Tris(benzylthiolato)bismuth. Efficient Precursor to Phase-Pure Polycrystalline Bi_2S_3

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Received November 19, 1997

Details of the synthesis, physical and spectroscopic characterization, and thermal decomposition of tris(benzylthiolato)bismuth, $(BnS)_3Bi$, Bn $= CH_2C_6H_5$, are presented. Results from pyrolysis of $(BnS)_3Bi$ demonstrate that this compound is a convenient precursor to phase-pure, polycrystalline Bi_2S_3 with low carbon and hydrogen contamination under mild thermal conditions (ca. 275 °C). Flow-tube pyrolysis produces small ($\sim$1 μm) spherical particles, whereas sealed-tube pyrolysis produces 6-μm diameter spherical particles composed of radiating acicular crystallites. Bi_2S_3 was characterized by X-ray powder diffraction and scanning electron microscopy.

Introduction

Bismuthinite, Bi_2S_3, is a direct band gap semiconductor with an E_g of 1.3 eV[1,2] that is useful in photovoltaic materials and photodiode arrays.[1,3−5] Bi_2S_3 also belongs to a family of solid-state materials with applications in thermoelectric-cooling technologies based on the Peltier effect. Currently, its heavier congener, Bi_2Te_3, is the benchmark material.[6a−c]

One of the more technologically important functions of Bi_2S_3 may be as a starting material for the synthesis of semiconductors based on sulfo salts of bismuth and related compounds.[7,8] For example, Kanatzidis and co-workers recently demonstrated that Bi_2S_3 is a useful precursor for ternary alkali metal sulfides.[7] The latter were found to be poor conductors of heat, but, surprisingly, Bi_2S_3 was shown to possess essentially metallic conduction.[7]

While most molecular precursor routes to Bi_2S_3 involve dithiocarbamates[1,9] or thiosulfates,[10] recent reports by Rees et al.[11a,b] and from our laboratory[12a,b] demonstrate that metal bis(benzylthiolates) produce metal sulfides in good ceramic yields and in unique forms or phases. For example, we have demonstrated the use of lead and cadmium bis(benzylthiolates) to produce nanocrystalline materials.[12] The high ceramic yields, mild reaction conditions, and low carbon contamination were attributed to the ease with which the volatile byproduct, bibenzylsulfide, forms.[12b] As part of our efforts to explore the potential of metal benzylthiolates as convenient sources of metal sulfides, we investigated tris(benzylthiolato)bismuth, $(BnS)_3Bi$,[13] Bn $= CH_2C_6H_5$, as a source of bismuthinite. The results presented in this paper show that $(BnS)_3Bi$, is a convenient precursor to highly crystalline bismuthinite.

Results and Discussion

Synthesis. $Bi(SBn)_3$, **1**, first prepared by Wieber and Baudis[13] by eq 1, was synthesized in our laboratory using eqs 2 and 3. All three routes are efficient. Compound **1** exhibits no extraordinary spectral features in the IR or NMR. UV−vis spectra show the expected peaks for π to π^* transitions of the benzyl moieties. In addition, there is an absorption at 357 nm, a charge-transfer band based on the values of λ_{max}, ϵ_{max}, and the dependence of the position of the band on solvent composition.[14] The peak is slightly red-shifted when the solvent polarity is increased (e.g., 365 nm in THF; 367 nm in acetone). Some spectral data are summarized in Table 1.

$$BiCl_3 + 3NaOC_2H_5 + 3BnSH \rightarrow Bi(SBn)_3 + 3NaCl + 3C_2H_5OH \quad (1)$$

$$BiCl_3 + 3NEt_3 + 3BnSH \rightarrow Bi(SBn)_3 + 3NEt_3HCl \quad (2)$$

$$BiCl_3 + 3BnSLi \rightarrow Bi(SBn)_3 + 3LiCl \quad (3)$$

The thermogravimetric analysis (TGA) results of **1** at 5 °C/min from 70 to 300 °C, under N_2, are shown in Figure 1. A very smooth decomposition occurs with an onset temperature

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(1) Nomura, R.; Kanaya, K.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 939.

