

Use of Lead Bis(butylthiolate) Compounds in a New Low-Temperature Route to Highly Crystalline Lead Sulfide: Identity and Source of Reaction Byproducts

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Highly crystalline lead sulfide has been prepared by the thermolyses of compounds of the general formula $Pb(SR)_2$. Three isomeric lead bis(butylthiolate) compounds have been isolated and characterized by IR, 1H NMR, and elemental analyses. Their solid-state decomposition, as well as their thermolysis in suspension in a refluxing hydrocarbon, has been studied. Decomposition has been carried out at temperatures as low as 190 °C. XRPD patterns and SEM micrographs of the obtained PbS are discussed. Elemental analysis and ESCA data indicate the presence of highly pure PbS. All gaseous byproducts have been isolated and identified, and the origins of their chemical production have been located.

Introduction

The preparation of single-source precursors for use in electronic and optical applications has been the focus of several recent efforts in the area of designed molecular routes to solid-state chemical materials. Single-source processing offers the potential advantage of simplified fabrication equipment, when compared with the use of multiple sources requiring exact control over stoichiometry.¹ Additional motivation for the use of single-source precursors may be found in the observation of unusual growth selectivities or metastable phase formation.² Likewise, site-selective doping of materials may be achieved by judicious choice of designed source molecules.³⁻⁶

Lead chalcogenides are known to be photoconductors. Among them PbS is the most widely studied compound. It is used extensively in photoconducting detectors. Lead sulfide-based detectors have a high response in the near-IR region (1-3 μm) and are utilized for applications such as spectrometric sensors, flame monitors, missile guidance systems, and numerous other devices.⁷ Pure crystalline lead sulfide previously has been prepared by several methods, all of which involve the use of two sources. Highly pure PbS is formed by the reaction of lead metal with elemental sulfur either under vacuum or in an inert gas atmosphere at high temperatures (>1000 °C). It also can be prepared by the reaction of H_2S , thiourea, or $(NH_4)_2S$ with lead salts. PbS obtained from these reactions often contains a stoichiometric excess of elemental sulfur as well

as water and has to be annealed at 800 °C to remove these impurities. Finally, the heating, annealing, or subliming of contaminated PbS often is used to obtain the pure compound.⁸ Examples of such conditions required to convert crude amorphous PbS into a pure crystalline form include 800 °C for 3-4 h or 400-600 °C for 3 weeks.⁸ Recently, PbS thin films have been prepared by atomic layer epitaxy using H_2S and certain lead salts (e.g., lead bromide, lead iodide, lead β -diketonate compounds) as starting materials.⁹ Each of these routes demands a vigorous pyrolysis to give pure PbS. No mention is found indicating that lead thiolates have been used for the preparation of pure lead sulfide.

Lead thiolates have been known for well over a century;¹⁰⁻¹³ however, it was not until 1971 that accurate data on their synthesis, stability, and simple chemistry were published.¹⁴ Very recently, after the present project was almost complete, the first lead bis(thiolate) was characterized by an X-ray structure determination.¹⁵ Several authors have reported that lead thiolates decompose forming a black precipitate;^{14,16} however, no details are given concerning the pyrolysis conditions and decomposition products. Herein, we report the preparation of three lead bis(thiolate) compounds, $Pb(SR)_2$ ($R = iso$ -butyl, sec -butyl, or $tert$ -butyl), and show that these compounds can be converted cleanly into high-purity lead sulfide in excellent yields both by solid-state decomposition and by heating a suspension of the appropriate lead bis(thiolate) compound in Decalin.

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Table 1. Summary of Thermogravimetric Analyses for Compounds 1-3 (10 °C/min, N₂ Atmosphere)

compound	residue at 500 °C, wt % of charge	
	observed	calculated
1 [Pb(S- <i>t</i> -Bu) ₂]	62.11	62.06
2 [Pb(S- <i>i</i> -Bu) ₂]	63.06	62.06
3 [Pb(S- <i>s</i> -Bu) ₂]	64.21	62.06

Experimental Methods

General Comments. All reactions were performed under N₂(g) using standard Schlenk methods. Ethanol and distilled water from an in-house system were degassed before use. Thiols (Aldrich Chemical Co.) were distilled and stored under nitrogen. Lead acetate trihydrate (Aldrich Chemical Co.) was used without further purification. Di-*tert*-butyl sulfide was prepared by the reaction of *tert*-butyl alcohol and *tert*-butyl thiol in aqueous solution.¹⁷ The new lead bis(thiolate) compounds utilized in the present study were prepared following a method described previously.¹⁴

IR spectra were obtained on a Perkin-Elmer 983 spectrometer using a Nujol mull of the compound and are reported in cm⁻¹. Gas chromatographs/mass spectra were taken with a Hewlett-Packard 5890 Series II, MS 5971 A gas chromatograph. ¹H NMR (300 MHz) spectra were recorded on a Gemini-300 spectrometer and processed on a Sun 4/110 data station. XRPD (X-ray powder diffraction) patterns were obtained with a Siemens Kristalloflex diffractometer. Scanning electron microscopy was performed on a JEOL JXA-840A microscope. Thermogravimetric analysis was carried out using a DuPont 931 thermogravimetric analyzer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. ESCA compositions were determined with a Perkin-Elmer PHI-5100 system on samples surface cleaned by Ar sputtering with a Perkin-Elmer Model 04-303A differential ion gun.


