choice of reaction temperatures was based on our previous work on PbS.^[22]

Optical properties

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The absorption spectra of the Bi_2S_3 particles synthesised from precursor 1 in 3.0 g of OLA at 190, 230, and 270 °C are shown in Figure 6. A strong blueshift with absorption band edges of 3.1, 3.09 and 2.9 eV were observed for particles synthesised at

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Figure 6. UV/Vis absorption spectra of OLA-capped Bi_2S_3 nanorods obtained from 1 at a) 190, b) 230 and c) 270.

190, 230 and 270 °C, respectively, compared to that of 1.3 eV (950 nm) for bulk Bi_2S_3 , characteristic of the quantum confinement. This shift can be explained by the presence of Bi_2S_3 nanocrystals in which at least one linear dimension is in the nanosize regime. A slight shift in the optical absorption associated with increasing reaction temperature is also observed, and indicates an increase in mean particle size with increasing temperature. A similar trend was observed when precursor 1 was thermolysed in HDA, DDA, and TOPO. No significant changes in the optical properties of the Bi_2S_3 particles were observed when precursor 2 was thermolysed in DDA, HDA, and TOPO with corresponding reaction parameters.

Structural and morphological characterisation

Powder X-ray diffraction (PXRD) studies on the powders obtained from precursor 1 in HDA at 190, 230, and 270 °C are shown in Figure 7. The (020), (120), (220), (101), (111), (021), (211), (002) and (240) peaks correspond to the pure orthorhombic phase of Bi_2S_3 (ICCD 03-065-2435). The strong and sharp peaks in the XRD patterns are an indication that the Bi₂S₃ particles are highly crystalline. The XRD data are in agreement with reported data for Bi₂S₃ nanostructures synthesised from dithiocarbamate precursors by other methods.^[13, 14, 16] We compared the PXRD patterns of the Bi₂S₃ particles prepared from precursor 1 at 270 °C in DDA, HDA, OLA and TOPO (Figure 8). All the particles were crystalline, except for OLAcapped Bi₂S₃, which exhibited broad peaks, typical of poorly crystalline particles. The broadening of the peaks in Figure 6c also implies a smaller grain size of the Bi₂S₃ crystals prepared in OLA compared to the other capping agents. This was confirmed by their average crystallite sizes estimated by applying the Scherrer formula to the (111) peak, which were 15.7 (OLA), 21.5 (TOPO); 21.9 (HDA) and 21.5 nm (DDA). A representative



Figure 7. PXRD patterns of ${\rm Bi}_2 S_3$ nanorods synthesised in HDA from 1 at 190, 230 and 270 $^\circ C.$



Figure 8. PXRD patterns of Bi_2S_3 nanorods synthesised from 1 at 270 $^\circ C$ in DDA, HDA, OLA and TOPO.

PXRD pattern for the material prepared from precursor **2** at a reaction temperature 230 °C is shown in the Supporting Information (Figure S8).

The morphology of the Bi_2S_3 nanostructures was studied by TEM. Figure 9 shows the images of Bi_2S_3 nanocrystals prepared from precursor 1 in DDA (C_{10}) at 190, 230 and 270 °C. It has been reported that at high temperatures the influence of the surface ligands is minimised through the dynamic bonding nature of the ligands, and as a result particles revert to thermodynamically stable morphologies such as spheres. Low-temperature routes offer more flexibility in shape control, and anisotropic-shaped particles such as rods are formed through judicious use of surfactants.^[22] We obtained Bi_2S_3 nanorods at the three different reaction temperatures (Figure 9a–c) using DDA as capping group. Similar results were obtained by Xie et al. by thermolysing bismuth tris(diethyldithiocarbamate) complexes at temperatures ranging from 115 to 170 °C. The formation of nanorods at all the temperatures could be attrib-



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Figure 9. TEM images of Bi_2S_3 nanoparticles synthesised from 1 in DDA at a) 190, b) 230 and c) 270 °C. d) Corresponding SAED pattern

Table 4. Lengths <i>L</i> and widths <i>W</i> of the Bi_2S_3 nanorods synthesised from 1 with various reaction parameters.					
Capping agent	<i>T</i> [°C]	<i>L</i> [nm]	<i>W</i> [nm]	Aspect ratio (± 0.1)	
DDA	190	161.9±0.3	16.5 ± 0.1	9.8	
DDA	230	154.7 ± 0.4	22.7 ± 0.1	6.8	
DDA	270	$76.1\pm\!0.5$	23.9 ± 0.1	3.2	
HDA	190	236.9 ± 0.2	20.3 ± 0.1	11.7	
HDA	230	217.2 ± 0.1	24.4 ± 0.1	8.9	
HDA	270	193.5 ± 0.3	49.9 ± 0.2	3.9	
OLA	190	252.6 ± 0.2	31.2 ± 0.1	8.1	
OLA	230	221.5 ± 0.2	36.4 ± 0.2	6.1	
OLA	270	194.2 ± 0.4	38.3 ± 0.2	5.1	
ТОРО	190	182.3 ± 0.2	29.2 ± 0.2	6.2	
ТОРО	230	106.6 ± 0.1	42.8 ± 0.2	2.4	
ТОРО	270	95.4 ± 0.3	44.1 ± 0.2	2.1	

