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Synthesis and Characterization of Volatile Bismuth β-Diketonate Compounds for Metal–Organic Chemical Vapor Deposition of Thin Films

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The synthesis of several new Bi(III) β-diketonate complexes is described. In this method the chelates of the anions of 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (H(fod)) and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (H(hfa)) are formed by refluxing 3 equiv of the protonated ligand with 1 equiv of triphenylbismuth. The same reaction with 1,1,1-trifluoro-2,4-pentanedione (H(tfa)) produced a mixed β-diketonate/phenyl ligand complex. The reaction products were characterized by thermogravimetric analysis, mass spectrometry, nuclear magnetic resonance spectrometry, and gas chromatography/mass spectrometry. Formation of bismuth-containing thin films using metal–organic chemical vapor deposition was demonstrated using the Bi(III) complex of fod. The films produced using this method were determined to contain 76% bismuth by Auger analysis, and no fluorine contamination was observed.

Introduction

Various metal oxides, in addition to the high-temperature superconductor with formulation $YBa_2Cu_3O_7$, have desirable superconducting properties. In fact, the material containing bismuth, $Bi_2(Sr,Ca)_3Cu_2O_x$, exhibits a T_c as high as 110 K.[1] The formation of thin films of this material has been investigated, and MOCVD has been used successfully to produce high-quality films.[2-4] This application has generated new interest in the development of additional volatile sources of bismuth.

In the MOCVD studies cited above, triphenylbismuth and triethoxybismuth were used as volatile sources of bismuth. While these compounds are relatively volatile and thermally stable (the alkoxide is somewhat moisture sensitive[5] during vaporization), it is not known what conditions are needed to decompose these materials to bismuth or bismuth oxide at the substrate. For example, while hydrolysis was sufficient to decompose the β-diketonate complexes of Sr, Ca, and Cu to form the oxides, addition of O_2 was necessary to convert the triphenyl bismuth to bismuth oxide at 550 °C. The bismuth triethoxide compound was decomposed at 910 °C in the work by Yamane et al.[4] Matchett et al., however, have recently studied a series of bismuth trialkoxides and have found that they are relatively volatile and that they can be decomposed to bismuth oxide via hydrolysis or via thermal decomposition at 200 °C followed by annealing at 600 °C.[6] Other known volatile bismuth compounds include complexes with diethyldithiocarbamate and its derivatives.[7-9] For example, the bismuth complex with a trifluorinated derivative of diethyldithiocarbamate has a sublimation point of 215–300 °C at atmospheric pressure with only 0.4% thermal decomposition.[9] These compounds, however, contain sulfur which may cause undesirable impurities in the thin films.

There has been very little information in the literature about β-diketonate complexes of bismuth, even though β-diketonates are the most common ligands used in forming other metal oxide high-temperature superconductors by MOCVD. Therefore, an investigation has been made to demonstrate that β-diketonates of Bi(III) are effective precursors for formation of films of superconducting oxides.

Experimental Section

Synthesis. *Reagents.* Triphenylbismuth was purchased from Alfa (Danvers, MA 01923). 1,1,1-Trifluoro-2,4-pentanedione (H(tfa)), 1,1,1,5,5,5-heptafluoro-2,4-pentanedione (H(hfa)), and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (H(fod)) were purchased from Aldrich. H(tfa) was distilled prior to use. Toluene was purchased from Mallinckrodt (Paris, KY 40361).

Synthesis of Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)bismuth(III). Triphenylbismuth (2.03 g, 4.6×10^{-3} mol), was completely dissolved in 50 mL of toluene. H(fod) (4.08 g, 1.4×10^{-2} mol) was added to this solution and the reaction was refluxed for 2 h. The reaction mixture turned from a pale yellow color to an intense yellow color during the reflux period. The toluene was removed by heating at 100 °C and directing a stream of N_2 over the surface of the solution. The remaining orange-yellow residue was redissolved in 30 mL of hexanes, the insoluble material was removed by filtration, and the solvent was allowed to evaporate to dryness. In some instances, the material was further purified by sublimation. The sample used in the MOCVD experiments was not sublimed. The sample prepared for elemental analysis was first sublimed at 150 °C and 5 Torr; this first fraction was discarded, and the sublimation continued at 200 °C and 5 Torr to give a yellow solid which was collected from the coldfinger. Elemental analysis was performed at the Microanalytical Laboratory at the University of Ilinois School of Chemical Sciences, and the results are as follows: Anal. Calcd for $C_{30}H_{30}O_6F_{21}Bi$: C, 32.92; H, 2.76; F, 36.45; Bi, 19.09. Found: C, 32.80; H, 2.75; F, 36.35; Bi, 18.81. Reactions in which only 2 equiv of ligand instead of three were also investigated.

