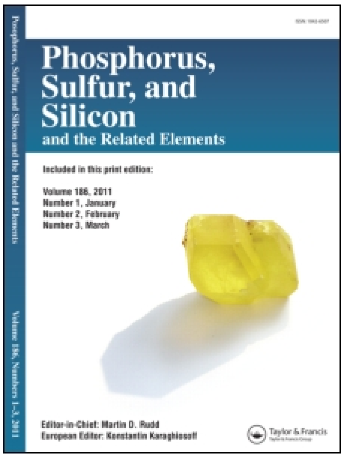

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NEW MOLECULAR - BASED ROUTES TO BINARY MAIN GROUP METAL SULFIDES

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Metal thiolates of the general formula $M(SR)_2$ (M = Pb, Zn, Cd) and Cl-Hg-SR (R = alkyl) have been prepared and characterized by IR and NMR spectroscopic techniques, TGA and, in selected cases, single crystal X-ray diffraction. The metal *bis*(thiolate) compounds can be converted into the related metal sulfides by thermolyses. The solid state materials have been characterized by XRPD, SEM and, in selected cases, by particle size determination. The volatile pyrolytic co-products have been isolated and characterized by GC/MS. The decomposition pathways of mercury chlorothiolates are more complicated and depend on the nature of the organic group present in Cl-Hg-SR.

Key Words: metal *bis*(thiolate), mercury chlorothiolate, single source precursor, decomposition studies, metal sulfide

INTRODUCTION

Many binary metal sulfides possess interesting electrical and optical properties such as semiconductivity, photoconductivity and luminescence.[1] Metal sulfides usually are prepared by the reaction of metal salts and H_2S in aqueous solution. However, metal sulfides prepared by this method frequently contain large amounts of impurities and often are amorphous. The reaction of metal alkyls and hydrogen sulfide leads to the formation of pure metal sulfides, however, problems persist due inhomogenous mixing of the starting materials, the intrensic high reactivity of the metal alkyls and the toxicity of hydrogen sulfide. Single source processing offers obvious advantages. While the single source precursor method has been explored extensively for 13-15 semiconductors in recent years,[2] single source precursors leading to 12-16 and 14-16 compounds have been studied much less extensively.

Metal thiolates - the sulfur analogs of metal alkoxides - possess the potential to serve as single source precursors for metal sulfides.[3] Due to their polymeric structures, many metal thiolates, including zinc- and cadmium thiolates, are insoluble in typical organic solvents, making their purification by recrystallization difficult and often impossible.[4] Two approaches can be envisioned to overcome these difficulties, one of which involves the choice of bulky organic groups to encourage the formation of compounds with a relatively low degree of association. This idea has been realized by Bochmann and coworkers who recently have prepared cadmium *bis*(supermesitylthiolate) and have shown that this soluble compound decomposes to give cadmium sulfide.[5] However, metal thiolates containing such bulky organic groups show a high degree of thermal stability and, therefore, high temperatures are required for their decomposition - in the case of $Cd(SMes^*)_2$ a temperature of about 450°C at 10^{-2} Torr is necessary. Complementing the synthesis of metal thiolates with bulky groups, the formation of adducts with Lewis bases can be used to obtain more soluble metal thiolate complexes. The Lewis base should be bonded only weakly to the metal center to insure that it can be cleaved easily under mild conditions, thereby not interfering with the decompostion process. Steigerwald and coworkers have reported that phosphine ligands fullfill these requirements for $Cd(SePh)_2$.[6] The present work describes the utilization of 1-methylimidazole to form soluble adducts of zinc- and cadmium *bis*(alkylthiolate) compounds and the decomposition of the unsolvated and solvated derivatives. The imidazole ligand was chosen because of its known role in the formation of soluble zinc mercapto complexes in biological systems.[7] Additionally, it has been reported recently that N-alkylimidazole solutions of chalcogens show a remarkable reactivity towards several elemental metals and metal sulfides.[8]

In contrast to zinc- and cadmium *bis*(thiolate) compounds,[9-11] the analogous base-free lead *bis*(thiolate) derivatives[12] as well as mercury chlorothiolates[9-11] are soluble in organic solvents. The syntheses, characterization and decomposition of these compounds are discussed.

