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Synthesis and characterization of thiosemicarbazone derivatives of methylbismuth(III) dichloride: generation of one dimensional micro-rods of bismuthinite from [$MeBiCl_2 \cdot n\{(C_6H_4OH)CHNNHCSNH_2\}$] by a solvothermal process

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Abstract

Reactions of methylbismuth(III) dichloride with thiosemicarbazones (TSC) in 1:1 and 1:2 molar ratios in anhydrous methanol yield [$MeBiCl_2.n\{RR'CNNHCSNH_2\}$] [where, R=R′=$CH_3$ and n=1 (**1**) or n=2 (**2**); R=C_6H_4OH, R′=H and n=1 (**3**) or n=2 (**4**); R=C_5H_4N, R'=CH_3 and n=1 (**5**) or n=2 (**6**)]. These monomeric adducts have been characterized by elemental analyses, Fourier transform infrared, nuclear magnetic resonance [^1H, $^{13}C\{^1H\}$] and fast atom bombardment mass spectrometry. The ligand appears to bind bismuth through sulfur and azomethine nitrogen atoms rendering penta- and hepta- coordination geometries, in (**1**, **3** and **5**) and (**2**, **4** and **6**), respectively, in the solution state. Low temperature (143–145°C) solvothermal transformation of (**3**) or (**4**) in refluxing xylene yields nano-structured flowers of amorphous bismuthinite (Bi_2S_3). Prolonged (~10 h) sintering at 150°C of the powder obtained from (**4**) yielded one-dimensional micro/nanorods of orthorhombic Bi_2S_3. All the materials were characterized by X-ray diffraction, scanning electron microscopy and energy-dispersive X-ray analyses.

Keywords: methylbismuth(III) dichloride adducts; micro Bi_2S_3; orthorhombic bismuthinite.

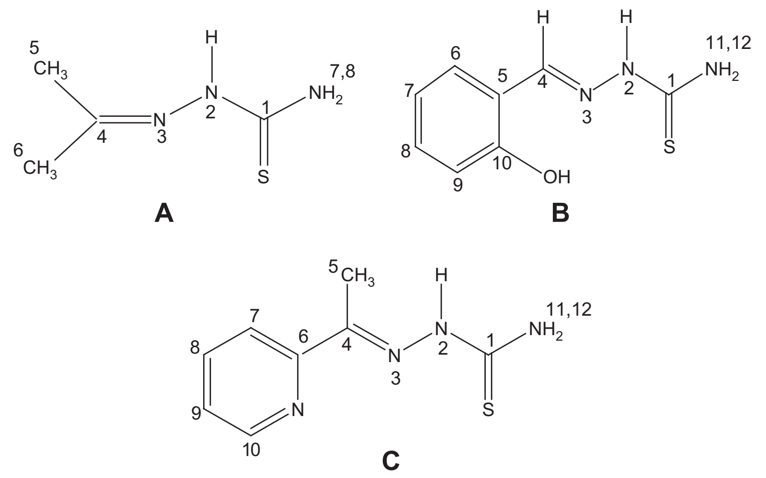
Introduction

One-dimensional nanostructured group-15 chalcogenide materials, such as Bi_2S_3, Bi_2Se_3 and Bi_2Te_3, are considered to be the most promising species for nanoscale devices (Wang et al., 2009; Kim et al., 2011). Although telluride materials exhibit predominant thermoelectric properties (Böttner et al., 2007; Lee et al., 2008), the toxic effect of tellurium necessitates the use of some alternate materials. Bismuth sulfide being a good semiconductor material (with a direct band gap of 1.3–1.7 eV) it has applications in photoelectrochemical cells (Mane et al., 1999; Ahire and Sharma, 2006), optoelectronic devices (Xi et al., 2009), thermoelectric cooling technologies (Zhao et al., 2008), etc.

Many approaches have been proposed for fabricating one-dimensional nanostructured Bi_2S_3 including template-assisted (Ota and Srivastava, 2005), solvothermal (Wei et al., 2006; Ma et al., 2007), thermolysis (Boudjouk et al., 1998), microwave irradiation (Lu et al., 2007), etc. Little is known, however, about the solvothermal process for the preparation of one-dimensional micro/nanorods of Bi_2S_3 using single source precursors (Xie et al., 2004). Interestingly, the single source precursor route not only provides a feasible reaction mechanism and the possibility to tailor the molecule for the desired nanocrystal morphology (Monteiro and Trindade, 2000; Han et al., 2007; Tahir et al., 2010), but also decreases the variable factors, such as the molar ratio of reactants, reaction temperature and anions of the metal salts.

Synthesis, characterization and applications of some methylbismuth(III) derivatives containing dithio ligands yielding interesting results have recently been reported by us. It has been observed that some of these derivatives behave as good precursors for the preparation of pure microcrystallites of bismuthinite (Bi_2S_3) at low temperature, as compared with the traditional high-temperature synthetic routes (Gupta et al., 2003; Jain and Bohra, 2006; Jain et al., 2006; Chaudhari et al., 2010).

Although details of the first bismuth(III) complex with a thiosemicarbazone derivative as a ligand were published in 1990 (Battaglia et al., 1990), their structural variations were only demonstrated in 1995 (Diemer et al., 1995). Methylbismuth(III) derivatives of thiosemicarbazones (TSCs), however, have not been reported in the literature (Chauhan, 1998). Herein, we report on the synthesis and characterization of single-source molecular precursors of TSCs of the types [$MeBiCl_2.n\{RR'CNNHCSNH_2\}$] (where, R=$CH_3$, C_6H_4OH or C_5H_4N and R′=CH_3 or H), for the preparation of pure, one-dimensional micro/nanorods of bismuthinite.



Scheme 1 Numbering scheme for TSC: (A) acetone thiosemicarbazone; (B) salicaldehyde thiosemicarbazone; (C) 2-acetylpyridine thiosemicarbazone.

Results and discussion

Reactions of $MeBiCl_2$ with TSCs in a 1:1 or 1:2 molar ratio in anhydrous methanol yield adducts of the type $[MeBiCl_2.n\{RR'CNNHCSNH_2\}]$

$$MeBiCl_2 + n\{RR'CNNHCSNH_2\} \xrightarrow{\text{Methanol}} \underset{\mathbf{(1–6)}}{[MeBiCl_2.n\{RR'CNNHCSNH_2\}]}$$

[where, $R=R'=CH_3$ and n=1 (**1**) or n=2 (**2**); $R=C_6H_4OH$, $R'=H$ and n=1 (**3**) or n=2 (**4**); $R=C_5H_4N$, $R'=CH_3$ and n=1 (**5**) or n=2 (**6**)] (Scheme 1).