(2) Black, J.; Conwell, E. M.; Seigle, L.; Spencer, C. W. *J. Phys. Chem. Solids* **1957**, *2*, 240.

(3) Farrugia, L. J.; Lawlor, F. J.; Norman, N. C. *Polyhedron* **1995**, *14*, 311.

(4) Nayak, B. B.; Acharya, H. N.; Mitra, G. B.; Mathur, B. K. *Thin Solid Films* **1983**, *105*, 17.

(5) Pawar, S. H.; Bhosale, P. N.; Uplane, M. D.; Tanhankar, S. *Thin Solid Films* **1983**, *110*, 165.

(6) (a) Ritter, J. J. *Inorg. Chem.* **1994**, *33*, 6419. (b) Ritter, J. J.; Maruthamuthu, P. *Inorg. Chem.* **1995**, *34*, 4278. (c) Ritter, J. J.; Maruthamuthu, P. *Inorg. Chem.* **1997**, *36*, 260.

(7) Chen, B.; Uher, C.; Iordanidis, L.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 1655.

(8) Kanischeva, A. S.; Mikhailov, Y. N.; Trippel, A. F. *Inorg. Mater.* **1981**, *17*, 1466.

(9) Lalia-Kantouri, M.; Manoussakis, G. E. *J. Therm. Anal.* **1984**, *29*, 1151.

(10) Cyaganski, A.; Kobylecka, J. *Thermochim. Acta* **1981**, *45*, 65.

(11) (a) Rees, W. S., Jr.; Kräuter, G. *J. Mater. Res.* **1996**, *11(12)*, 3005. (b) Kräuter, G.; Neumueller, B.; Goedken, V.; Rees, W. S., Jr. *Chem. Mater.* **1996**, *8*, 360.

(12) (a) Jarabek, B. R.; Grier, D. G.; Simonson, D. L.; Seidler, D. J.; McCarthy, G. J.; Boudjouk, P. *Advances in X-ray Analysis*, (CD-ROM), 40; Plenum Publishing Corporation: New York, 1997; (b) Boudjouk, P.; Simonson, D.; Seidler, D. J.; Jarabek, B. R.; Grier, D. G.; McCarthy, G. J.; Keller, L. P. *Chem. Mater.*, in press.

(13) Wieber, V., Baudis, U. *Z. Anorg. Allg. Chem.* **1976**, *423*, 47.

(14) Drago, R. *Physical Methods in Chemistry*; Saunders: Philadelphia, 1997.

S0020-1669(97)01463-8 CCC: \$15.00

Table 1. Selected Spectroscopic Data for $Bi(SBn)_3$

^1H NMR (ppm)	^{13}C NMR (ppm)	IR (cm^{-1}) (KBr)	UV−vis (λ_{max}, ϵ_{max}), CH_2Cl_2
$CDCl_3$; 4.81(s), 7.16−7.28 (m)	$CDCl_3$; 33.80, 127.42, 128.91, 129.09, 143.46	3025, 1599, 1491, 1451, 1229, 1065, 696, 677, 559	(1.04×10^{-4} M); 357 nm 6346 L mol^{-1} cm^{-1}