RESULTS AND DISCUSSION

Zinc- and Cadmium Bis(thiolate) Compounds

Zinc- and cadmium *bis*(alkylthiolate) compounds have been prepared by the reaction of the metal acetates with the appropriate thiol in aqueous ethanol (eq. 1).

$$M(OOCCH_3)_2 * n\,H_2O \;+\; 2\,R\text{-}SH \;\text{------------>}\; M(SR)_2 \;+\; HOOCCH_3 \qquad (1)$$

M = Zn, R = *i*Pr, *t*Bu; M = Cd, R = *i*Pr, *t*Bu, Bz

TABLE 1

Thermogravimetric analyses of zinc and cadmium *bis*(thiolate) compounds

compound	weight residue	
	observed	calculated
$Zn(S\textit{i}Pr)_2$	46.8 %	45.2 %
$Zn(S\textit{t}Bu)_2$	42.4 %	40.0 %
$Cd(S\textit{i}Pr)_2$	55.5 %	54.9 %
$Cd(S\textit{t}Bu)_2$	49.2 %	49.6 %
$Cd(SBz)_2$	42.5 %	40.2 %

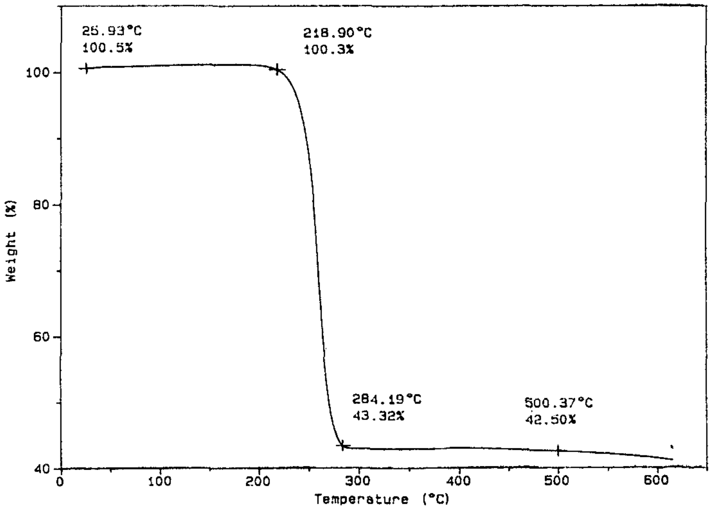

FIGURE 1 TGA plot of $Cd(SBz)_2$ (10°C/min, N_2 atmosphere)

The reaction affords the homoleptic metal thiolates in good yields as colorless powders which are virtually insoluble in typical organic solvents. The decomposition of the prepared compounds first was studied by thermogravimetric analysis. The TGA-plots show a sharp decline in weight beginning at about 200°C. The observed weight loss suggests that in each case the desired binary metal sulfide is formed. Figure 1 shows the TGA plot for $Cd(SBz)_2$ and Table 1 summarizes the results of the thermogravimetric analyses. Decompostion then was carried out by heating samples of the prepared compounds under vacuum (250°C, 4h). The volatile co-products were trapped and analyzed by GC/MS. The solid state material was characterized by XRPD and SEM measurements. Dialkylsulfides were found to be the only volatile product of the decomposition. In the case of the metal *bis*(*t*-butylthiolate) compounds, however, several volatile decomposition products were isolated. By heating a freshly prepared sample of di-*t*-butyl sulfide to 250-300°C for 4h it was shown that this compound was unstable at the temperature present during the metal thiolate thermolysis process and decomposes, forming dialkyldisulfide, coupled alkane, olefin and thiol. The XRPD patterns of the obtained solid state materials were indicative of cubic zinc sulfide (Wurzite) (Figure 2) and hexagonal CdS (Greenockite) (Figure 3), respectively. However, the decomposition of $Cd(SBz)_2$ leads to the formation of the relatively uncommon cubic CdS (Hawleyite).

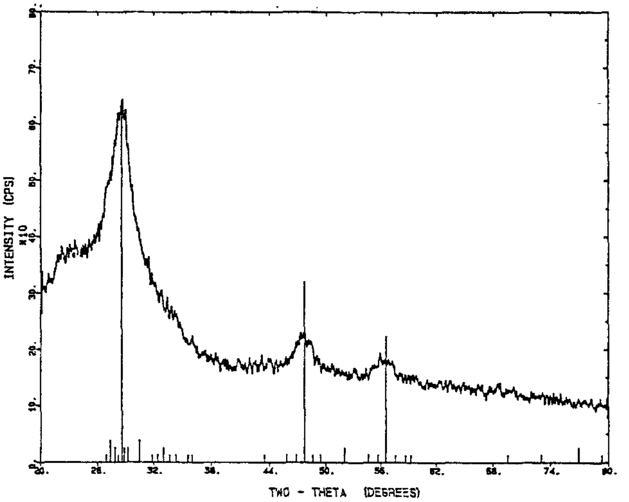

FIGURE 2 XRPD pattern of ZnS (from $Zn(SiPr)_2$, 250°C, 4 h)

Decomposition also was carried out by heating a suspension of the prepared zinc- or cadmium *bis*(*t*-butylthiolate) in decalin (b. p. 190°C) for 3 days. A complete conversion into the respective metal sulfide was observed. The XRPD patterns of the obtained solid state materials resemble those of the metal sulfides obtained by solid state decompostion. The size of the formed metal sulfide particles was determined. Figure 4 shows the particle size distribution found for ZnS.