The above reactions are quite facile, quantitative and lead to the formation of adducts. These are colored solids that are sparingly soluble in dichloromethane but soluble in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF). They were further purified by recrystallization from a mixture of THF and n-hexane. These solids were characterized by elemental analyses, Fourier transform infrared, nuclear magnetic resonance (NMR) [^1H, $^{13}C\{^1H\}$] and fast atom bombardment (FAB) mass studies. Elemental analyses correspond to the expected formulae. FAB mass studies indicate their monomeric nature. The ν (C=N) band of the TSCs at 1600–1620 cm^{-1} shifts in the spectra of the complexes to 1590–1600 cm^{-1} (a shift of 10–20 cm^{-1}), indicating coordination of the azomethine nitrogen to the metal. Similarly, the uncomplexed TSC exhibits a ν (C=S) band at 790–835 cm^{-1}, which also shifts to 765–795 cm^{-1} in the bismuth complexes (a shift of 25–40 cm^{-1}), suggesting coordination of the thione sulfur with the metal. Both the ^1H and $^{13}C\{^1H\}$ NMR spectra of these complexes exhibit marginal downfield shifts compared to the free TSC. The absence of any significant shift in the heteroaryl ring proton/carbon resonance in the $^1H/^{13}C\ \{^1H\}$ NMR spectra of complexes (**5**) and (**6**) suggests that the heteroatom (nitrogen ring) is not taking part in coordination with the central bismuth atom in the solution state.

Attempts to obtain good quality crystals of these products were not successful. On the basis of above studies, however, penta-(**1**, **3** and **5**) and hepta-(**2**, **4** and **6**) coordination geometry around bismuth may tentatively be assumed in the solution. It is possible that bismuth halide bridges exist in the solid state to give a higher coordination number than assumed in the solution. The tentative structures of $[MeBiCl_2.\{(C_6H_4OH)CHNNHCSNH_2\}]$ (**3**) and $[MeBiCl_2.2\{(C_6H_4OH)\text{-}CHNNHCSNH_2\}]$ (**4**) in solution are shown in Figure 1.

Thermogravimetric analysis

Thermogravimetric analysis of the two representative single-source molecular precursors, (**3**) and (**4**) was carried out (Figure 2). For both complexes, the decomposition appears to be complete at about 900°C.

The TG curve of (**3**) revealed three-step decomposition, with a minimal weight loss of 3.76% (calc. 3.26%) at a temperature of 0–150°C due to the elimination of a methane molecule (possibly due to $MeBiCl_2.LH \rightarrow CH_4 + BiCl_2.L$). In the second step, i.e., from 150°C to 350°C, although quite speculative the weight loss of 35.91% (calc. 35.81%) could be due to the elimination of half molecules of $BiCl_3$ and HCl (possibly from the decomposition of the $BiCl_2.L$ that forms). Major weight loss of 38.40% (calc. 34.89%) occurred in the final step in the of 350–900°C temperature range, which may be due to

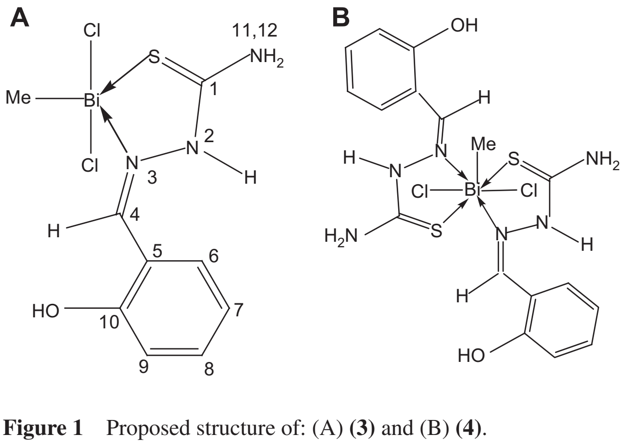


Figure 1 Proposed structure of: (A) (**3**) and (B) (**4**).

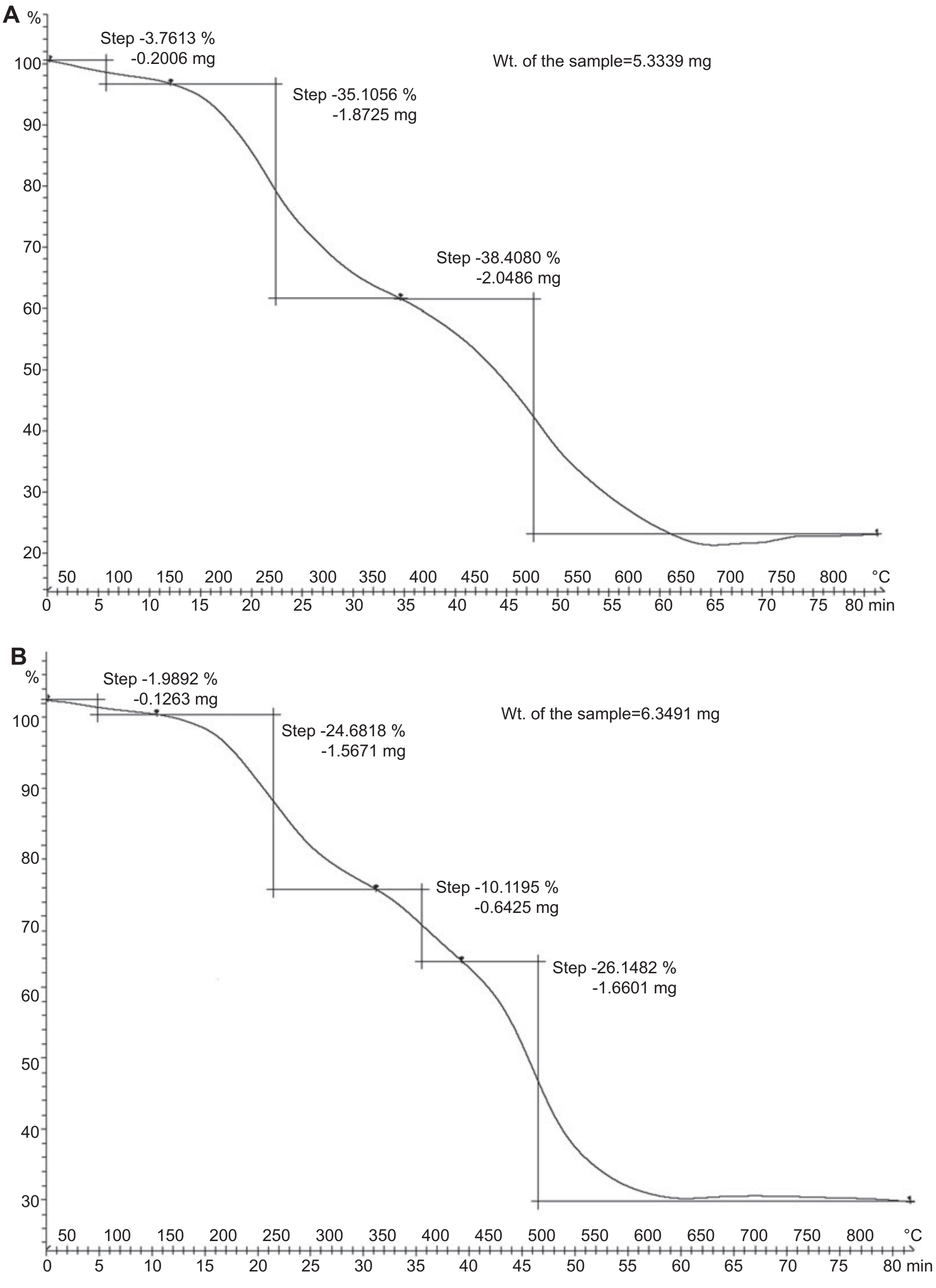


Figure 2 TG curve (weight % vs. temperature °C) of: (A) **(3)** and (B) **(4)**.