Syntheses. *Pb(S-*t*-Bu)₂ (1); t-Bu = -C(CH₃)₃*: A solid sample of 9.48 g of Pb(OOCCH₃)₂·3H₂O (25 mmol) was dissolved in a mixture of 50 mL of distilled water and 200 mL of ethanol. The reaction mixture was heated to 60 °C, and 4.51 g of *tert*-butyl thiol (5.6 mL, 50 mmol) was added, and the heating was continued for 1 h. After this cooled to ambient temperature, a yellow precipitate was collected by filtration, washed with a small amount of cold ethanol, and dried under vacuum; yield 6.54 g (68%); mp 210 °C (dec), lit. 180–185 °C (dec)¹³ and 260 °C (dec).¹⁸ IR (Nujol, NaCl plates) 1207 (m), 1157 (s), 1077 (m), 1023 (s), 928 (w), 871 (w), 816 (w); ¹H NMR (CDCl₃) 1.52 (s).

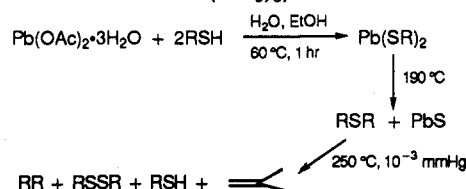
*Pb(S-*i*-Bu)₂ (2); i-Bu = -CH₂CH(CH₃)₂*: The preparation was carried out as described above using 9.48 g of Pb(OOCCH₃)₂·3H₂O (25 mmol) and 4.51 g of isobutyl thiol (5.6 mL, 50 mmol); yield 7.5 g of a yellow precipitate (78%); mp 98 °C. Elemental analysis (calcd): C 24.85% (24.92%); H 4.70% (4.71%). IR (Nujol, NaCl plates) 1235 (m), 1162 (m), 1103 (w), 1061 (m), 941 (w), 917 (w), 847 (w), 803 (w); ¹H NMR (CDCl₃) 1.02 (d, 6H), 2.78 (octet, 1H), 3.46 (d, 2H).

*Pb(S-*s*-Bu)₂ (3); s-Bu = -CH(CH₃)CH₂CH₃*: The preparation was carried out as described above using 9.48 g of Pb(OOCCH₃)₂·3H₂O (25 mmol) and 4.51 g of *sec*-butyl thiol (5.4 mL, 50 mmol); yield 4.0 g (41.6%) of a yellow oil, solidifies when cooled to 5 °C; mp 53–55 °C. Elemental analysis (calcd): C 23.77% (24.92%); H 4.34% (4.71%). The compound decomposes when exposed to light. IR (Nujol, NaCl plates) 1287 (m), 1270 (m), 1216 (s), 1140 (s), 1049 (m), 1006 (w), 990 (w), 949 (w), 840 (w), 790 (w); ¹H NMR (CDCl₃) 1.00 (t, 3H), 1.39 (d, 3H), 1.67 (quintet, 2H), 3.90 (sextet, 1H).

Thermolyses. To determine the decomposition temperatures of the prepared compounds, thermogravimetric analyses were performed (Table 1, Figure 1, and in the supplementary material (see paragraph at end of paper)). Decompositions then were carried out in the solid state and by heating a suspension of each of the prepared compounds in Decalin.

Table 2. Summary of Volatile Decomposition Products Isolated and Identified from Vacuum Thermolyses of Compounds 1-3 at 250 °C for 4 h

compound	RSR	RSSR	RSH	RR	
1 [Pb(S- <i>t</i> -Bu) ₂]		91.2%	traces	8.8%	traces
2 [Pb(S- <i>i</i> -Bu) ₂]	68.8%	25.6%	traces	3.0%	2.5%
3 [Pb(S- <i>s</i> -Bu) ₂]	47.0%	37.6%	2.9%	traces	11.2%

Scheme 1. Summary of Observed Chemical Transformations Related to Compound 1 (R = C(CH₃)₃)

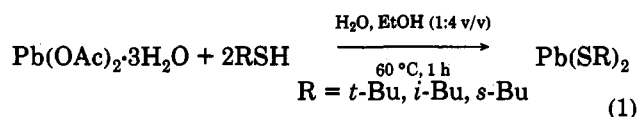
Solid-State Decomposition. Samples of the prepared compounds (1.5 g) were placed in a flask and heated under vacuum (0.2 Torr) to 250 °C for 4 h. The volatile decomposition products were trapped in a flask cooled by liquid nitrogen. After 4 h black solids remained in the heated flasks. These solids were weighed and characterized by X-ray powder diffraction (Figure 2 and in the supplementary material). The volatile products were characterized by GC/MS (Table 2).