As mentioned above, all of the zinc- and cadmium *bis*(thiolate) compounds were found to be insoluble in typical organic solvents as initially prepared. However, in the presence of 1-methylimidazole, three of the five prepared metal *bis*(thiolate) derivatives readily are soluble in toluene. Upon removal of the solvent, the imidazole adducts are isolated (Table 2). Thermogravimetric analysis was performed to examine the decomposition of the adducts. In the case of $[Cd(SBz)_2]_2 * L$ (L = 1-methylimidazole), the imidazole ligand is cleaved off under mild conditions. The -- now uncoordinated -- $Cd(SBz)_2$ decomposes in the usual manner (Figure 5).

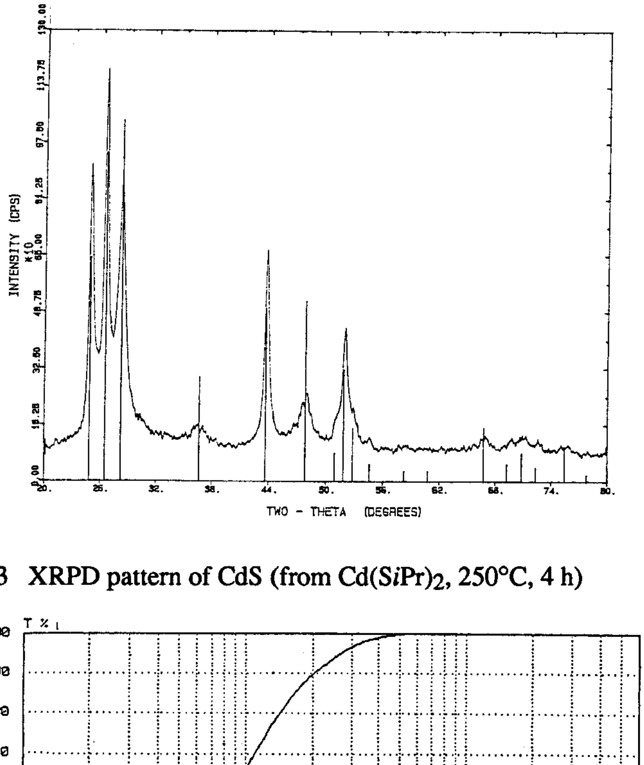

FIGURE 3 XRPD pattern of CdS (from $Cd(S\textit{i}Pr)_2$, 250°C, 4 h)

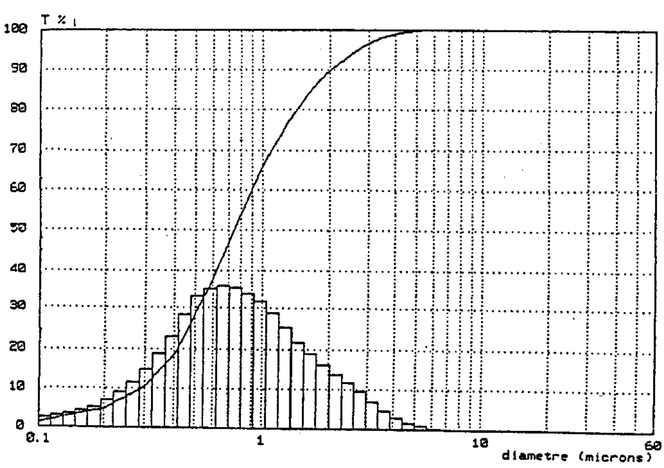

FIGURE 4 Particle size distribution in ZnS (from $Zn(S\textit{t}Bu)_2$ in decalin, 190°C, 3 days)