the complete loss of the ligand moiety resulting in the formation of 1/2 Bi_2S_3. The overall weight loss corresponding to the formation of 1/2 Bi_2S_3 was 74.00% (observed: 78.07%).

The TG curve of **(4)** exhibits four weight loss events. The weight loss of 1.98% in the 0–150°C range may be due to elimination of a methane molecule (calc. 2.33%). The next step is followed by a weight loss of 24.68% at a temperature range of 150–350°C. This could be due to the loss of a TSC molecule without sulfur, which is in agreement with the calculated value (23.79%). In the third step, a weight loss of 10.11% in the 350–440°C temperature range may be due to the loss of two HCl molecules (10.65%). In the final step (at 440–900°C) complete decomposition takes place leading to the formation of 1/2 Bi_2S_3 (obs. 26.14%; calc. 25.83%). The overall weight loss corresponds quite well to the formation of 1/2 Bi_2S_3 (obs.: 62.91%, calc. 62.60%).

Material characterization

The solvothermal processes for **(3)** and **(4)** have been carried out in xylene (143–145°C) for the preparation of pure bismuthinite (Bi_2S_3). When **(3)** or **(4)** is refluxed for 2 h in xylene under inert media, black powder was obtained. Powder XRD (Figure 3), SEM and EDX (Figure 4) analyses indicate the formation of Bi_2S_3 microspheres. These microspheres are quite similar to those from the reported morphology (Zhou et al., 2006; Phuruangrat et al., 2009). It may be assumed that these microspheres are the spherical assembly of linear (one-dimensional) projections (i.e., nanorods) growing by a splitting crystal growth mechanism (Tang and Alivisatos, 2006). A comparison of the XRD patterns of Bi_2S_3 (Figure 3) obtained from the precursors **(3)** and **(4)** with the reported patterns [PDF # 17-0320], indicates the formation of the orthorhombic Bi_2S_3 in both cases. No impurities, such as Bi_2O_3, Bi, etc., were detected. The XRD (Figure 3) and SEM images (Figure 4) exhibit better uniformity in particle morphology and crystallinity of Bi_2S_3 obtained from precursor **(4)** as compared to (**3**). Keeping this in mind, only Bi_2S_3 obtained from **(4)** was further sintered at 150°C to examine the occurrence of morphological changes over time. It is worth mentioning here that experiments indicate that sintering at 150°C for at least 10 h appears to be essential to get crystalline microrods. The diffraction peaks of Bi_2S_3 microrods obtained from **(4)**, after refluxing in xylene followed by sintering at 150°C for ~10 h, are narrower and sharper (Figure 3c), indicating the formation of a highly crystalline orthorhombic Bi_2S_3 (Table 1). The average size of the crystallite, as calculated by the Debye Scherrer equation, was found to be ~23 nm.

The EDX analysis of these samples are in agreement with the composition of Bi_2S_3 (Figure 4) [calc., Bi, 81.3; S, 18.7%]; found Bi, 80.0; S, 20.0% (in Bi_2S_3 obtained from **3**); found Bi, 79.9; S, 20.1% (in Bi_2S_3 obtained from **4**) and found Bi, 79.8; S, 20.2% (obtained after sintering the powder from **(4)** at 150°C for ~10 h).

The absorption spectra of Bi_2S_3 obtained from **(4)** as well as that of the crystalline Bi_2S_3 microrods obtained from **(4)** after sintering at 150°C for ~10 h are shown in Figure 5. Plots of hν vs. $(\alpha h\nu)^2$ show the energy band gaps of 4.93 eV and 4.37 eV calculated by Tauc relation for amorphous and crystalline Bi_2S_3 (Figure 6), respectively. Bismuth sulfide generally exhibits a direct band gap of 1.3–1.7 eV, depending on its morphology. The high values of band gaps are quite unusual but are very similar to the reported values (Zhao et al., 2004; Dong et al., 2008). Although XRD patterns do indicate the formation of pure Bi_2S_3, the high values of band gaps could be due to the presence of some impurities containing C=N and/or C=S functions.

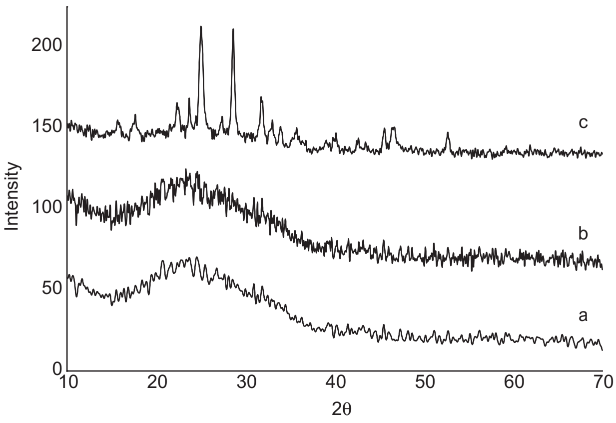


Figure 3 XRD patterns of Bi_2S_3 obtained from; (a) (**3**); (b) (**4**); and (c) after sintering of the powder obtained from **(4)** at 150°C for ~10 h.

Conclusions

Adducts of methylbismuth(III) dichloride with TSCs exhibit penta- and hepta- coordination states around bismuth(III) in the solution state. One-dimensional microrods of bismuthinite have been successfully synthesized by solvothermal processes using the single-source molecular precursors $[MeBiCl_2.n\{(C_6H_4OH)CHNNHCSNH_2\}]$ (n=1 and 2). The formation of pure bismuthinite from these precursors at refluxing xylene temperature indicates their potential application in material synthesis.

Experimental

All manipulations for the synthesis and characterization of the complexes were carried out under strictly anhydrous conditions. The solvents and reagents (Sigma-Aldrich Co. LLC., St. Louis, Missouri, USA) used were dried and purified by conventional methods (Vogel, 1989). Appropriate precautions were taken when handling hazardous chemicals and solvents. $MeBiCl_2$ (Althaus et al., 2001) and TSCs (Anderson et al., 1951) were prepared according to methods given in the literature. Chloride was estimated using Volhard's method (Vogel, 1989).