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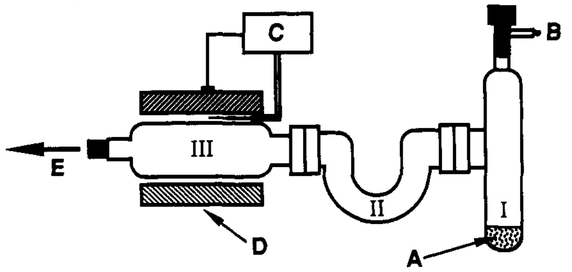

Figure 1. Schematic diagram of hot-wall reactor used for MOCVD of bismuth. Regions I, II, and III can be thermostated at various temperatures during a MOCVD experiment. The precursor is shown at point A; B represents the inlet for carrier gas; C shows the thermocouple assembly; D represents the quartz-halogen lamps; E shows where the vacuum pump is attached.

Synthesis of Other Bi(III) β-Diketonate Chelates. A synthesis procedure similar to that used for $Bi(fod)_3$ was followed. Three equiv of either H(hfa), H(tfa), or H(thd) (1.9×10^{-2} mol) and 1 equiv of triphenylbismuth (6.0×10^{-3} mol) were refluxed in 25 mL of toluene for 2 h. The toluene was then allowed to evaporate. Orange-yellow residues were collected from the reaction mixtures which contained either H(hfa) or H(tfa). After the solvent was removed from the reaction mixture containing H(thd) and triphenylbismuth, a white crystalline solid and a clear yellow liquid remained. The yellow liquid tested positive for free (protonated) β-diketone, as indicated by the red color which developed upon reaction with an ethanol solution of $FeCl_3$. The melting point of the white solid matched that of triphenylbismuth (78 °C). From these results it was concluded that no reaction with H(thd) occurred under these conditions, presumably due to the lower acidity of the enolate proton of this ligand.

Characterization of Reaction Products. Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TG-2 system. The apparatus was purged with helium at a flow of 80 mL/min, and the furnace was heated at a rate of 20 °C/min up to 500 °C.

Mass spectra were obtained using a VG-7070EQ high-resolution mass spectrometer. The spectra were calibrated against perfluorotri-*n*-butylamine or Ultramark, a high mass range standard containing high molecular weight perfluoro polyethers (SCM Specialty Chemicals). The powdered complexes were introduced into the source of the mass spectrometer using a direct insertion probe. The probe was heated until sufficient ion current was obtained. The source temperature was 250–300 °C. Methane was used as a reagent gas to obtain the negative chemical ionization spectra.

Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker WM250 250-MHz spectrometer. Deuterated chloroform (Aldrich) was used as the solvent, except for the hfa complexes, which were insoluble in chloroform and were dissolved in perdeuterated acetone (Aldrich).

Combined gas chromatography/mass spectrometry experiments were performed using a HP 5988A GC/MS instrument with high mass capability. A 5-m long column was cut from a single fused-silica capillary column that was coated with a cross-linked poly(dimethylsilicone) stationary phase (HP-1, 0.2-mm i.d., 0.11-μm film thickness). The mass spectrometer ion source was maintained at 250 °C, and the transfer line and injection port were both operated at 225 °C. The column temperature was programmed from 125 to 200 °C at 4 °C/min. Microliter-sized aliquots of solutions consisting of approximately 0.2 g of the chelate dissolved in 10 mL of hexanes were injected into the injection port and split 15 to 1 before entering the capillary column, resulting in approximately 2–3 μg of the analyte entering the column.