uted to bonding to metal ions.^[15] The dimensions of the Bi_2S_3 nanostructures obtained under different reaction conditions with a variety of capping groups are summarised in Table 4.

The DDA-capped Bi₂S₃ nanostructures obtained at 190 °C are rods with average length of 161.9 ± 0.3 nm and average breadth of 16.5 ± 0.1 nm (Figure 9a). When the temperature was raised to 230 °C, a slight increase in the breadth (22.7 ± 0.1 nm) and decrease in the length (154.7 ± 0.4 nm) of the rods was observed (Figure 9b). At 270 °C, the aspect ratio of the rods decreased further (Figure 9c). The darker, opaque regions of the rods observed in the TEM images indicate overlap or stacking of rods. The selected-area electron diffraction (SAED) pattern confirmed the formation of a highly crystalline single Bi₂S₃ nanorod (Figure 9d), and energy-dispersive X-ray analysis revealed a Bi:S molar ratio of 30.88:48, close to the expected 2:3 molar ratio of Bi₂S₃ (Supporting Information, Figure 9).

The carbon chain length of the amine was increased from C_{10} (DDA) to C_{16} (HDA). When complex **1** was thermolysed in HDA at the same reaction temperatures (190–270 °C), no significant change in the Bi₂S₃ morphology was revealed by TEM

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Figure 10. TEM images of Bi_2S_3 nanorods synthesised from 1 in HDA at a) 190, b) 230 and c) 270 °C. d) Corresponding HRTEM image.

(Figure 10). Overall the average breadth of the rods increased with increasing length of the carbon chain. The HDA-capped Bi_2S_3 nanorods obtained at 190 °C appeared to be agglomerated, and stacking was also observed. The aspect ratio also increased compared to the DDA-capped Bi_2S_3 rods. When synthesised at 230 °C the distinct nanorods have equal lengths with some degree of alignment (Figure 10b). Larger and more irregularly shaped particles were obtained at 270 °C (Figure 10c). The HRTEM image of a single nanorod synthesised at 230 °C (Figure 10d) shows distinct lattice fringes with a lattice spacing of 0.311 nm, assigned to the (211) lattice plane.

When precursor 1 was thermolysed in TOPO, spherical Bi_2S_3 particles were expected at high temperature according to the thermodynamic growth regime. Monteiro et al. reported the synthesis of spherical Bi_2S_3 when a bismuth tris(alkyldithiocarbamate) complex was thermolysed in TOPO at 150 °C.^[7] However rod-like morphologies were obtained at 190 and 230 °C when thermolysis of 1 was carried out in TOPO (Supporting Information, Figure S10). The higher temperature of 270 °C gave less anisotropic morphologies with higher degrees of agglomeration. Similar results were obtained when precursor 2 was thermolysed in DDA, HDA, OLA and TOPO, and the representative images for samples prepared at 230 °C are shown in Figure 11.

The role of dodecanethiol (DT) in the formation of rodshaped nanostructures has been reported previously for Bi_2S_3 and $Cu_{2-x}S.^{[18,41,42]}$ In our work, decomposition of the bismuth complexes at high temperatures allowed the sulfur atoms of DT to react with the Bi^{3+} ions. This coordination of sulfur to the metal can control the reaction chemical potential of the solution. High chemical potentials result in thermodynamically less stable elongated structures. We thermolysed both complexes in HDA at 230 °C without the addition of DT. The absence of DT resulted in the formation of poorly crystalline bismuth sulfide nanoparticles, as observed by TEM (Supporting Information, Figure 11).



Figure 11. TEM images of a) DDA-, b) HDA-, c) OLA- and d) TOPO-capped Bi_2S_3 nanoparticles synthesised from 2 at 230 °C.