Decomposition in a Refluxing Suspension of Decalin. Samples of the prepared compounds (1–3 g) were placed into flasks containing 30 mL each of Decalin. The resultant suspensions were heated to reflux temperature (190 °C). Compound 1 is insoluble in Decalin, whereas compounds 2 and 3 partially dissolve in hot Decalin. After about 2 h the formation of a black precipitate was observed. The heating was continued for 3 days. After cooling to ambient temperature, the precipitate was separated by filtration, dried under vacuum and characterized by XRPD and SEM (Figures 2 and 3).

Decomposition of Di-*tert*-butyl Sulfide. Di-*tert*-butyl sulfide¹⁷ (5 g) was sealed under vacuum (0.1 Torr) in a heavy-walled glass ampule. The ampule was heated to 300 °C for 5 h. The decomposition products were characterized by GC/MS (eq 6).

Results and Discussion

Compounds of the general formula Pb(SR)₂ (R = -C₄H₉) have been prepared by the reaction between Pb(OOCCH₃)₂·3H₂O and the appropriate thiol in aqueous ethanol (eq 1 and Scheme 1). The preparation of Pb(S-*t*-Bu)₂ was



reported first over 6 decades ago.^{13,18} It is a crystalline yellow solid which is insoluble in most typical organic solvents but quite soluble in chlorinated hydrocarbons. The compound decomposes at 210 °C prior to melting. Both Pb(S-*i*-Bu)₂ and Pb(S-*s*-Bu)₂ are yellow solids which are soluble in typical organic solvents and melt prior to decomposition.

Whereas Pb(S-*t*-Bu)₂ exhibits no pronounced sensitivity toward photodecomposition, Pb(S-*i*-Bu)₂ decomposes very slowly upon continual exposure to ambient laboratory light (1–2 weeks). However, Pb(S-*s*-Bu)₂ was found to possess enhanced light sensitivity. It decomposes during a period of hours when exposed to ambient light. Solutions of compounds 2 or 3 in organic solvents are even more light sensitive. The prepared lead bis(butylthiolate) compounds are not air sensitive and can be stored in the dark for extended periods of time. Such solid-state, in-the-dark

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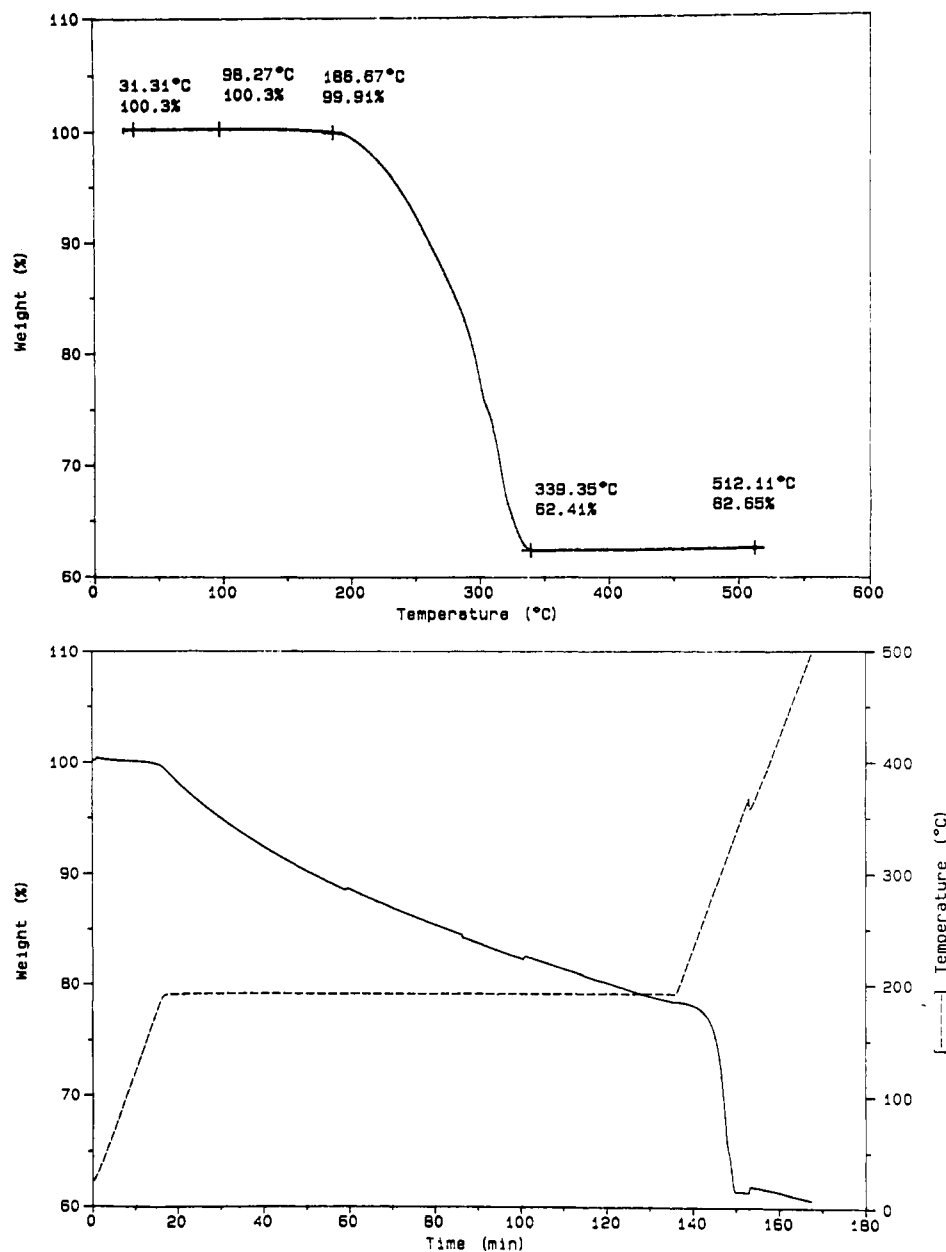