MOCVD Experiments. Chemical vapor deposition of $Bi(fod)_3$ to make thin films of bismuth was performed by using a hot-wall type chemical vapor deposition apparatus (Figure 1). A high-speed diffusion pump based vacuum system was employed to ensure a 10^{-8}–10^{-7}-Torr base pressure before every MOCVD experiment was initiated. The temperature and pressure of the reaction chamber were monitored, respectively, by a thermocouple controller and by a combination of ion and cold cathode gauges.

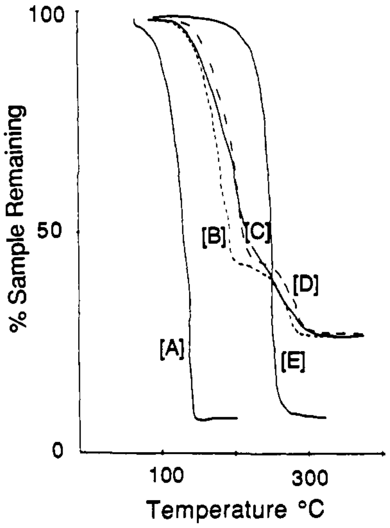

Figure 2. Thermogravimetric analysis of fod compounds of Bi(III). Thermogram A is H(fod) alone; B is $Bi(fod)_3$ sublimed at 170 °C; C (solid line) is product from synthesis starting with two moles of ligand; D (dashed line) is original $Bi(fod)_3$ product; E is triphenylbismuth. Thermograms were obtained with a flow rate of 80 mL/min helium and a temperature program of 20 °C/min.

In a typical deposition experiment, the bismuth(III) source compound, $Bi(fod)_3$, was initially placed in a bubbler chamber (region I) at room temperature. An initial sublimation to purify the $Bi(fod)_3$ was subsequently performed by heating region I to 80–95 °C at 10^{-7}–10^{-6} Torr. The source compound was thus carried to region II, maintained at dry ice temperature, where it recondensed. The quartz-halogen lamps were then activated and the reaction chamber, region III, was heated to temperatures in the range 400–450 °C. Deposition was carried out on Pyrex substrates by heating region II to approximately 90 °C and performing MOCVD at a working pressure of 1 Torr. The deposition rate for the films produced by this procedure was 10 nm/min. No carrier gas was used in these experiments. Auger analysis of the films was performed with a Perkin-Elmer Model PH1660 scanning Auger microprobe. The sputtering beam used in this analysis was an Ar beam (3 kV, 1.2 μA/cm²).

Results

Reaction of H(fod) with Triphenylbismuth. *Thermal Analysis.* The residue obtained initially from the reaction of triphenylbismuth with H(fod) melted between 72–80 °C. A sample that had been sublimed had a sharper melting point (88–90 °C). As the sample was heated above 230 °C, a color change from cloudy yellow to orange-brown was observed. The complex made with 2, rather than 3, equiv of H(fod) exhibited similar behavior upon heating. The thermogravimetric analysis of $Bi(fod)_3$ showed that a relatively sharp weight loss, down to 40–45% sample remaining, occurred near 200 °C. A more gradual weight loss to a final residue of 20–25% sample remaining occurred between 250 and 300 °C. The thermogravimetric analysis was similar for all samples of fod complexes of bismuth prepared, including the sample that had been sublimed, the complex made from 2 equiv of ligand, and the residue from a reaction that had been refluxed in the absence of oxygen (Figure 2).

Mass Spectral Analysis. The electron ionization mass spectrum of $Bi(fod)_3$ showed ions at *m/z* 799, $Bi(fod)_2^+$; 504, $Bi(fod)^+$, and 209, Bi^+. The negative chemical ionization mass spectrum showed ions at *m/z* 1389, $Bi(fod)_4^-$; 1094, $Bi(fod)_3^-$; 613, $[Bi(fod)_2\text{-}186]^-$, and 295, $(fod)^-$. The mass spectral results of the sublimed complex and of the crude product are very similar. The electron ionization mass spectrum of the complex made from 2, rather than