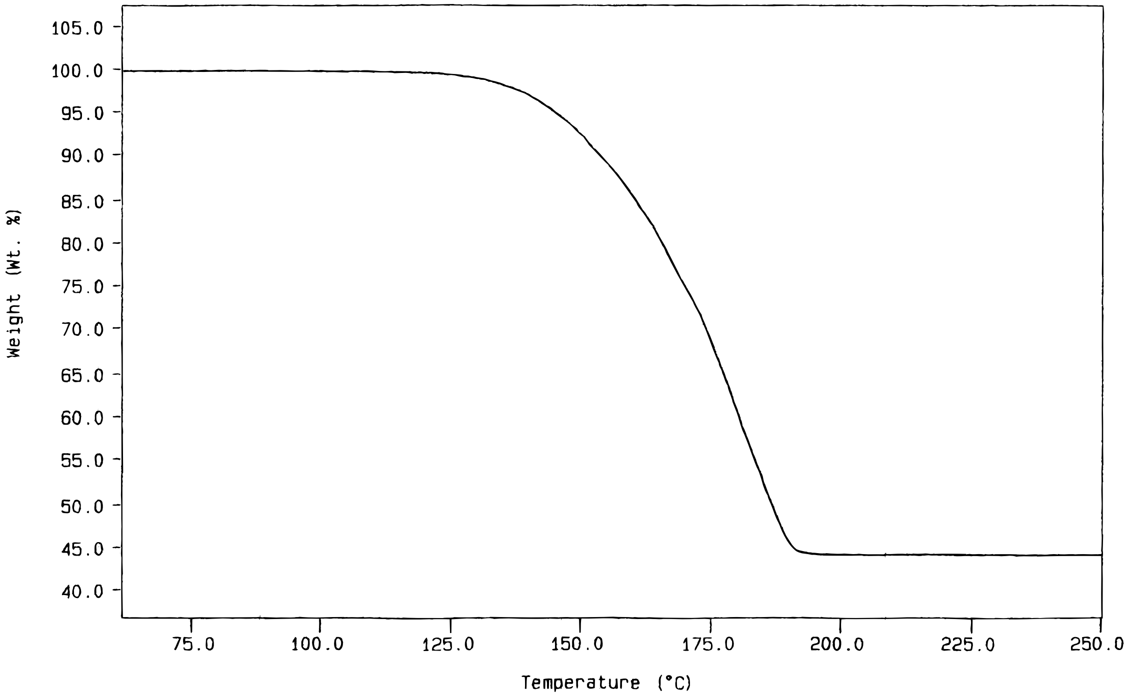

Figure 1. TGA of $(BnS)_3Bi$ under N_2.

of approximately 152 °C and completion temperature of approximately 193 °C. Moreover, the first derivative of the TGA curve confirms that decomposition occurs as a single event, in contrast to the multistep decomposition of alkali metal thiosulfatobismuthates.[10] The amount of mass loss, 55.68 mass %, is in excellent agreement with the calculated value of 55.57 mass % based on eq 4 for the production of Bi_2S_3. This suggests an efficiency of production of Bi_2S_3 for **1** slightly higher than that of the majority of dithiocarbamate complexes which exhibit differences of as much as 5 mass % between the calculated and actual mass losses.[1,9]

$$2Bi(SBn)_3 \rightarrow Bi_2S_3 + 3Bn_2S \qquad (4)$$

Thermolysis of **1** in a conventional flow pyrolysis apparatus at 275 °C for 5 h produced bismuthinite and benzylsulfide. The ceramic yield was 99% of the theoretical yield with a mass recovery (nonvolatile + volatile products) of >91%. X-ray powder diffraction (XRPD) confirmed that the solid ceramic product was phase pure (Figure 2). No peaks attributable to crystalline bismuth, sulfur, or the oxides of these elements were observed. Carbon and hydrogen contamination were below 1% and 0.5%, respectively. The alkali metal thiosulfatobismuthates of Bi gave crystalline Bi_2S_3, elemental sulfur, and alkali metal sulfates at 200 and 320 °C,[10] while the decomposition of tris(*N*,*N*-disubstituted dithiocarbamate) complexes of Bi gave Bi_2S_3 ceramics with 1−9% carbon incorporation.[9]

Benzylsulfide was the only volatile product detected. These observations lead us to believe that the reaction is dominated by a simple reaction mechanism. We suggest that an intramolecular nucleophilic displacement of benzyl by sulfur is a key step (Figure 3). A similar mechanism was proposed to explain the facile decomposition of the benzylthiolates of lead, cadmium, and zinc.[12]