Infrared spectra (4000–400 cm^{-1}) were recorded as dry KBr pellets on a SHIMADZU, Fourier transform Infrared 8400 spectrometer (Shimadzu Corp., Tokyo, Japan) in KBr powder. NMR [^1H and $^{13}C\{^1H\}$] data were collected on a JEOL FX 300 FT NMR spectrometer (Jeol USA Inc., PA, USA) in DMSO solution at frequencies of 300.4 and 75.45 MHz, respectively, using tetramethylsilane as an internal standard. The FAB mass spectra of all the complexes were obtained on a JEOL SX 102/DA-6000 mass spectrometer data system (Jeol Ltd., Tokyo, Japan) using argon/xenon (6 kv, 10 mA) as the FAB gas and m-nitrobenzylalcohol as the matrix. Microanalyses were carried out on a Heracus Carlo Erba 1108 analyzer (Elemental microanalysis Ltd., Okehampton, UK). X-ray diffraction (XRD) analysis was carried out on a Philips PW 1820 diffractometer (PANalytical B.V, Almelo, Netherlands) operating with Cu-K_α radiation at λ 1.54056. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis were performed on an EDX-coupled scanning electron microscope QUANTA 200 FEG (FEI Co., Oregon, USA). Thermogravimetric analysis was performed on a Mettler Toledo Star SW701 (Mettler-Toledo International Inc., Columbus, OH, UK) with the heating rate being 25–900/10°C under nitrogen atmosphere. Absorption spectra were recorded on a USB2000 spectrometer (Ocean Optics, Dunedin, FL, USA) at room temperature using OOIBase32 software (Ocean Optics, USA).

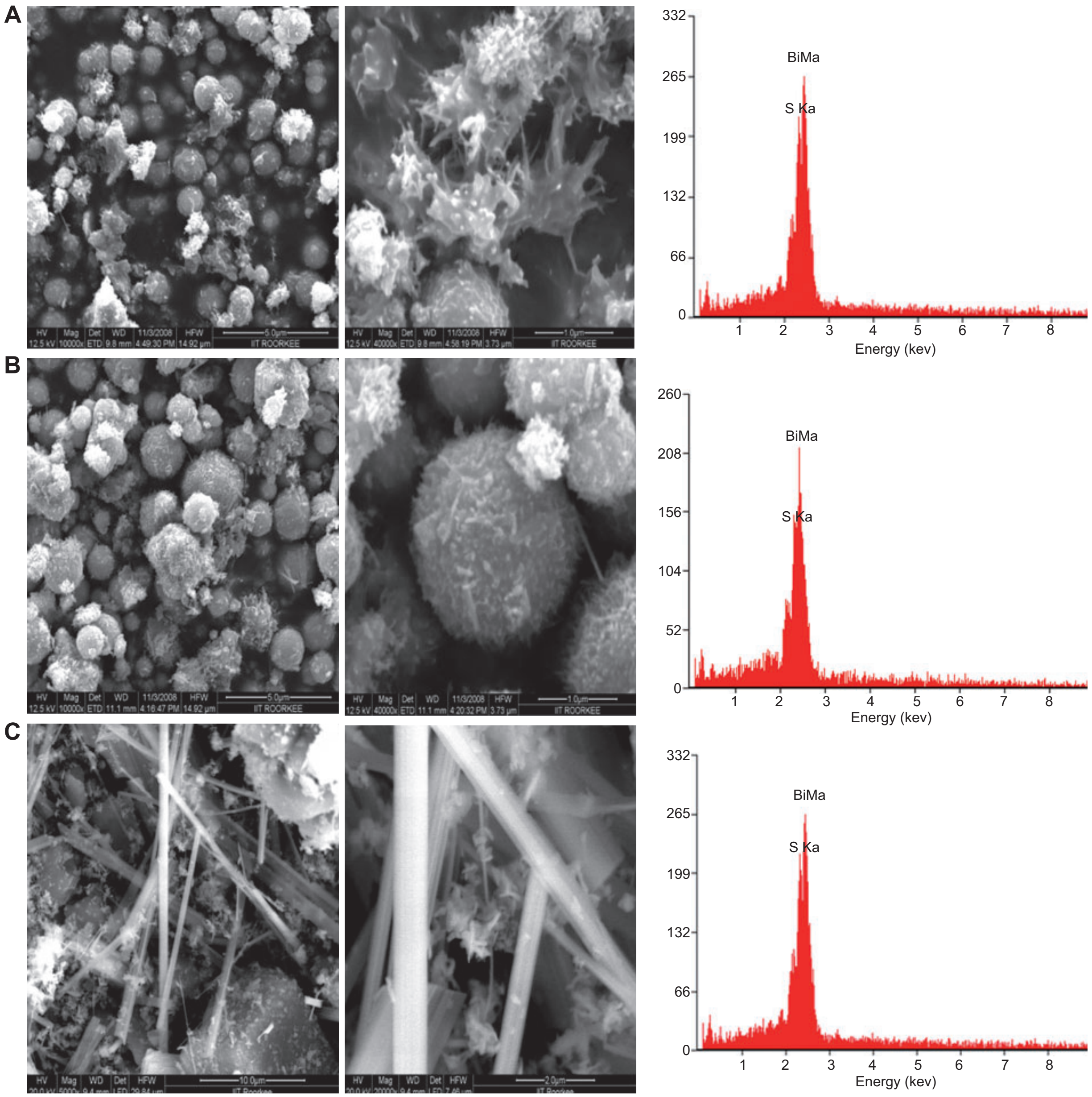


Figure 4 SEM and EDX images of Bi_2S_3 obtained from: (A) **(3)**; (B) **(4)**; and (C) after sintering of the powder obtained from **(4)** at 150°C for ~10 h.

Preparation of $[MeBiCl_2.\{(CH_3)_2CNNHCSNH_2\}]$ (1)

A solution of $MeBiCl_2$ (2.21 g, 7.49 mmol) in methanol (~15 ml) was added to a solution of $[(CH_3)_2CNNHCSNH_2]$ (0.98 g, 7.46 mmol) in methanol (~30 ml). The solution immediately turned yellow. The reaction mixture was stirred for 5 h. The solvent was stripped off under vaccum to give a yellow foamy solid that was washed with n-hexane to yield yellow colored powder.

Table 1 XRD data of Bi_2S_3 obtained from **(4)** after sintering at 150°C for ~10 h.