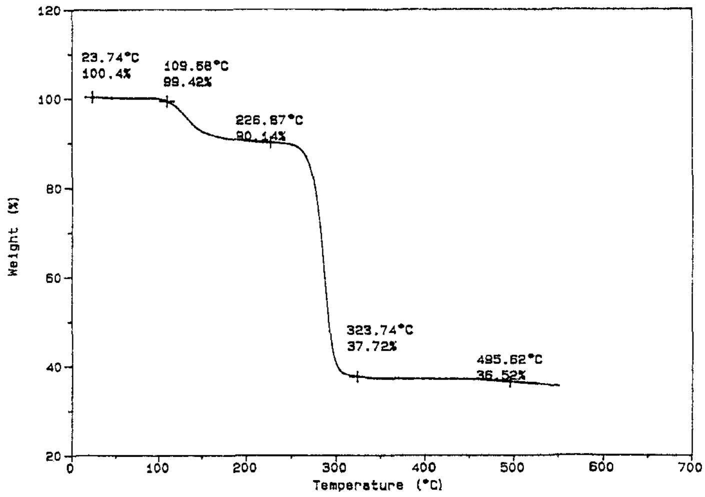

FIGURE 5 TGA plot of $[\mathrm{Cd(SBz)_2}]_2 * \mathrm{L}$ (10°C/min, N_2 atmosphere)

TABLE 2

1-Methylimidazole adducts of zinc and cadmium *bis*(thiolate) compounds

metal *bis*(thiolate) compound	imidazole adduct
$\mathrm{Zn(S}\mathit{i}\mathrm{Pr)_2}$	$\mathrm{Zn(S}\mathit{i}\mathrm{Pr)_2} * 2\ \mathrm{L}$
$\mathrm{Cd(S}\mathit{i}\mathrm{Pr)_2}$	$\mathrm{Cd(SiPr)_2} * \mathrm{L}$
$\mathrm{Cd(SBz)_2}$	$[\mathrm{Cd(SBz)_2}]_2 * \mathrm{L}$

L = 1-methylimidazole

However, in case of the imidazole adducts of $\mathrm{Zn(S}\mathit{i}\mathrm{Pr)_2}$ and $\mathrm{Cd(S}\mathit{i}\mathrm{Pr)_2}$, higher temperatures had to be applied to cleave off the imidazole ligands, presumably due to the fact that in these compounds the metal complex/ligand ratio is 1:2 and 1:1, respectively, as compared to 2:1 in the case of $\mathrm{Cd(SBz)_2}$.

Lead Bis(thiolate) Compounds

Lead *bis*(thiolate) compounds can be prepared analogous to the zinc- and cadmium *bis*(thiolate) derivatives by the reaction of lead acetate and thiol in aqueous ethanol (eq. 2).[13]

$$Pb(OOCCH_3)_2 * 3\,H_2O \quad + \quad 2\,R\text{-}SH \quad \text{--------->} \quad Pb(SR)_2 \quad + \quad 2\,HOOCCH_3 \qquad (2)$$

R = *t*Bu, *i*Bu, *s*Bu

TABLE 3

Thermogravimetric analyses of lead *bis*(thiolate) compounds

compound	weight residue observed	calculated
$Pb(StBu)_2$	62.1 %	62.1 %
$Pb(SiBu)_2$	63.1 %	62.1 %
$Pb(SsBu)_2$	64.2 %	62.1 %

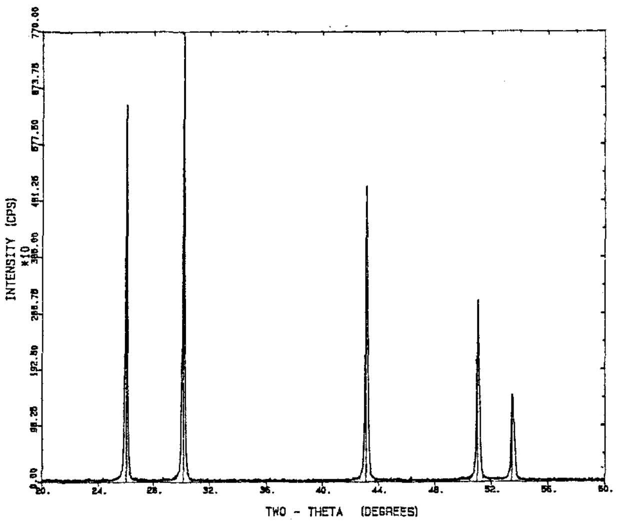

FIGURE 6 XRPD pattern of PbS (from $Pb(StBu)_2$, 250°C, 4 h)

The compounds are yellow crystalline solids, which are soluble in polar organic solvents. The thermogravimetric analyses show that lead *bis*(butylthiolate) compounds decompose at about 200°C to give lead sulfide (Table 3). The solid state decomposition under vacuum (250°C, 4h) yields highly crystalline cubic lead sulfide (Galena) as revealed by XRPD (Figure 6) and SEM[11-12] measurements, respectively. Decomposition also can be achieved by refluxing a suspension of the lead *bis*(butylthiolate) compounds in decalin for 3 days. The recovered lead sulfide is highly crystalline, as indicated by XRPD analysis.