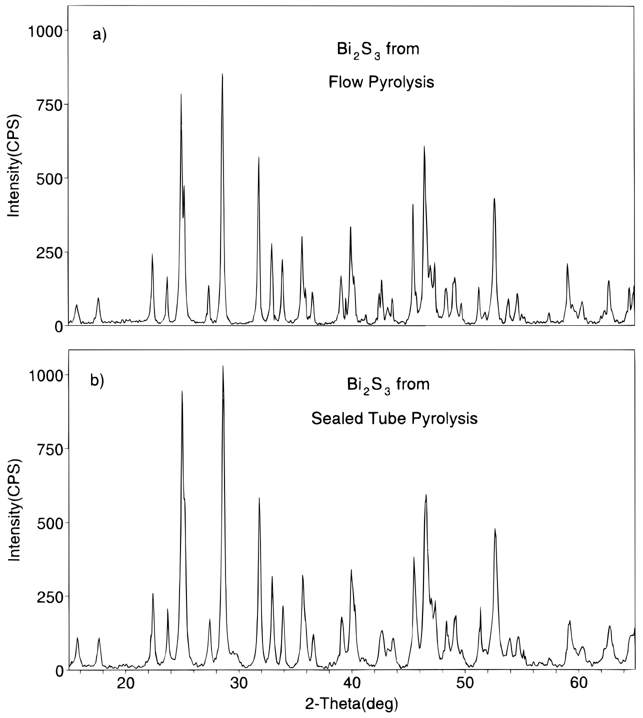

Figure 2. (a) X-ray diffractogram of pure Bi_2S_3 prepared from pyrolysis of $(BnS)_3Bi$ at 275 °C under 1 atm of N_2 for 5 h. (b) X-ray diffractogram of pure Bi_2S_3 prepared from pyrolysis of $(BnS)_3Bi$ at 260 °C at 0.05 Torr for 5 h.

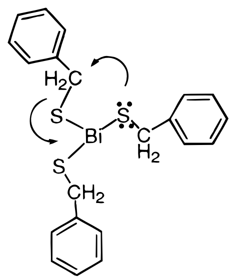

Figure 3. Mechanism for decomposition of tris(benzylthiolato)bismuth.

Table 2. Comparison of Lattice Parameters for Bi_2S_3

space group	*a* (Å)	*b* (Å)	*c* (Å)	vol ($Å^3$)	reference
Pbnm	11.12	11.25	3.97	496.6	15
Pbnm[a]	11.147	11.305	3.981	501.67	8
Pbnm	11.149	11.304	3.981	501.72	PDF # 17-0320
Pbnm	11.1472(7)	11.2947(10)	3.9823(4)	501.39	this study[b]
Pbnm	11.156(1)	11.292(15)	3.9850(1)	501.97	this study[c]

[a] Reported as *Pmcn*, a different orientation of the same unit cell. [b] Reaction conditions: 275 °C, 5 h, under 1 atm of N_2. [c] Reaction conditions: 260 °C, 5 h, under vacuum (0.05 Torr).

Pyrolysis of **1** in a sealed tube under vacuum (0.05 Torr) gave essentially the same results but with a more complex mixture of volatile organic products. Again, Bi_2S_3 with low carbon and hydrogen contamination, less than 1% and 0.5% respectively, was the only crystalline phase present, but the ceramic yields were slightly lower, 90% of theoretical, compared to the flow pyrolysis. The organic residue contained Bn_2S and Bn_2S_2 in an approximately 1:1 ratio as well as trace quantities of other organic materials that could not be isolated and identified. The total mass balance was 80%.

X-ray Powder Diffraction. A comparison of the known unit cell constants found in the literature[8,15] for Bi_2S_3 and those obtained via unit cell analysis for the powders in this study are shown in Table 2. The Bi_2S_3 is highly crystalline, with an average crystallite size of >1000 nm as determined using the Scherrer equation, i.e., no small crystallite size peak broadening was observed.

Phase Morphology. The electron micrographs (parts a and b of Figure 4) of the Bi_2S_3 under flow pyrolysis conditions show aggregates of botryoidal particles of approximately 1 μm in diameter. At higher magnification, the surface mophology of the nearly spherical aggregates can be seen with low profile 0.1−0.2 μm projections.

The morphology of the clusters produced under sealed conditions is quite different. They consist of spherical aggregates with a diameter of 5−6 μm with acicular crystallites radiating from the center in a uniform size distribution (Figure 5). The acicular crystallites are approximately 3 μm long by 0.25 μm wide.

One may be led to believe that the differing morphologies under the same temperature and length of synthesis are due only to the pressure differences in the respective conditions of the two syntheses. Gas-phase nucleation of the Bi_2S_3 under equilibrium conditions (sealed-tube reaction) cannot be ruled out. However, monitoring the reaction by observation shows no evidence for the sublimation of **1** but rather a similar condensed-phase decomposition as witnessed under flow pyrolysis conditions. Gas-phase interactions after volatile organic evolution or a two-stage decomposition mechanism may account for the differences in phase morphology.