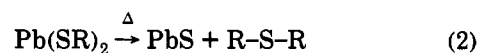
Figure 1. TGA plots for lead bis(butylthiolate) compounds: (a, top) compound 1; (b, bottom) compound 1, isothermal profile.

stability persists for at least several months and, perhaps, indefinitely. A comment regarding the photosensitivity is warranted, in light of the apparent lack of a trend correlating radical stability (t -Bu > s -Bu > i -Bu) with the observed decomposition rates of the lead bis(butylthiolate) compounds (s -Bu \gg i -Bu \gg t -Bu). Proton abstraction from an α -carbon atom on sulfur previously has been postulated as a mechanism in the cleavage of the S-S bond in dialkyl disulfides.^{19,20} Thus, the absence of such α -C-H moieties for the t -Bu example imparts stability, relative to the s -Bu (BDE for R-H: 94 kcal/mol) and i -Bu cases (BDE for R-H: 97 kcal/mol).²¹

Each compound (1-3) gave the expected spectroscopic data (1 H NMR and IR). The Pb-S stretch in this type of

compound is expected to be observed²² in the IR region at 320 cm^{-1} , a frequency outside the range of the spectrometers available for the present work. The 1 H NMR resonances are shifted 0.9 ppm from the parent thiols, as predicted based on the electronegativity difference between lead and hydrogen (1.6 and 2.2, respectively).^{23,24}

Thermogravimetric analyses suggest that compounds 1-3 decompose cleanly to form PbS (eq 2). To probe the



nature of this decomposition, an isothermal experiment was conducted (Figure 1b). Indication of the nature of

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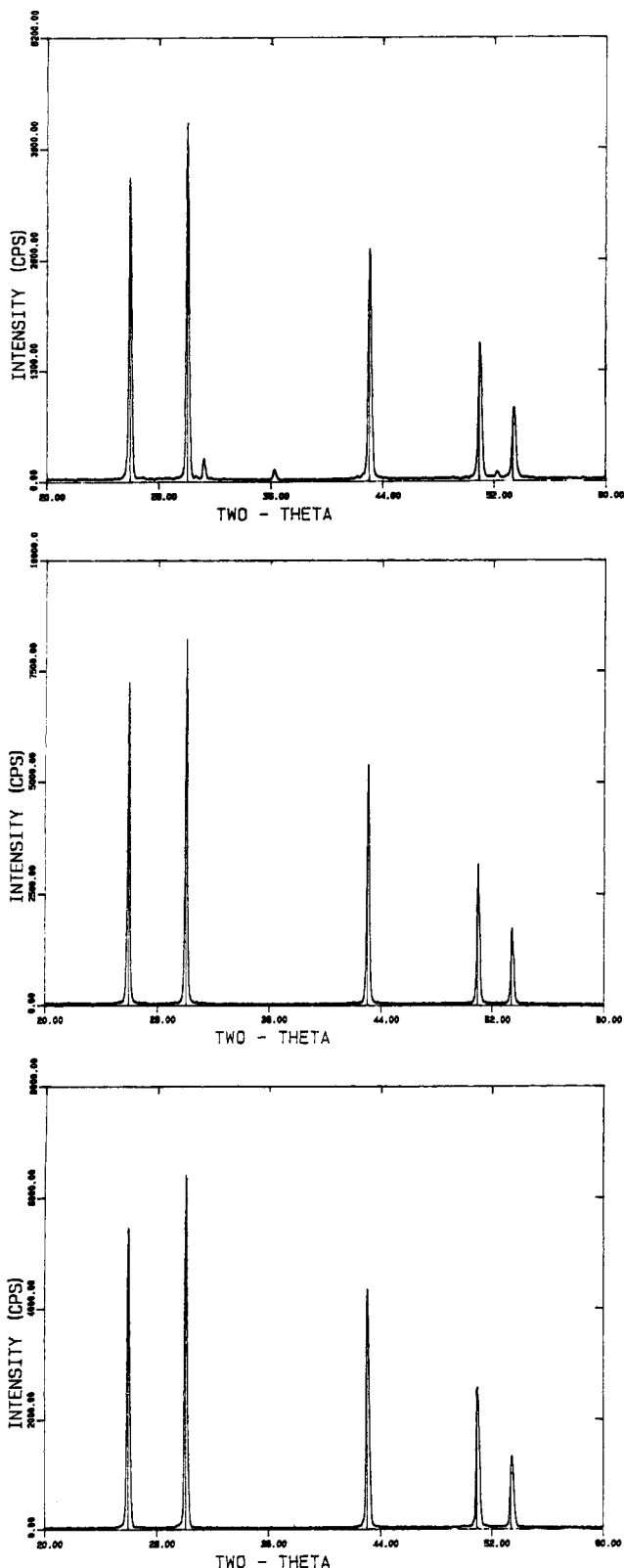