Trindade and co-workers also observed that the coordinating solvent plays a significant role in the final morphology of the Bi₂S₃ nanoparticles.^[7] They obtained Bi₂S₃ nanofibers when bismuth (III) dithiocarbamate complexes were thermolysed in ethylene glycol. The use of p-xylene, 2-ethoxyethanol and 4ethylpyridine also gave fibre-type Bi₂S₃ particles. The high guality of the Bi₂S₃ nanostructures shows that the use of SSPs is effective. The synthetic route allows for the manipulation of shape and properties. We have done extensive work on the use of heterocyclic metal dithiocarbamate complexes in various coordinating solvents.^[19,21,22] Our experience has shown that long-chain alkyl amine ligands are effective in producing anisotropic nanostructures. We have used hexadecylamine (HDA), dodecylamine (DDA) and oleylamine (OLA) to synthesise elongated CdS^[19] and PbS^[22] nanostructures. In this work we have shown that the judicious choice of capping groups in combination with DT is essential to obtain good-quality nanorods. We have also shown that the bulky nature of the heterocyclic precursor is also important in the decomposition pathway to the nanostructures. In general, SSPs behave better than the multisource precursors, partly due to the absence of prereactions, built-in stoichiometry, high purity and decomposition at a single temperature, because most of the SSPs are solid crystalline materials.

Conclusion

Heterocyclic bismuth dithiocarbamate complexes *catena*-(μ_2 -ni-trato-*O*,*O*')bis(piperidinedithiocarbamato)bismuth(III) (1) and tetrakis(μ -nitrato)tetrakis[bis(tetrahydroquinolinedithiocarbamato)bismuth(III)] (2) have been synthesised and characterised. The single-crystal X-ray structures of both complexes were determined; that of 1 is based on a 1D coordination polymer, whereas 2 is a cyclic tetramer. High-quality Bi₂S₃ nanorods were obtained by thermolysis of 1 and 2 with variation of the temperature and the capping agent. The optical properties of

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the materials obtained under all reaction conditions confirmed the quantum-confined nature of the particles. The length of the carbon chain of the amine used as capping agent affects the optical properties and size of the Bi_2S_3 nanorods. The orthorhombic phase and the crystalline nature of the synthesised particles were confirmed by PXRD. We envisage further investigating the use of these precursors for the deposition of Bi_2S_3 thin films by aerosol-assisted chemical vapour deposition.

Experimental Section

Chemicals

Hexadecylamine (HDA), dodecylamine (DDA), oleylamine (OLA), trin-octylphosphine oxide (TOPO), acetonitrile, 1,2,3,4-tetrahydroquinoline (98%), piperidine (99%), bismuth nitrate tetrahydrate, and 1-dodecanethiol were purchased from Sigma-Aldrich. Petroleum ether, methanol (99.5%), dichloromethane, carbon disulfide (99.5%), chloroform, sodium hydroxide (98%) and acetone were purchased from Merck and used without any further purification.

Instrumentation

Microanalysis was performed with a PerkinElmer automated model 2400 series II CHNS/O analyser. IR spectra were recorded with a Bruker FTIR Tensor 27 spectrophotometer directly on small samples of the compounds in the range 200–4000 cm⁻¹. TGA was carried out at a heating rate of 20 °C min⁻¹ with a PerkinElmer Pyris 6 instrument up to 600 °C in a closed perforated aluminium pan under N₂ gas flow.

Optical absorption measurements were carried out with a PerkinElmer Lambda 1050 UV/Visible NIR spectrophotometer. The samples were placed in silica cuvettes (1 cm path length), and hexane was used as reference solvent. TEM and HRTEM were performed with JEOL 1010 TEM and JEOL 2100 HRTEM microscopes. Samples were prepared by placing a drop of dilute solution of nanoparticles on Formvar-coated Cu grids (150 mesh) for TEM and holey carbon grids for HRTEM. The samples were allowed to dry completely at room temperature and viewed at accelerating voltages of 100 kV (TEM) and 200 kV (HRTEM), and images were captured digitally with a Megaview III camera and stored and measured by using Soft Imaging Systems iTEM software (TEM) and a Gatan camera and Gatan software (HRTEM). PXRD patterns were recorded in the high-angle 2θ range of 20–60° by using a Bruker AXS D8 Advance X-Ray diffractometer, equipped with nickel-filtered $Cu_{K\alpha}$ radiation (λ = 1.5406 Å) at 40 kV, 40 mA, and at room temperature.