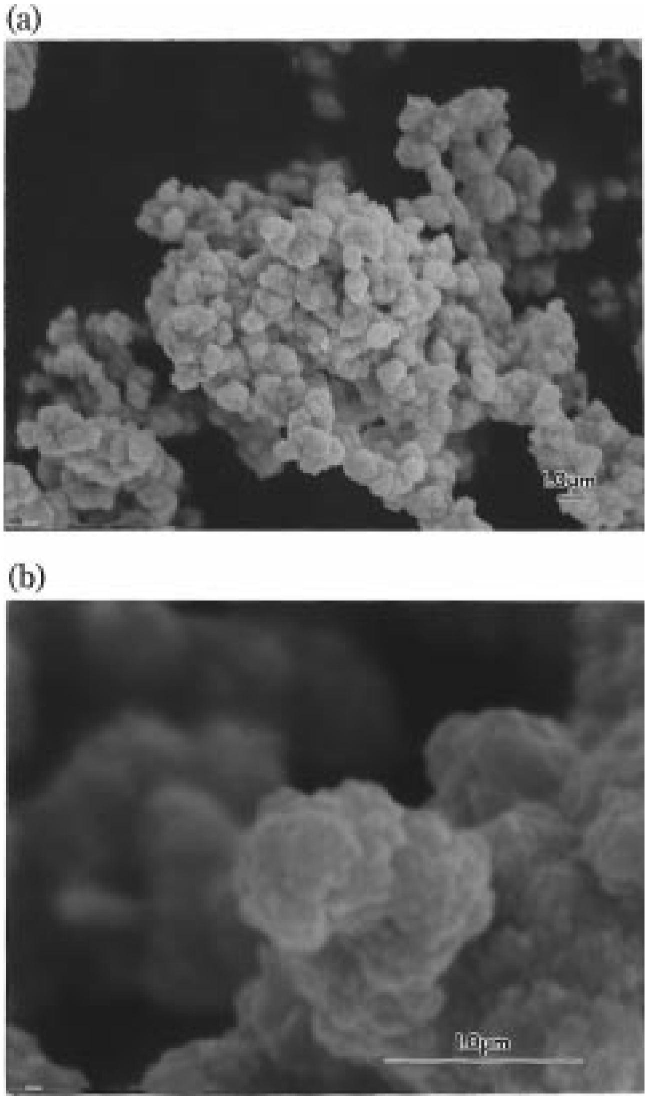

Figure 4. (a) SEM (15 kV magnification 5000×, reproduced at 74% of original size) of Bi_2S_3 obtained from the flow pyrolysis of $(BnS)_3Bi$. (b) SEM (15 kV magnification 35000×, reproduced at 74% of original size) of Bi_2S_3 obtained from the flow pyrolysis of $(BnS)_3Bi$.

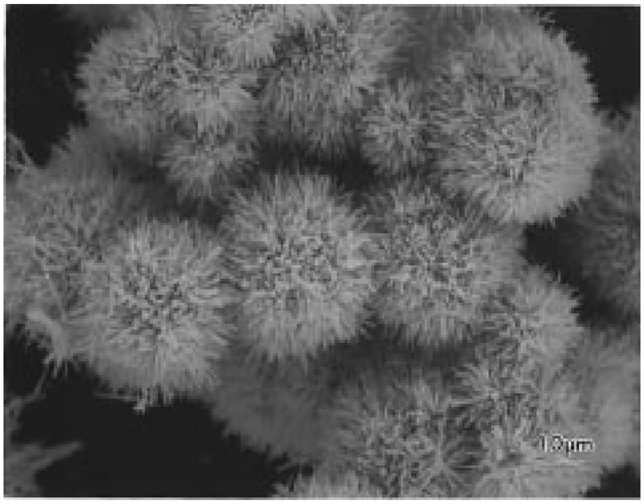

Figure 5. SEM (10 kV magnification 5000×, reproduced at 74% of original size) of Bi_2S_3 obtained from the sealed-tube pyrolysis of $(BnS)_3Bi$.