Figure 2. XRPD patterns of PbS obtained by the decomposition of lead bis(butylthiolate) compounds: (a, top) compound 3 (250 °C, solid state, 4 h); (b, middle) compound 3 (400 °C, solid state, 4 h); (c, bottom) compound 1 (refluxing Decalin suspension, 3 days).

the conversion is given by the pseudo-one-step profile obtained. Table 1 lists the TGA results, and Figure 1 shows the TGA plot obtained from compound 1 (see supplementary material for data related to compounds 2 and 3). The solid-state decomposition of each compound

Table 3. Summary of Yields of PbS Obtained from the Solid-State Decompositions of Compounds 1-3 at 250 °C for 4 h

compound	charge, g	residue of PbS, g	
		observed	calculated
1 [Pb(S- <i>t</i> -Bu) ₂]	1.50	0.95 (63.3%)	0.93 (62.0%)
2 [Pb(S- <i>i</i> -Bu) ₂]	1.50	0.90 (60.0%)	0.93 (62.0%)
3 [Pb(S- <i>s</i> -Bu) ₂]	0.81	0.50 (62.0%)	0.50 (62.0%)

Table 4. Summary of Elemental Analysis Data for PbS Produced by Pyrolysis of Compounds 1-3 at 250 °C for 4 h

compound ^a	% H found	% C Found
1	<0.5	<0.5
2	<0.5	<0.5
3	<0.5	<0.5

^a Precursor compound utilized in synthesis of PbS. Elemental analysis is for final ceramic material produced by pyrolysis of the respective compounds.

yields highly crystalline cubic PbS (Galena), which possesses the NaCl structure. Table 3 lists the yield of PbS obtained from each decomposition in the solid state.

The chemical purity of the PbS was examined by elemental analysis (Table 4) and ESCA (Figure 4). The PbS precursors, compounds 1-3, contain only C, H, S, and Pb (Experimental Section). The elemental analyses indicate no detectable quantities (<0.5%) of either carbon or hydrogen in the ceramic materials. Typical values observed for lead and sulfur were 86.53% and 13.30%, respectively. These correspond to 86.60% and 13.40%, respectively, as calculated values for pure PbS. ESCA data indicate an almost exact 1:1 Pb:S ratio (1.00:0.96), and, in some samples, trace quantities of oxygen and/or carbon. These latter two presumably result from post-synthesis atmospheric handling of the materials.

The XRPD pattern of PbS obtained from the solid-state decomposition of Pb(S-*t*-Bu)₂ at 250 °C for 4 h does not indicate any crystalline impurities (supplementary material, virtually identical to that presented in Figure 2c). The decompositions of Pb(S-*i*-Bu)₂ and Pb(S-*s*-Bu)₂, at the same temperature, yield slightly impure PbS, as judged by XRPD. These crystalline impurities were identified as Pb (Figure 2a and supplementary material). However, if the thermolyses are carried out at a moderately elevated temperature (400 °C) for 4 h, X-ray pure PbS is obtained (Figure 2b).

If Pb(S-*t*-Bu)₂ is suspended in Decalin and heated at the reflux temperature (190 °C) for 3 days, crystalline PbS is formed. The XRPD pattern of the PbS obtained from the decomposition of a suspension of Pb(S-*t*-Bu)₂ in Decalin reveals highly crystalline material (Figure 2c). As with the PbS formed during the solid-state decompositions of Pb(S-*i*-Bu)₂ or Pb(S-*s*-Bu)₂ at 250 °C, the PbS formed during the thermolyses of these compounds in refluxing Decalin contains minor crystalline impurities (see supplementary material).

Several possible explanations can be put forward regarding this observation of trace amounts of the impurity phase Pb. At the present time, it is suggested that either the PbS initially formed [at 250 °C in the solid state thermolysis of Pb(S-*i*-Bu)₂ or Pb(S-*s*-Bu)₂] is subjected to further reaction by atmospheric handling, or its crystallization is incomplete at this stage. No appreciable change was observed upon longer term (24 h) heating of solid samples neat at 250 °C; therefore, we conclude that the observation of crystalline impurities is thermodynamic