2θ	d (Å)	hkl	Crystal structure
24.960	3.5644	130	Orthorhombic
28.615	3.1169	211	(*a*=1.0376 nm, *b*=1.1386 nm, *c*=0.4128 nm)
31.744	2.8164	221	

[Yield 98%; m.p. 120°C; Elemental analysis (obs.) C, 14.16; H, 2.67; N, 9.50; Cl, 16.61, (cal.) C, 14.09; H, 2.84; N, 9.86; Cl, 16.64; ^1H NMR (DMSO-d_6, 300.4 MHz) 1.57 [s, 3H, BiMe], 1.89, 1.91 [s, 3H, 3H, H-5,6], 7.54 [br, 1H, H-7], 8.04 [br, 1H, H-8], 9.94 [br, 1H, H-2]; ^{13}C- NMR (DMSO-d_6, 75.45 MHz), 18.01 [C-5], 25.47 [C-6], 74.69 [BiMe], 152.24 [C=N], 178.69 [C=S]; IR (KBr, cm^{-1}) 427s [ν (Bi-N)], 490s [ν (Bi-C)], 765s [ν (C=S)], 1590s [ν (C=N)], 3145s [ν (N-H) 2°amine], 3200s [ν_{as} (N-H) 1°amine], 3380m [ν_s (N-H) 1°amine]; MS 410 $[BiCl_2\{(CH_3)_2CNNCSNH_2\}]^+$, 390 $[MeBiCl\{(CH_3)_2CNNHCSNH_2\}]^+$, 354 $[MeBi\{(CH_3)_2CNNHCSNH_2\}]^+$, 339 $[Bi\{(CH_3)_2CNNCSNH_2\}]^+$, 241 $[BiS]^+$, 131 $[(CH_3)_2CNNHCSNH_2]^+$, 115 $[(CH_3)_2CNNHCS]^+$]. The product was dissolved in

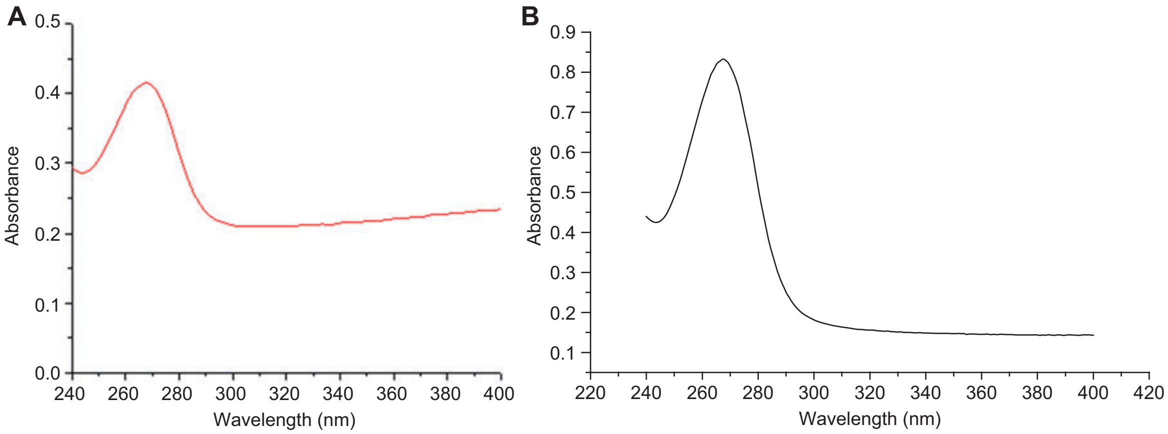


Figure 5 Absorption spectra of: (A) **(4)**; and (B) after sintering **(4)** at 150°C for ~10 h.

~15 ml of THF and ~2 ml of n-hexane was added. The mixture was kept over night to yield amorphous powder.

All other methylbismuth(III) adducts were prepared using a similar route and their synthetic and analytical details are given below.

[MeBiCl$_2$.2(CH$_3$)$_2$CNNHCSNH$_2$] (2)

This was prepared by similar route, using MeBiCl$_2$ (2.06 g, 6.89 mmol) and [(CH$_3$)$_2$CNNHCSNH$_2$] (1.83 g, 13.93 mmol) to yield a yellow foamy solid.

[Yield 99%; m.p.75°C**;** Elemental analysis (obs.) C, 19.38; H, 3.68; N, 14.80; Cl, 12.81, (cal.) C, 19.40; H, 3.80; N, 15.08; Cl, 12.72; ^{1}H NMR (DMSO-d$_6$, 300.4 MHz) 1.56 [s, 3H, BiMe], 1.88, 1.90 [s, 6H, 6H, H-5,6], 7.54 [br, 2H, H-7], 8.01 [br, 2H, H-8], 9.93 [br, 2H, H-2]. 13C-NMR (DMSO-d$_6$, 75.45 MHz)- 18.03 [C-5], 25.48 [C-6], 74.20 [BiMe], 152.36 [C=N], 178.54 [C=S]; IR (KBr, cm^{-1}) 426s [ν (Bi-N)], 485m [ν (Bi-C)], 770s [ν (C=S)], 1591s [ν (C=N)], 3170s [ν (N-H) 2°amine], 3225s [ν_{as} (N-H) 1°amine], 3378m [ν_s (N-H) 1°amine]; MS 541 [BiCl$_2${(CH$_3$)$_2$CNNHCSNH$_2$}{(CH$_3$)$_2$CNNCSNH$_2$}]$^+$, 410 [BiCl$_2${(CH$_3$)$_2$CNNCSNH$_2$}]$^+$, 339 [Bi{(CH$_3$)$_2$NNSCNH$_2$}]$^+$, 241 [BiS]$^+$, 131 [(CH$_3$)$_2$CNNHCSNH$_2$]$^+$, 115 [(CH$_3$)$_2$CNNHCS]$^+$].

[MeBiCl$_2$.{(C$_6$H$_4$OH)HCNNHCSNH}] (3)

A solution of MeBiCl$_2$ (2.54 g, 8.61 mmol) in methanol (~15 ml) was added to a solution of [(C$_6$H$_4$OH)CHNNHCSNH$_2$] (1.68 g, 8.60 mmol) in methanol (~30 ml). The solution immediately turned red. The reaction mixture was stirred for 5 h. The solvent was stripped off under vacuo to give a red foamy solid, which was washed with n-hexane to yield a red-colored powder.