Table I. Mass Spectra of fod Compounds of Bi(III)

	electron ionization			chemical ionization		
	m/z	% base	ion	*m/z*	% base	ion
$Bi(fod)_3$	209	79	Bi^+	256	61	$[fod\text{-}39]^-$
	239	50	$[fod\text{-}57]^+$	295	100	fod^-
	296	18	$H(fod)^+$	798	2	$Bi(fod)_2^-$
	446	10	$[Bi(fod)\text{-}57]^+$	1054	3	$[Bi(fod)_3\text{-}39]^-$
	504	13	$Bi(fod)^+$	1094	25	$Bi(fod)_3^-$
	519	8	unidentified	1389	5	$Bi(fod)_4^-$
	687	21	$[Bi(fod)_2\text{-}112]^+$			
	799	100	$Bi(fod)_2^+$			
$Bi(fod)_2Ph$	127	91	$[fod\text{-}169]^+$	256	68	$[fod\text{-}39]^-$
	209	93	Bi^+	257	10	
	239	46	$[fod\text{-}57]^+$	276	10	$[fod\text{-}19]^-$
	286	65	$BiPh^+$	295	100	fod^-
	301	55	unidentified	296	32	
	303	26	unidentified	876	5	$Bi(fod)_2Ph^-$
	360	15	unidentified	1094	17	$Bi(fod)_3^-$
	427	14	unidentified	1172	10	$Bi(fod)_3Ph^-$
	504	13	$Bi(fod)^+$	1390	25	$Bi(fod)_4^-$
	524	11	$FBi(fod)^+$			
	542	20	$F_2Bi(fod)^+$			
	582	89	$Bi(fod)Ph^+$			
	583	18				
	597	17	unidentified			
	799	100	$Bi(fod)_2^+$			
	800	31				

3, equiv of ligand contained (in addition to the ions listed above) the following ions, one of which is indicative of a mixed ligand product: 582, $BiPh(fod)^+$; 363, $BiPh_2^+$; and 286, $BiPh^+$. The mass spectral data for the fod complexes of Bi(III) are shown in Table I. The electron ionization spectra are similar to what one would expect for these types of compounds, except that the large abundance of the bare metal ion, Bi^+, is unusual for β-diketonate metal complexes (although Sn^+ was observed in the mass spectra of Sn(II) β-diketonate complexes synthesized in a similar manner[10]). The negative chemical ionization spectrum of $Bi(fod)_3$ is dominated by the ion corresponding to the free ligand, H(fod), and the presence of the $Bi(fod)_4^-$ ion, in addition to the expected molecular ion for the tris compound, is also somewhat unique.

NMR Spectrometry. There are several peaks in each region of the NMR spectrum of the original product obtained from the reaction in which 3 equiv of ligand/equiv of triphenylbismuth are used. For example, in the methine region, there are peaks occurring at 6.06 (corresponding to the methine proton of H(fod)), 5.97, and 5.70 ppm. The major peak in the spectrum (from the protons on the *tert*-butyl group of the fod) appears at 1.21 ppm as a large peak with a shoulder upfield (Figure 3). The resonance at 14.97 ppm is due to the enol proton of unreacted H(fod). The NMR spectrum of material sublimed at 160 °C dissolved in $CDCl_3$ is similar. It is important to note that there are no peaks in the phenyl region of the spectrum for any of these samples. The sample of mixed-ligand complex made from only 2 equiv of H(fod), however, does show several peaks in the 7–8 ppm region of the spectrum that are similar to the resonances of triphenylbismuth, in addition to the methine and *tert*-butyl peaks, as expected.

Gas Chromatography/Mass Spectrometry. The results from the analysis of the $Bi(fod)_3$ reaction by gas chromatography/mass spectrometry are shown in Figure 4. There are two peaks in this chromatogram. The retention time and mass spectra of the first peak, appearing early in the chromatogram, correspond to the protonated ligand, H(fod). The second compound eluted with a peak maximum at 6.5 min and exhibits a mass spectrum similar to that obtained from direct insertion probe mass spectrometry