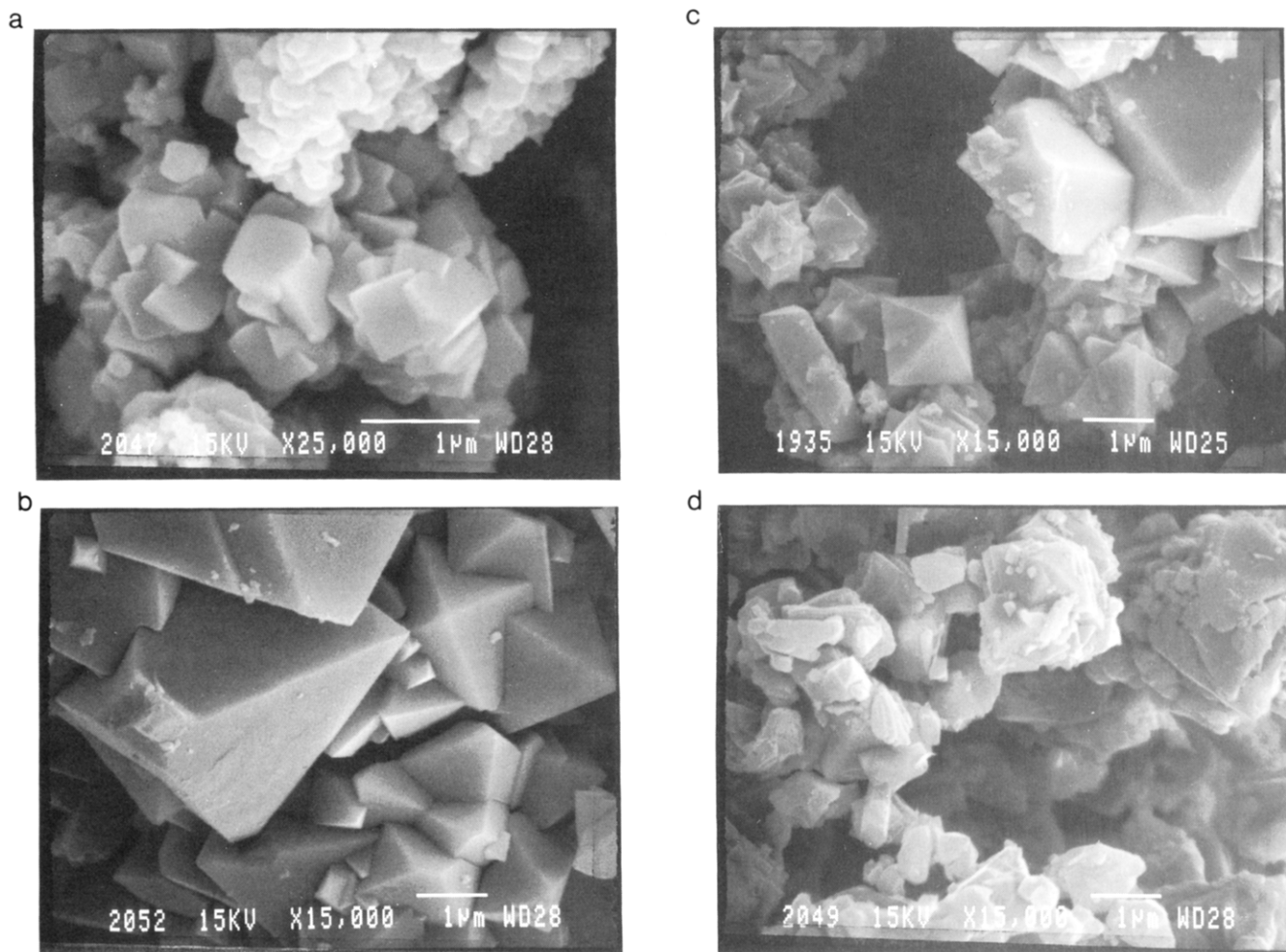


Figure 3. SEM micrographs of PbS obtained by the decomposition of lead bis(butylthiolate) compounds in the solid state (a and b) and in refluxing Decalin (c and d): (a) compound 1 (250 °C); (b) compound 3 (400 °C); (c) compound 1; (d) compound 2.