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(15) Kupcik, V.; Vesela-Novakova, L. *Tschermaks Mineral Petrog. Mitt.* **1970**, *14* (1), 55.

Conclusions

Tris(benzylthiolato)bismuth, Bi(SBn)$_3$, was prepared by two new routes and subjected to flow- and sealed-tube pyrolysis. Product analysis shows that this compound is a convenient source of highly crystalline, phase-pure bismuthinite, Bi_2S_3, with low contamination. Flow-tube pyrolysis produces small, 1-μm diameter, nearly spherical aggregates, whereas sealed-tube pyrolysis produces 5−6-μm diameter aggregates composed of radiating acicular crystallites.

Experimental Section

General. Benzylthiol and *n*-butyllithium were purchased from Aldrich (Milwaukee, WI) and used as received. Triethylamine was dried over CaH_2, distilled, and stored over molecular sieves prior to use. Bismuth trichloride was purchased from Strem (Newburyport, MA) and used as received. Mercaptans and their compounds are toxic and irritating. Thus, protective clothing and gloves should be worn when handling them. All reactions and manipulations were performed in a fume hood in conjunction with standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under a dry nitrogen atmosphere immediately before use. Toluene was distilled over sodium metal under a dry nitrogen atmosphere immediately before use.

Flow pyrolyses were performed using a Lindberg model 55035 programmable tube furnace, 36 cm long and 3 cm in diameter with a 55 × 2.5 cm Vycor silica glass tube placed inside. One end of the tube was fitted with a one-holed septum connected to a dry nitrogen source and sealed with Parafilm. Nitrogen flow was monitored at the exit of the tube by a mineral oil bubbler. The flow was set to approximately 50 mL/min, and the tube was purged at this rate for at least 0.5 h before introduction of the sample. The sample to be pyrolyzed was placed in a Coors porcelain boat which had been oven-dried at 120 °C and cooled under a stream of dry nitrogen in the tube furnace. Typical sample sizes were 500−800 mg. The crucible containing the sample was placed in the tube at the center of the furnace. For all samples, the oven was programmed to ramp at a rate of 10 °C/min to 120 °C, held at this temperature for 1 h to remove moisture, and then ramped at a rate of 5 °C/min to 275 °C. This temperature was maintained for 5 h before the oven was allowed to cool to room temperature. The volatile products were condensed near the exit of the tube by using dry ice and were collected by washing the tube with acetone and hexane.

Sealed-tube pyrolyses were carried out in a vacuum sealable 20-mL glass hydrolysis tube in a temperature-controlled sandbath. The hydrolysis tube and Teflon stopcock were oven-dried at 120 °C for at least 3 h before use. The tube and stopcock were allowed to cool during five pump/purge cycles. The sample was then placed in the tube under N_2, followed by evacuating and sealing the reaction vessel at 0.05 mmHg. The sealed tube was placed in the sandbath and brought to 260 °C and held there for 5 h. The reaction vessel was allowed to reach room temperature slowly by turning off the heat supply and leaving it in the sandbath. The tube was opened under N_2, rinsed with dry, distilled toluene (3 × 5 mL), and then rinsed with dry hexane (3 × 5 mL). The rinsings were collected with a glass pipet and transferred to a preweighed beaker. Solvent was removed in vacuo or under a stream of air and the remaining residue was analyzed by ^{1}H NMR. The ceramic was air-dried and weighed prior to characterization by XRPD.

NMR spectra were obtained on a JEOL GSX270 spectrometer at the following frequencies: ^{1}H (270.17 MHz), ^{13}C (67.94 MHz). Typical samples were prepared as 0.1−0.2 M solutions in $CDCl_3$. Chemical shifts are reported relative to Me_4Si and are in ppm. UV−vis spectrum were obtained on an IBM 9340 UV−vis spectrophotometer scanning from 700−200 nm. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy series spectrometer and are reported in cm^{-1}.