[Yield 98%, m.p. 120°C; Elemental analysis (obs.) C, 22.36; H, 2.66; N, 8.33; Cl, 14.50, (cal.) C, 22.05; H, 2.47; N, 8.57; Cl, 14.46; ^{1}H NMR (DMSO-d$_6$, 300.4 MHz) 1.56 [s, 3H, BiMe], 6.80 [m, 2H, H-7,8], 7.21 [d, 1H, H-6], 7.91 [m, 2H, H-9,4], 8.10 [br, 1H, H-11], 8.35 [br, 1H, H-12], 9.93 [br, 1H, H-2], 11.37 [br, 1H, OH]; ^{13}C-NMR (DMSO-d$_6$, 75.45 MHz), 74.09 [BiMe], 116.14 [C-6], 119.43 [C-7], 120.38 [C-8], 126.84 [C-9], 131.32 [C-5], 139.95 [C-10], 156.52 [C=N], 177.50 [C=S]; IR (KBr, cm^{-1}) 418m [ν (Bi-N)], 475m [ν (Bi-C)], 780m [ν (C=S)], 1600s [ν (C=N)], 3175m [ν (N-H) 2°amine], 3290m [ν_{as} (N-H) 1°amine], 3425 [ν_s (N-H) 1°amine]; MS 474 [BiCl$_2${(C$_6$H$_4$OH)CHNNCSNH$_2$}]$^+$, 418 [MeBi{(C$_6$H$_4$OH) CHNNCSNH$_2$}]$^+$, 403 [Bi{(C$_6$H$_4$OH)CHNNCSNH$_2$}]$^+$, 340 [MeBiCONNCSNH$_2$]$^+$, 276 [MeBiC$_2$N$_2$]$^+$, 241 [BiS]$^+$, 136 [C$_6$H$_4$OHCNHNH$_2$]$^+$, 120 [C$_6$H$_4$OHCNH]$^+$, 105 [C$_6$H$_4$OHC]$^+$**]**.

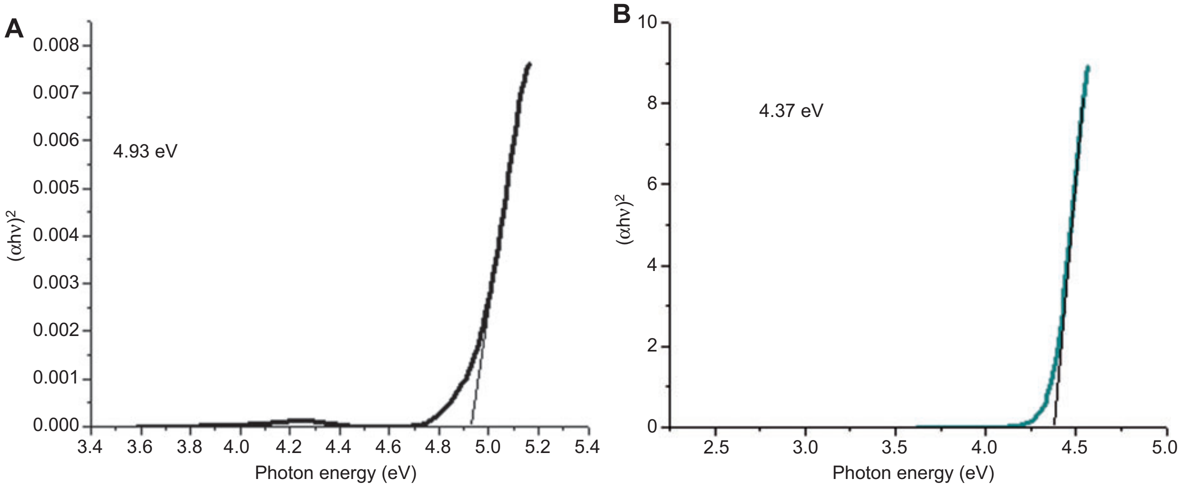


Figure 6 Plots of hν vs. (αhν)^2 for: (A) **(4)**; and (B) after crystallization of **(4)** at 150°C for ~10 h.

$[MeBiCl_2.2\{(C_6H_4OH)CHNNHCSNH_2\}]$ (4)

This was prepared by the above route using $MeBiCl_2$ (1.89 g, 6.40 mmol) and $[(C_6H_4OH)CHNNHCSNH_2]$ (2.52 g, 12.81 mmol), to yield red-colored solid.

[Yield 97%, m.p. 110°C; Elemental analysis (found) C, 30.03; H, 3.04; N, 12.14; Cl, 10.55, (cal) C, 29.79; H, 3.09; N, 12.26; Cl, 10.34; ^1H NMR (DMSO-d_6, 300.4 MHz) 1.64 [s, 3H, BiMe], 6.90 [m, 4H, H-7,8], 7.28 [d, 2H, H-6], 7.98 [m, 4H, H-9,4], 8.16 [br, 2H, H-11], 8.43 [H-12], 9.99 [H-2], 11.44 [br, 2H, OH]; ^{13}C-NMR (DMSO-d_6, 75.45 MHz), 73.97 [BiMe], 116.16 [C-6], 119.45 [C-7], 120.38 [C-8], 126.85 [C-9], 131.32 [C-5], 139.94 [C-10], 156.53 [C=N], 178.08 [C=S]; IR (KBr, cm^{-1}) 417m [ν (Bi-N)], 465m [ν (Bi-C)], 785m [ν (C=S)], 1598s [ν (C=N)], 3170m [ν(N-H) 2°amine], 3395m [ν_{as} (N-H) 1°amine], 3420 [ν_s (N-H) 1°amine]. MS- 669 $[BiCl_2\{(C_6H_4OH)CHNNHCSNH_2\}\{(C_6H_4OH)CNNHCSNH_2\}]^+$, 597 $[MeBiCl_2\{(C_6H_4OH)CHNNHCSNH_2\}\{(C_6H_4OH)HC\}]^+$, 533 $[BiCl_2\{(C_6H_4OH)CHNNHCSNH_2\}\{NCS\}]^+$, 474 $[BiCl_2\{(C_6H_4OH)CHNNCSNH_2\}]^+$, 340 $[Bi\{NNHCSN\}\{CS\}]^+$, 241 $[BiS]^+$, 136 $[C_6H_4OHCHNHNH_2]^+$, 120 $[C_6H_4OHCNH]^+$, 105 $[C_6H_4OHC]^+$].

$[MeBiCl_2.(C_5H_4N)C(CH_3)NNHCSNH_2]$ (5)

A solution of $MeBiCl_2$ (1.68 g, 5.69 mmol) was stirred with $[(C_5H_4N)C(CH_3)NNHCSNH_2]$ (1.11 g, 5.71 mmol) in methanol to yield a yellow foamy solid.