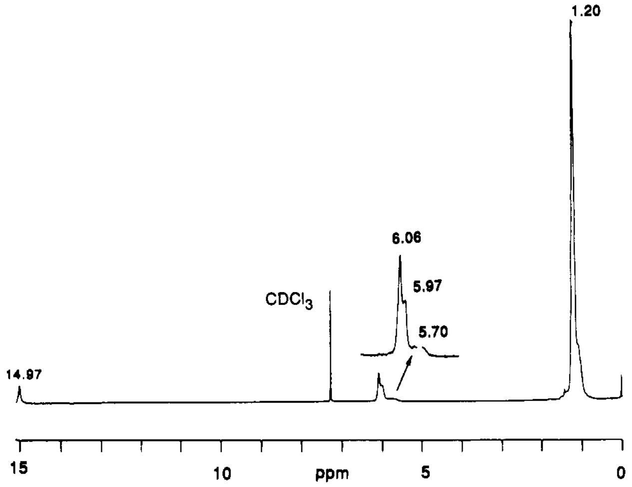

Figure 3. NMR spectrum of fod chelate of Bi(III). The ^1H NMR spectrum of the original product from the reaction of 3 equiv of H(fod) with 1 equiv of triphenylbismuth is shown.

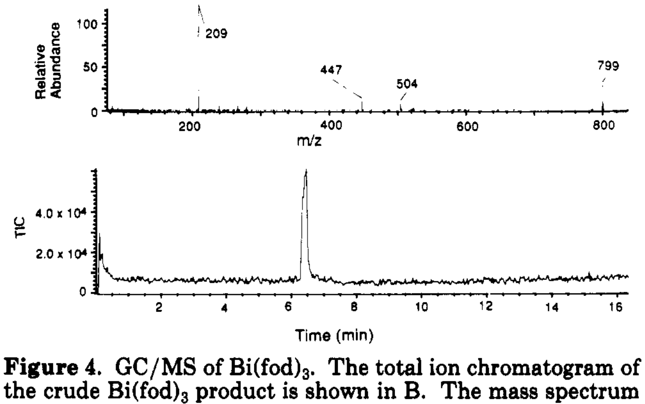

Figure 4. GC/MS of $Bi(fod)_3$. The total ion chromatogram of the crude $Bi(fod)_3$ product is shown in B. The mass spectrum of the chromatographic peak at 6.5 min is shown in A. The ions at *m/z* equal to 799, 504, and 209 correspond to $Bi(fod)_2^+$, $Bi(fod)^+$, and Bi^+, respectively. These data were obtained using a 5-m HP-1 column. The injection port and transfer line were maintained at 225 °C, and the oven was programmed from 125 to 200 °C at a rate of 4 °C/min, after a solvent delay of 1 min.

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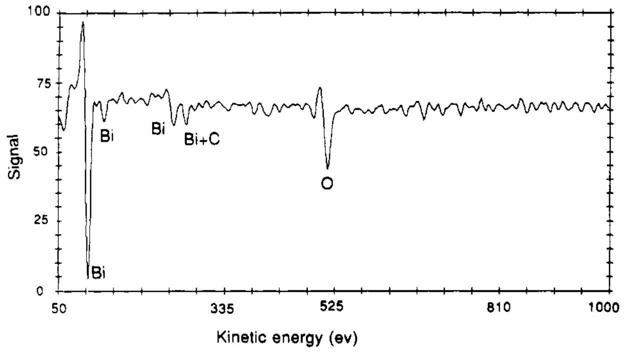

Figure 5. Auger spectrum of bismuth film made from $Bi(fod)_3$. This spectrum was obtained after sputtering surface for 20 min with an Ar beam.

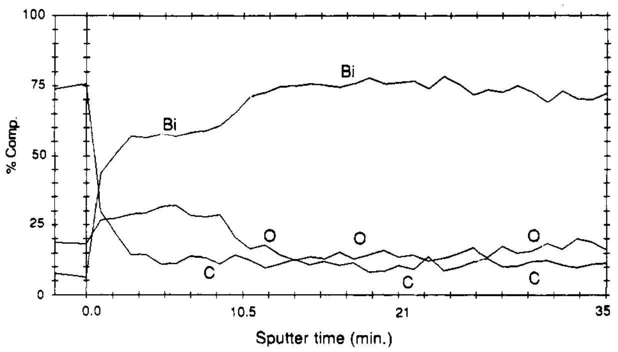

Figure 6. Atomic composition profiles of bismuth film. Graph shows percent composition of film by Auger analysis as a function of sputtering time.

of the reaction product, with ions at m/z 799, 504, and 209, corresponding to $Bi(fod)_2^+$, $Bi(fod)^+$, and Bi^+.