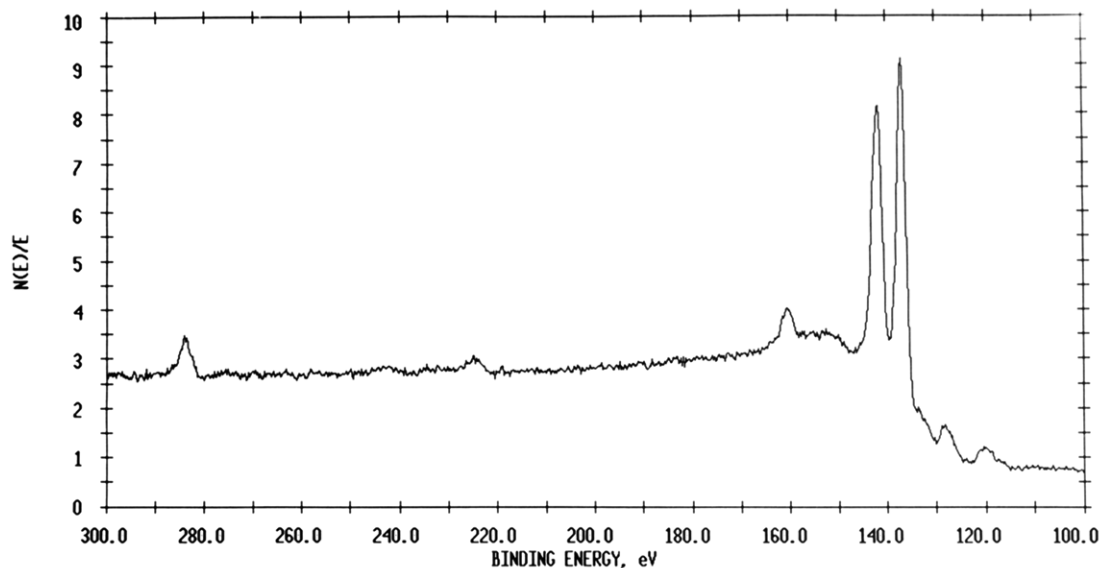


Figure 4. ESCA survey scan of PbS produced by thermolysis of compound 3 at 250 °C for 4 h.

and not kinetic in origin. The boiling point of Decalin (190 °C) is well below the temperatures utilized in the neat solid-state pyrolyses. Thus, it is evident that even milder thermal conditions than 250 °C are sufficient to effect this transformation from $\text{Pb}(\text{SR})_2$ into a ceramic material. Furthermore, these thermolyses in suspension in an inert medium were carried out under an atmosphere of ultrapure nitrogen, thereby avoiding any disadvanta-

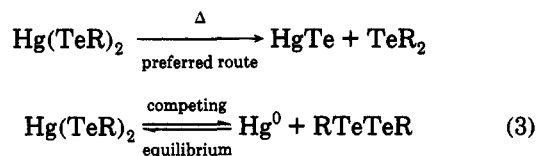
geous incorporation of oxygen from the reaction atmosphere. Combined with the observation of traces of PbO in the samples prepared in vacuo (0.2 Torr), this lends some support to the notion that the PbO observed by XRPD is formed due to postsynthesis oxidation of the elemental lead-containing ceramic material.

The properties of nanocrystals are known to differ from those of the bulk.²⁵ The observation of minor crystalline

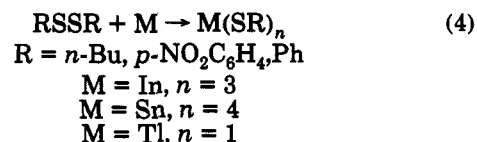
impurities present in the thermolysis products of either compound 2 or compound 3 at 250 °C may result from the initial small size of the PbS crystallites produced in this molecules-to-materials synthetic scheme. If higher temperatures are demanded for the annealing of such nanoparticles into larger agglomerates, then the observation of impurity phases due to potential postsynthesis oxidation is expected. It has not escaped our attention that RS-capped clusters,^{26,27} which may be present in these early stages of crystal growth, would be thermodynamically unstable,^{28,29} with respect to atmospheric oxidation.

The observation of traces of elemental lead is somewhat more difficult to rationalize, although a comparable process involving the expulsion of RS-SR from surface-capping RS- groups can be envisioned. Whatever the origin of these observations, conversion to crystalline PbS is complete after heating the Pb(SR)₂ compounds directly at 400 °C for 4 h. In any discussion, however, it must be remembered that crystalline PbS has not been reported previously to be formed quickly at any temperature below 800 °C.⁸ Such thermal extremes utilized in other, prior work are >450–550 °C above those observed here for the rapid thermal decompositions of lead bis(butylthiolate) compounds.

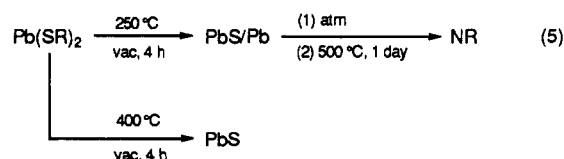
A related process (eq 3), reported by Steigerwald,³⁰ has been documented to lead to the formation of elemental metal by the reductive elimination of a dialkyldichalcogenide from a bis(alkylchalcogenide) metal complex. At



first examination, it appeared somewhat doubtful that the reverse reaction, oxidative addition, was operative in the present system. Initial higher temperatures (see below) render the material free of crystalline impurities of metallic lead. The difficulty with the organometallic equilibrium route (eq 3) is the residence time of RSSR at 250–350 °C under dynamic vacuum. It seems highly unlikely, due to its vapor pressure, that such a species would persist. For example, each of the dibutyl disulfide structural isomers utilized in the present investigation has a boiling point of <220 °C at 1 atm of pressure.³¹ Although well documented by Tuck³² (eq 4), oxidative additions of dialkyl or diaryl disulfides to main-group metals traditionally are effected in a hydrocarbon medium (e.g., toluene), not heterogeneously in a vapor phase/solid phase environment. By examination of the redox potentials of the four elements



under consideration (In -0.338 V, Sn -0.136 V (0 → +2), +0.15 V (+2 → +4), Tl -0.336 V, Pb -0.126 V),³³ it is evident that chemistry comparable to that observed in solution by Tuck is thermodynamically favored for the case of Pb. The present data best can be understood by the presence of RSSR surface adsorbed onto crystalline Pb at 250 °C. Exposure of this species to the atmosphere results in an oxidation of the dibutyl disulfide and concomitant loss of the reverse pathway (eq 3) to secure Galena. Thus, annealing to higher temperatures after ambient atmospheric oxidation does not cause reaction of the residual elemental lead. Alternatively, direct heating to 400 °C converts the initial RSSR-capped Pb into PbS and RSR (eq 5).