[Yield 98%, m.p. 101°C; Elemental analysis (obs.) C, 22.08; H, 2.49; N, 11.28; Cl, 14.63, (cal.) C, 22.10; H, 2.68; N, 11.45; Cl, 14.49; ^1H NMR (DMSO-d_6, 300.4 MHz) 1.55 [s, 3H, BiMe], 2.37 [s, 3H, H-5], 7.43 [t, 1H, H-9], 7.85 [t, 1H, H-8], 8.19 [br, 1H, H-11], 8.40, 8.42 [m, 2H, H-7,12], 8.58 [d, 1H, H-10], 10.39 [br, 1H, H-2]; ^{13}C-NMR (DMSO-d_6, 75.45 MHz), 73.98 [BiMe], 12.37 [C-5], 121.80 [C-9], 124.54 [C-7], 138.51 [C-8], 146.57 [C-10], 147.41 [C-6], 153.30 [C=N], 178.99 [C=S]; IR (KBr, cm^{-1}) 405s [ν (Bi-N)], 475s [ν (Bi-C)], 795m [ν (C=S)], 1600vs [ν (C=N)], 3180s [ν(N-H) 2°amine], 3300s [ν_{as} (N-H) 1°amine], 3325s [ν_s (N-H) 1°amine]. MS-474 $[BiCl_2\{C_5H_4N(CH_3)CNNHCSNH_2\}]^+$, 454 $[MeBiCl\{C_5H_4N(CH_3)CNNHCSNH_2\}]^+$, 380 $[BiCl_2\{CNNCSNH_2\}]^+$, 241 $[BiS]^+$, 136 $[C_5H_4NC(CH_3)NHNH_2]^+$, 120 $[C_5H_4NC(CH_3)NH]^+$, 105 $[C_5H_4NC(CH_3)]^+$].

$[MeBiCl_2.2(C_5H_4N)C(CH_3)NNHCSNH_2]$ (6)

This was prepared by the above similar route using of $MeBiCl_2$ (2.07 g, 6.88 mmol) and $[(C_5H_4N)C(CH_3)NNHCSNH_2]$ (2.72 g, 14.00 mmol) to yield a yellow foamy solid.

[Yield 99%, m.p. 110°C; Elemental analysis (obs.) C, 29.67; H, 3.25; N, 16.01; Cl, 10.49, (cal.) C, 29.88; H, 3.39; N, 16.39; Cl, 10.37; ^1H NMR (DMSO-d_6, 300.4 MHz) 1.55 [s, 3H, BiMe], 2.37 [s, 6H, H-5], 7.43 [t, 2H, H-9], 7.85 [t, 2H, H-8], 8.20 [br, 2H, H-11], 8.40 [m, 4H, H-7, 12], 8.59 [d, 2H, H-10], 10.40 [br, 2H, H-2]; 13C-NMR (DMSO-d_6, 75.45 MHz) 73.98 [BiMe], 12.19 [C-5], 121.32 [C-9], 124.18 [C-7], 137.44 [C-8], 146.57 [C-10], 147.83 [C-6], 153.30 [C=N], 179.02 [C=S]; IR (KBr, cm^{-1}) 420m [ν (Bi-N)], 480s [ν (Bi-C)], 790m [ν (C=S)], 1598vs [ν (C=N)], 3170s [ν (N-H) 2°amine], 3300s [ν_{as} (N-H) 1°amine], 3350s [ν_s (N-H) 1°amine]. MS- 669 $[BiCl_2\{C_5H_4N(CH_3)CNNHCSNH_2\}\{C_5H_4N(CH_3)CNNH_2CSNH_2\}]^+$, 649 $[MeBiCl_2\{C_5H_4N(CH_3)CNNCS\}\{C_5H_4N(CH_3)CNNCS\}]^+$, 613 $[MeBiCl\{C_5H_4N(CH_3)CNNCS\}\{C_5H_4N(CH_3)CNNCS\}]^+$, 454 $[MeBiCl\{(CH)CNNCS\}\{(CH_2)CNNCS\}]^+$, 418 $[MeBiCl\{CH)CNNCS\}\{H_2NNS\}^+$, 402 $[BiCl\{CCNNCS\}\{H_2NNS\}]^+$, 241 $[BiS]^+$, 136 $[C_5H_4NC(CH_3)NHNH_2]^+$, 120 $[C_5H_4NC(CH_3)NH]^+$, 105 $[C_5zH_4NC(CH_3)]^+$].

Synthesis of Bi_2S_3 micro-rods

In a typical experiment, xylene (~10 ml) in a three-necked flask was degassed at refluxing temperature under a nitrogen atmosphere for 30 min. A weighed quantity of **(3)** (52 mg) was added to this and the mixture was refluxed for 2 h. It was then gradually cooled. After cooling to room temperature, the product was centrifuged, the supernatant liquid was decanted and the residue was washed with methanol (20 ml). The residue was also washed several times with an acetone-hexane mixture. Finally, it was dried under reduced pressure and characterized as pure Bi_2S_3. A similar procedure was adopted for **(4)**, taking 56 mg of sample. The amorphous black residue obtained from **(4)** was subjected to crystallization by sintering in air at 150°C for ~10 h.

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References

Ahire, R. R.; Sharma, R. P. Photoelectrochemical characterization of Bi_2S_3 thin films deposited by modified chemical bath deposition. *Indian J. Eng. Mater. Sci*. **2006**, *13,* 140–144.

Althaus, H.; Breunig, H. J.; Lork, E. Syntheses and chemistry of methylantimony and methylbismuth dihalides: an extended two-dimensional framework in the crystal structure of CH_3BiCl_2 and molecular units in the structures of $[CH_3ECl_2$(2,2'-bipyridine)] (E = Sb, Bi). *Organometallics* **2001**, *20*, 586–589.

Anderson, F. E.; Duca, C. J.; Scudi, J. V. Some heterocyclic thiosemicarbazones. *J. Am. Chem. Soc*. **1951**, *73*, 4967–4968.

Battaglia, L. P.; Corradi, A. B.; Pelizzi, C.; Pelosi, G.; Tarasconi, P. Chemical and structural investigations on bismuth complexes of 2,6-di-acetylpyridine bis(2-thenoylhydrazone) and 2,6-di-acetylpyridine bis(thiosemicarbazone). *J. Chem. Soc. Dalton Trans*. **1990**, *12*, 3857–3860.

Böttner, H.; Ebling, D.; Kölbel, H.; Schubert, A.; Gavrikov, A.; Mahlke, A.; Nurnus, J. Formation of nanometer scale layers of V-VI (Bi_2Te_3-related) compounds based on amorphous precursors. *Proc. Estonian. Acad. Sci. Eng*. **2007**, *13*, 354–362.

Boudjouk, P.; Remington, M. P. Jr.; Grier, D. G.; Jarabek, B. R.; McCarthy, G. J. Tris(benzylthiolato)bismuth. Efficient precursor to phase-pure polycrystalline Bi_2S_3. *Inorg. Chem*. **1998**, *37*, 3538–3541.

Chaudhari, K. R., Yadav, N., Wadwale, A., Jain, V. K., Bohra, R. Monoorganobismuth(III) dithiocarboxylates: synthesis, structures and their utility as molecular precursors for the preparation of Bi_2S_3 films and nanocrystals. *Inorg. Chim. Acta*. **2010**, *363*, 375–380.