Reaction of H(hfa) and H(tfa) with Triphenylbismuth. Bismuth complexes made with H(hfa) did not melt; rather they decomposed at approximately 190 °C. Some weight loss does occur in the TGA, over a wide temperature range, 200–400 °C; however, over 50% of the sample remained at 500 °C. The electron ionization spectrum of $Bi(hfa)_3$ showed peaks corresponding to $Bi(hfa)_2^+$, 623; $FBi(hfa)^+$, 435; and Bi^+, 209; the negative chemical ionization spectrum showed the molecular ion at m/z 830. The NMR spectrum of $Bi(hfa)_3$ showed only a small broad peak at about 6 ppm for the methine peak of the ligand.

The residue initially isolated from the reaction of three equivalents of triphenylbismuth with H(tfa) had a melting point of 86–90 °C. The original material isolated lost weight upon heating in a broad transition, 200–500 °C, with several plateaus down to about 50% sample remaining. The thermograms of sublimed material, however, generally exhibited less thermal decomposition. The EI mass spectrum of this compound showed ions corresponding to $BiPh_2^+$, $Bi(tfa)Ph^+$, and $Bi(tfa)Ph_2^+$ as well as $Bi(tfa)^+$ and $Bi(tfa)_2^+$. The NMR spectrum showed fairly intense resonances in the phenyl region, a broad methine peak at approximately 5.6, and a singlet at 2.15 ppm. From these data it was concluded that the reaction of triphenylbismuth with H(tfa) was not complete, giving a mixed-ligand complex. While the reaction of triphenylbismuth with H(hfa) did appear to give the tris chelate, the Bi(III) chelate made from H(fod) was more thermally stable. Therefore $Bi(fod)_3$ was the precursor of choice for the MOCVD of bismuth-containing films.

Formation of Thin Films of Bismuth Using $Bi(fod)_3$. The material deposited on the glass walls of the MOCVD reactor from the decomposition of $Bi(fod)_3$ was a uniform light brown film with a lustrous appearance. The Auger spectrum of the region of the film where the temperature was the most uniform during deposition is shown in Figure 5. The results show a large bismuth peak and smaller peaks from carbon and oxygen. It is significant that fluorine is not present as a major peak, as the possibility of fluorine contamination is a concern when fluorinated precursors are used. Figure 6 shows the percent atomic composition (taking into account the relative sensitivity factors) of the film as a function of sputtering time. The film contains a higher percentage of carbon and oxygen before sputtering, presumably from atmospheric contamination. However, after several minutes of sputtering, a constant percent of bismuth (73%), carbon (15%), and oxygen (12%) is maintained, indicating a relatively uniform film. Regions of the film produced on the edge of the hottest deposition zone contained slightly more carbon contamination, with an atomic composition of 66% Bi, 25% C, and 9% O. The carbon and oxygen contamination may be reduced or eliminated if hydrogen is used as a carrier gas during the deposition experiment. For example, using the same apparatus the purity of copper films deposited from β-diketonate precursors increased from 70% to greater than 99% when changing from 10% H_2 in Ar to 100% H_2 as a carrier gas.[11]

Discussion

We have successfully synthesized the Bi(III) chelates of fod by the reaction of 3 equiv of β-diketone/mol of triphenylbismuth. All of the phenyl groups were displaced by these β-diketones. This is the first example of the synthesis of a volatile β-diketonate complex of Bi(III) suitable for use as a MOCVD precursor. Previous studies have shown that bismuth can be extracted from aqueous solution using β-diketones as complexing agents. For example, bismuth ion can be extracted from aqueous solution at high pH into benzene using benzoylacetone and dibenzoylmethane.[12] Thenoyltrifluoroacetone will extract Bi(III) above pH 2.35.[13] One problem with using the traditional methods for synthesizing Bi(III) β-diketonate complexes[14] is that many bismuth salts hydrolyze in aqueous solution in the pH range needed to deprotonate the β-diketone ligand. An alternative procedure used to synthesize complexes of aluminum[15] and boron[16] is simply to mix a trialkylated metal compound with the β-diketone ligand. Generally the dialkyl complexes were formed. The reaction of Sn(II) organometallic complexes with β-diketones yields the bis chelates.[10] For example, the reaction between $Sn(OCH_3)_2$ or bis(methylcyclopentadienyl)tin(II) and 2 equiv of H(acac), H(tfa), or H(hfa) results in the bis (β-diketonate) Sn(II) complex and 2 equiv of methanol or methylcyclopentadiene. These Sn(II) compounds are relatively volatile and appear to be monomeric, unlike other oxygenated complexes of Sn(II) that form oligomers via oxygen bridging. Because of these encouraging results,

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ligand displacement was used for the synthesis of bismuth β-diketonate complexes.