Single-crystal X-ray structure analysis

Flat, yellow, needle-like single crystals measuring about $0.35 \times 0.20 \times 0.15$ mm for 1 and $0.40 \times 0.16 \times 0.12$ mm for 2 were mounted on the goniometer of a Bruker Apex II Duo CCD diffractometer by using a 500 µm-long needle mount and a 200 µm-diameter cryoloop (MiTeGen), respectively, after initial suspension and selection in Paratone oil. Intensity data were collected with Mo_{ka} radiation from an Incoatec microsource (IuS, Quazar mirror optics) at 100 K for complex 1 and 296 K for complex 2. The structures were solved by direct methods with SHELXS^[39] running in Olex2.^[40] The structures were refined by least-squares methods (SHELXL).^[39] All non-H atoms were refined anisotropically; H atoms were included in calculated positions, assigned isotropic thermal parameters (U_{iso} for H atoms = 1.2 U_{iso} for the attached C atom) and allowed to ride on their parent carbon atoms by using the standard HFIX parameters

in SHELXL. In the case of **2**, the tetrahydroisoquinoline ring containing atoms N1 and C1–C9 was slightly disordered with two puckered half-chair conformations. The disorder was resolved by using two positions for C8 and C9 (C8A and C8B; C9A and C9B) with standard SHELXL restraints (79 in total). Solvent-accessible voids exist in the structure of **2** and the total solvent-accessible volume per cell is 220.9 Å³ (4.6%). The largest voids located at the special positions (0.500,0.000,0.500) and (0.500,0.500,-0.000) have volumes of 51.4 Å³ and contain a disordered water molecule (9.9 electrons). The electron density, however, was not allocated to the solvent in the final structural model. Crystal data and structure refinement parameters are presented in Table 1. CCDC 1425649 (1) and 418494 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Preparation of the ligands

Carbon disulfide (0.1 mol, 6.0 mL) was added in small portions to an equimolar mixture of sodium hydroxide (4.0 g, 0.1 mol) and the corresponding amine (piperidine, tetrahydroquinoline, 0.1 mol) cooled in an ice bath. After 15 min, a precipitate was formed and was then dried in air and recrystallised from acetone/petroleum ether. The final product was collected, washed with chloroform and suction-dried.

Na(S2CPip): Yield: 92%. Significant IR bands: $\tilde{\nu}$ = 3377 (O–H), 967 (C=S), 1468 cm⁻¹ (C=N); elemental analysis (%) calcd for C₆H₁₄NS₂O₂Na: C 32.86, H 6.43, N 6.39; found: C 32.91, H 6.53, N 6.20.

Preparation of bismuth complexes

Bi(NO₃)₃·4H₂O (2.43 g, 5 mmol) was suspended in deionised water (15 mL), and the suspension added dropwise to a solution of the corresponding dithiocarbamate ligand (10 mmol) in deionised water (25 mL). The mixture was stirred at room temperature for 1 h. The yellow precipitate that formed was collected by filtration and recrystallised from chloroform/methanol (3:1).

Complex 1: Yield: 62%. Significant IR bands: $\tilde{\nu} = 964 \text{ cm}^{-1}$ (C=S), 1473 (C=N),: 365 cm⁻¹ (Bi–S); elemental analysis (%) calcd for Bi(C₆H₁₀NS₂)₂NO₃·2H₂O: C 24.36, H 3.41, N 7.10; found: C 24.37, H 3.24, N 6.95; m.p. 279 °C.

Complex **2**: Yield: 68 %. Significant IR bands: $\tilde{v} = 960$ (C=S), 1475 (C=N), 388 cm⁻¹ (Bi–S); elemental analysis (%) calcd for Bi(C₁₀H₁₀NS₂)₂·NO₃: C 34.93, H 2.93, N 6.11; found: C 34.8, H 2.86, N 6.06; m.p. 270 °C.

Preparation of HDA-capped Bi₂S₃ nanoparticles

Complex 1 or complex 2 (0.3 g) was dissolved in OLA (3.0 mL) and the solution injected into HDA (3.0 g) and DT (0.2 mL) in a threenecked flask at 190 °C. The mixture turned to a blackish liquid and a drop in temperature of 25–30 °C was observed. The reaction was allowed to stabilise at 190 °C. After 2 h of reaction, heating was stopped and methanol was added, resulting in the formation of a flocculent precipitate. The precipitate was separated by centrifugation, washed several times with acetone/methanol and dispersed in toluene to give dark gray HDA-capped Bi₂S₃ nanoparticles. The reaction was repeated at 230 °C and 270 °C. The above re-

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action procedure was repeated with DDA, OLA and TOPO as capping agents.

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FULL PAPER

Nanoparticles

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Heterocyclic Bismuth(III) Dithiocarbamato Complexes as Single-Source Precursors for the Synthesis of Anisotropic Bi₂S₃ Nanoparticles



Bismuth sulfide nanorods: Two bismuth(III) dithiocarbamato complexes were synthesised and characterised by elemental analysis, FTIR spectroscopy, thermogravimetric analysis and single-crystal XRD. Both complexes were used as single-source precursors for the synthesis of capped Bi₂S₃ nanoparticles at different temperatures. High-quality, crystalline, long and short Bi₂S₃ nanorods were obtained (see figure) depending on the thermolysis temperature, which was varied from 190 to 270 °C.

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