Chauhan H. P. S. Chemistry of diorganodithiophosphate (and phosphinate) derivatives with arsenic, antimony and bismuth. *Coord. Chem. Rev.* **1998**, *173*, 1–30.

Diemer, R.; Dittes, U.; Nuber, B.; Seifried, V.; Opferkuch, W.; Keppler, B. K. Synthesis, characterization and molecular structures of some bismuth(III) complexes with thiosemicarbazones and dithiocarbazonic acid methylester derivatives with activity against helicobacter pylori. *Metal Based Drugs* **1995**, *2*, 271–292.

Dong, L.; Chu, Y.; Zhang, W. A very simple and low cost route to Bi_2S_3 nanorods bundles and dandelion-like nanostructures. *Mater. Lett*. **2008**, *62*, 4269–4272.

Gupta, A.; Sharma, R. K.; Bohra, R.; Jain, V. K.; Drake, J. E.; Hursthouse, M. B.; Light, M. E. Synthesis and characterization of methylbismuth(III) complexes containing dithio ligands: crystal and molecular structure of $[MeBi\{S_2COMe\}_2]$ and transformation of $[MeBi\{S_2CO^iPr\}_2]$ to Bi_2S_3. *J. Organomet. Chem.* **2003**, *678*, 122–127.

Han, Q.; Chen, J.; Yang, X.; Lu, L.; Wang, Xi. Preparation of uniform Bi_2S_3 nanorods using xanthate complexes of bismuth (III*)*. *J. Phys. Chem.* **2007,** *111*, 14072–14077.

Jain, A. K.; Bohra, R. Synthesis and characterization of some methylbismuth (III) O,O-alkylenedithiophosphates: convenient transformation of $[MeBi\{S_2PO\text{-}(CH_2)_4\text{-}O\}_2]$ and $[MeBi\{S_2POCH(CH_3)CH_2C(O)(CH_3)_2\}_2]$ to Bi_2S_3. *Appl. Organomet. Chem*. **2006**, *20*, 411–415.

Jain, A. K.; Sharma, V.; Bohra, R.; Sukumar, A. A.; Raju, V. S.; Drake, J. E.; Hursthouse, M. B.; Light, M. E. Synthesis and characterization of methylbismuth(III) complexes containing dithio ligands: crystal and molecular structure of $[MeBiCl(S_2CNEt_2)]$ and transformation of some $[MeBi(S_2CNR'_2)_2]$ to Bi_2S_3. *J. Organomet. Chem*. **2006**, *691*, 4128–4134.

Kim, F. S.; Ren, G.; Jenekhe, S. A. One-dimensional nanostructures of pi-conjugated molecular systems: assembly, properties, and applications from photovoltaics, sensors, and nanophotonics to nanoelectronics. *Chem. Mater*. **2011**, *23*, 682–732.

Lee, J. M.; Farhangfar, S.; Lee, J. Y.; Cagnon, L.; Scholz, R.; Gösele, U.; Nielsch, K. Tuning the crystallinity of thermoelectric Bi_2Te_3 nanowire arrays grown by pulsed electrodeposition. *Nanotechnology* **2008**, *19*, 365701 (8 pp).

Lu, J.; Han, Q.; Yang, X.; Lu, L.; Wang, X. Microwave-assisted synthesis and characterization of 3D flower-like Bi_2S_3 superstructures. *Mater. Lett*. **2007**, *61*, 2883–2886.

Ma, X.; Liu, L.; Mo, W.; Liu, H.; Kou, H.; Wang, Y. Surfactant-assisted solvothermal synthesis of Bi_2S_3 nanorods. *J. Cryst. Growth*. **2007**, *306*, 159–165.

Mane, R. S.; Sankapal, B. R.; Lokhande, C. D. Photoelectrochemical (PEC) characterization of chemically deposited Bi_2S_3 thin films from non-aqueous medium. *Mater. Chem. Phys*. **1999**, *60*, 158–162.

Monteiro, O. C.; Trindade, T.; Preparation of Bi_2S_3 nanofibers using a single-sorce method. *J. Mater. Sci. Letter,* **2000,** *19*, 859–861.

Ota, J. R.; Srivastava, S. K. Low temperature micelle-template assisted growth of Bi_2S_3 nanotubes. *Nanotechnology* **2005**, *16*, 2415–2419.

Phuruangrat, A.; Thongtem, T.; Thongtem, S. Characterization of Bi_2S_3 nanorods and nano-structured flowers prepared by a hydrothermal method. *Mater. Lett*. **2009**, *63*, 1496–1498.

Tahir, A. A.; Ehsan, M.; Mazhar, M.; Wijayantha, K. G. U.; Zeller, M.; Hunter, A. D. Photoelectrochemical and photoresponsive properties of Bi_2S_3 nanotube and nanoparticle thin films, *Chem. Mater*. **2010,** *22*, 5084–5092.

Tang, J.; Alivisatos, A. P. Crystal splitting in the growth of Bi_2S_3. *Nano. Lett*. **2006**, *6*, 2701–2706.

Vogel, A. I. Textbook of Quantitative Inorganic Analysis, 5th edition; Longman: London, 1989.

Wang, D.; Hao, C.; Zheng, W.; Ma, X.; Chu, D.; Peng, Q.; Li, Y. Bi_2S_3 nanotubes: facile synthesis and growth mechanism. *Nano. Res*. **2009**, *2*, 130–134.

Wei, F.; Zhang, J.; Wang, L.; Zhang, Z. Solvothermal growth of single-crystal bismuth sulfide nanorods using bismuth particles as source material. *Cryst. Growth Des*. **2006**, *6*, 1942–1944.

Xi, Y.; Hu, C.; Zhang, X.; Zhang, Y.; Wang, Z. L. Optical switches based on Bi_2S_3 nanowires synthesized by molten salt solvent method. *Solid State Communications* **2009**, *149*, 1894–1896.

Xie, G.; Qiao, Z.; Zeng, M.; Chen, X.; Gao, S. A single-source approach to Bi_2S_3 and Sb_2S_3 nanorods via a hydrothermal treatment. *Cryst. Growth Des*. **2004**, *4*, 513–516.

Zhao, L.; Zhang, B.; Liu, W.; Zhang, H.; Li, J. Enhanced thermoelectric properties of bismuth sulfide polycrystals prepared by mechanical alloying and spark plasma sintering. *J. Solid State Chem*. **2008**, *181*, 3278–3282.

Zhao, W.; Zhu, J.; Zhao, Y.; Chen, H. Photochemical synthesis and characterization of Bi_2S_3 nanofibers. *Mater. Sci. Eng. B*. **2004**, *110*, 307–312.

Zhou, X.; Zhao, X.; Zhang, D.; Chen, S.; Guo, X.; Ding, W.; Chen, Y. Hollow microscale organization of Bi_2S_3 nanorods. *Nanotechnology* **2006**, *17*, 3806–3811.