TGA was performed on a Perkin-Elmer 7 Series/Unix Thermogravimetric Analyzer. The instrument was brought under control at 70 °C, and scans were run at a ramp rate of 5 °C/min to 300 °C. Typical sample sizes were 5−10 mg. The onset of decomposition was calculated on the basis of a default trigger value of 1% of the starting sample mass. Melting points were taken on a Thomas−Hoover capillary melting point apparatus and are uncorrected. Combustion analysis was performed by Galbraith Laboratories, Knoxville, TN. Scanning electron microscopy was performed on plasma sputtered (Au) samples using a JEOL JSM6300V instrument. X-ray powder patterns were recorded from hexane slurry samples mounted on glass slides, using a Philips automated diffractometer with a graphite diffracted-beam monochromator, variable divergence slit and using Cu Kα (α = 1.5418 Å) radiation. NIST 660 lanthanum hexaboride (LaB_6) was used as an internal *d* spacing standard.

Syntheses of ($C_6H_5CH_2S)_3Bi$ (1). Method A. To a dry, 250-mL round-bottomed flask equipped with a stir bar and a nitrogen inlet was placed $BiCl_3$ (10.0 g, 31.7 mmol), followed by the addition of 100 mL of toluene. Triethylamine (9.62 g, 13.3 mL, 95.1 mmol) was added to the white slurry changing the color to dark yellow. The reaction mixture was allowed to stir at room temperature for 15 min after the addition was complete. Benzylthiol (11.81 g, 11.2 mL, 95.1 mmol) was added dropwise at room temperature, causing a change in color to light yellow and finally to a brown/green. The resulting mixture was stirred at room temperature for 1 h and then refluxed for 8 h to give a thick black solid with yellow streaks. After one week at ambient conditions under N_2, a bright yellow crystalline solid was observed. Recrystallization from CH_2Cl_2 afforded the title compound in 38% yield (7.0 g). Workup of the mother liquor led to the isolation of another 6.20 g (72% total yield) of analytically pure **1** which decomposes in the presence of light. Mp 87−89° C [lit. 88−90° C].[13] ^{1}H NMR ($CDCl_3$, 270 MHz) δ 4.81 (s, 2H, PhC*H*$_2$), 7.16−7.28 (m, 5H, Ph*H*) [lit. (CCl4) δ 4.93 (s), 7.33 (s)].[13] ^{13}C NMR ($CDCl_3$, 67.94 MHz) δ 33.80 (Ph*C*H$_2$), 127.42 128.91, 129.09, 143.46 (Ar). IR (KBr, cm^{-1}) 3025 w, 1599 w, 1491 s, 1451 s, 1229 s, 1065 s, 1026 w, 762 s, 696 vs, 677 vs, 559 s. UV−vis (1.04×10^{-4} M, CH_2Cl_2): λ_{max} 357 nm, ϵ_{max} 6346, log ϵ 3.80.

Method B. Benzylthiol (3.97 g, 3.8 mL, 32 mmol) was dissolved in THF (10 mL) under N_2 in a 100-mL round-bottomed flask equipped with a stir bar and a nitrogen inlet. *n*-BuLi (20 mL, 32 mmol) was then added dropwise to the reaction mixture. An exothermic reaction occurred, and the reaction was allowed to stir at room temperature for 4 h. $BiCl_3$ (3.36 g, 10.66 mmol) was placed in a dry, 25-mL round-bottomed flask equipped with a stir bar and a nitrogen inlet and dissolved in 10 mL of THF. The $BiCl_3$ solution was then added dropwise to the solution of LiSBn at room temperature. An exothermic reaction occurred with the formation of a white precipitate and an orange solution. The reaction was allowed to stir at room temperature for 6 h. Filtration via cannula and removal of the solvent in vacuo gave **1** as an orange solid. Passing a solution (CH_2Cl_2) of this solid through a 4-in. column of silica gel gave a clear yellow solution. Removal of the solvent in vacuo produced **1** in 61% yield (3.75 g) as a yellow crystalline, light-sensitive solid. Analytical data matches that of **1** produced by method A.

Acknowledgment. Financial support from the Department of Energy (Grant DE-FG02-91ER75674), the Office of Naval Research (Grant NOO14-96-1 1271), and the National Science Foundation (Grant OSR 9452892) is gratefully acknowledged. We thank Brian Very for technical assistance and Tom Freeman and Scott Payne for obtaining the electron micrographs.

IC971463H