An interesting intermediate in the path from the elemental forms of metal and sulfur to metal sulfide has been identified very recently by Rauchfuss.³⁴ In his case, polythio anions act as mineralizers. For example, S₆²⁻ and S₃²⁻ were implicated in the preparation of PbS_x²⁻ (12 < x ≤ 14), a species attributed to Pb(S_y)₂²⁻ (y = 6 or 7), from a combination of a solution of N-methylimidazole and lead with one of magnesium and S₈.³⁵ Also, this research group has been able successfully to isolate intermediates in the case of copper, utilizing pyridine (L) as the stabilizing ligand to intercept [LCu]₄(S₆)₂ on the route from metallic copper and S₈ to Covellite (CuS).³⁶ Due to the apparently simple nature of the decomposition of the Pb(SR)₂ precursors to Galena utilized in the present study (Figure 1), combined with the isolation of near-stoichiometric metal sulfide from preparative-scale processes (Table 3), it would not appear that polythio anions are implicated in this instance. For example, one would anticipate the observation of sulfur evaporation (150–200 °C, 1 atm)³⁶ from the thermal decomposition of the polythioanions. Such events are unobserved in the current examples (Figure 1).

SEM micrographs show that highly crystalline material is formed at 250 °C as well as 400 °C (Figure 3). Likewise, the SEM photomicrographs of the PbS obtained from the thermolysis of a suspension of compound 1 in boiling Decalin indicate the presence of well-formed crystalline-appearing material. This material, produced at 190 °C, has an apparent average crystal size of 1 (±10%) μm. No debris resembling amorphous components of the reaction products was observed by SEM.

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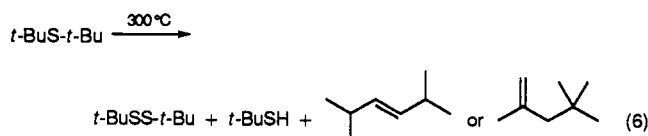
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The volatile products of the solid-state decomposition were trapped in a flask cooled by liquid nitrogen and characterized by GC/MS. Accounting for the results of the thermogravimetric analyses and the decomposition patterns of other metal thiolates,³⁷⁻⁴⁰ the thermolyses were expected to occur according eq 2. For compounds 2 and 3, this would appear to be the primary pathway. However, dialkyl sulfide was not observed in the isolated gaseous reaction byproducts from compound 1. A mixture containing dialkyl disulfide (R-S-S-R) and coupled alkane (R-R), together with trace quantities of thiol (R-SH) and olefinic hydrocarbons was collected under dynamic vacuum (Table 2).

To verify if these observed products were the primary reaction products of the decomposition of molecular precursor 1 to the solid-state PbS or, rather, were instead secondary reaction products due to subsequent premature decomposition of the primary reaction byproducts prior to analysis, an investigation of this potential side process was conducted. To examine the thermal stability of dibutylsulfides, freshly prepared di-*tert*-butyl sulfide was heated in a sealed vessel under static vacuum to 300 °C for 4 h. It was observed that this compound is unstable under these conditions. The carbon-sulfur bond is cleaved and di-*tert*-butyl disulfide, *tert*-butyl thiol, and a hydrocarbon which, as determined by GC/MS analysis of the reaction product mixture, appears to be a coupled product containing one site of unsaturation are formed (eq 6). The



observation of the formation of a coupled alkene in this instance presumably is due to the static pressure present in the sealed vessel, as compared with the experiments above (Table 2), which were performed under dynamic vacuum. The thermolysis of R₂S-type compounds usually

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involves the rupture of C-S bonds⁴¹ and has been explored extensively by previous investigators.⁴²

Summary and Conclusions

This work indicates that lead bis(butylthiolate) compounds are suitable single-source precursors for the preparation of lead sulfide. They can be synthesized in good yields and are air stable. Pb(S-*t*-Bu)₂ decomposes at temperatures as low as 190 °C and forms highly crystalline pure PbS. Temperatures of about 400 °C are necessary to obtain pure crystalline PbS from Pb(S-*i*-Bu)₂ and Pb(S-*s*-Bu)₂; however, this temperature still is well below that previously required for the preparation of crystalline PbS. XRPD patterns and SEM micrographs confirm the high crystallinity of the obtained PbS. The byproducts of the decompositions are volatile and can be removed easily. All byproducts have been isolated and identified by GC/MS and the sources of their chemical formation have been discerned.

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Supplementary Material Available: TGA plots for compounds 2 and 3, XRPD plots for PbS obtained from decomposition of compound 1 (solid state, 250 °C), compound 2 (solid state, 250 °C; in refluxing Decalin) and compound 3 (refluxing Decalin) (6 pages). Ordering information is given on any current masthead page.

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