The most promising compound synthesized, in terms of precursors for MOCVD, was $Bi(fod)_3$. From these results, it appears that the reaction between 3 equiv of H(fod) and 1 equiv of triphenylbismuth produces the tris chelate. The mass spectral, NMR, GC/MS, and thermogravimetric analyses all indicate that the crude product appears to contain an extra fod ligand, perhaps existing as the tetrakis complex, $HBi(fod)_4$, or as an adduct with the fourth ligand only weakly associated. If the reaction product is carefully sublimed, however, the tris chelate is obtained. The following equilibrium may exist and be driven to the right as temperature is increased:

$$H[Bi(fod)_4] \text{ or } Bi(fod)_3{\cdot}xH(fod) \overset{\Delta}{\rightleftharpoons} Bi(fod)_3 + xH(fod)$$

Elemental analysis of the residue remaining after sublimation or after use as a source for MOCVD indicates that some of the tris chelate decomposes to form a ligand-deficient nonvolatile species. Efforts were not made to remove the excess ligand from the chelate before using it as a MOCVD precursor, because the chelate was presublimed as part of the deposition experiment, and as has been noted previously,[17] the presence of excess ligand can improve the vaporization of the precursor compounds and is not detrimental to thin film formation. As postulated earlier for stabilization of Ba(II) complexes, the presence of excess ligand may also serve to repair ruptured chelate rings.[18]

In conclusion, the reactions of triphenylbismuth with several β-diketones have been investigated, and the reaction products have been characterized. The reaction with H(fod) to make $Bi(fod)_3$, perhaps via a tetrakis or ligand adduct intermediate species, was successful in producing a volatile chelate of bismuth that is a suitable precursor for making bismuth-containing thin films by MOCVD.

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Registry No. $BiPh_3$, 603-33-8; $Bi(Fod)_3$, 141364-07-0; $Bi(hfa)_3$, 141364-06-9; Bi, 7440-69-9; $Bi(Fod)_2Ph$, 142188-44-1.

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Bulk Semiconductors from Molecular Solids: A Mechanistic Investigation

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We report on the mechanism of the solid-state conversion of a series of II/VI precursors of general formula $(R_4N^+)_4[S_4M_{10}(SPh)_{16}]^{4-}$ (R = Me, Et; M = Cd, Zn) to the bulk metal sulfide structure. On heating in vacuum or inert atmosphere, we find that the solid-state conversion proceeds in two discrete reaction steps. The first step, ~200 °C, can be characterized as a nucleophilic substitution or elimination initiated by the attack of a fragment of the anion cluster on the tetraalkylammonium counterion. The intermediate solid produced in this step consists of charge neutral $M_{10}S_{16}Ph_{12}$ clusters that retain the primary cluster size present in the starting material but appear to aggregate to varying degrees in the solid or solution. The intermediate cluster has very different chemical and physical properties from the starting material and, therefore, suggests some new possible routes to the preparation of bulk II/VI semiconductor films and powders from molecular precursors.

Introduction

The preparation of crystalline solids via the consolidation of molecular precursors is an increasingly important branch of solid-state chemistry.[1] II/VI compound semiconductors have been a favorite subject for such studies because of interest in the evolution of their electronic properties as the consolidation process proceeds. Consequently, a wide variety of molecular precursor approaches to these materials has been described.[2,3] Nevertheless, whether the goal is crystalline thin films via MOCVD or microcrystalline powders via solution- or solid-state reactions, detailed information on the mechanisms of the transformation from molecules to bulk II/VI solids is limited. In this paper we report on the mechanism of the solid-state conversion of a particular series of II/VI precursors of general formula $(R_4N^+)_4[S_4M_{10}(SPh)_{16}]^{4-}$ to the bulk metal sulfide structure. On heating, in vacuum or

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