Mercury Chlorothiolates

Mercury dichloride reacts with one equivalent of thiol to yield mercury chlorothiolates (eq.3).

$$HgCl_2 + R\text{-}SH \text{ --------> } Cl\text{-}Hg\text{-}SR + HCl \qquad (3)$$

R = *i*Pr, *neo*-Pent, Bz

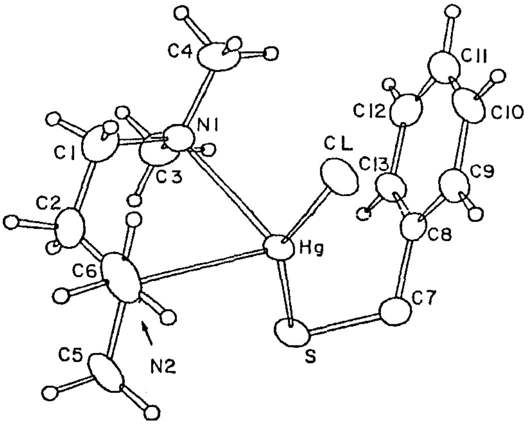

FIGURE 7 Solid state structure of ClHgSBz * TMEDA

The mercury chlorothiolates are colorless crystalline solids which are soluble in many polar and potentially coordinating solvents. Several of the prepared compounds have been characterized by single crystal X-ray diffraction. The benzyl derivative is soluble in tetramethylethylenediamine (TMEDA) and crystallizes as a monomeric TMEDA adduct

(Figure 7). Mercury chloro-*i*-propylthiolate crystallizes solvent-free, forming a polymeric chain as reported earlier.[14] The structure of the neopentyl derivative also contains a polymeric chain. This compound crystallizes from pyridine as an adduct (Figure 8).

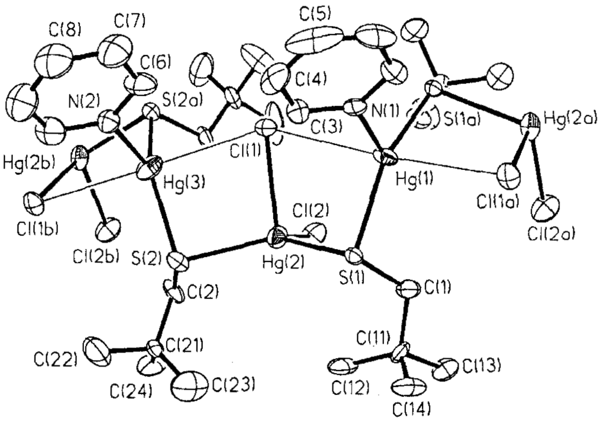

FIGURE 8 Solid state structure of ClHgS*neo*-Pent * Py

Samples of the unsolvated compounds were heated under vacuum (200°C, 4h). The *i*-propyl and neopentyl derivatives decompose to yield Hg_2Cl_2 and organosulfur compounds. The benzyl derivative forms highly crystalline black mercury sulfide (Metacinnabar), as determined by XRPD analysis, and benzylchloride. The metastable black HgS is converted slowly into the stable orange mercury sulfide (Cinnabar). We attribute the observed differences in the decomposition pathways to the higher stability of benzyl radicals, as compared to *i*-propyl and neopentyl radicals, assuming a radical decomposition process.

CONCLUSION

The prepared metal *bis*(alkylthiolate) compounds are useful single source precursors for the preparation of binary main group metal sulfides. They are obtained easily and in good yields. The reported compounds are stable towards water and oxygen. Their decomposition proceeds under mild conditions and yields crystalline and pure metal sulfides. The co-products are volatile and can be removed easily. The decomposition pathways of mercury chlorothiolates greatly depend on the organic group present in the studied compound. Apparently, compounds containing groups forming relatively stable radicals decompose to yield the desired mercury sulfide.

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REFERENCES

1. R. A. Smith, *Semiconductors, 2nd ed.*, Cambridge University Press, Cambridge, 1978.
2. A. H. Cowley and R. A. Jones, *Angew. Chem. Int. Engl. Ed.*, **28**, 1208 (1989).
3. K. Osakado and T. Yamamoto, *Inorg. Chem.*, **30**, 2328 (1991).
4. I. Dance, *Polyhedron*, **5**, 1037 (1986).
5. M. Bochmann, K. Webb, M. Harman and M. B. Hursthouse, *Angew. Chem. Int. Engl. Ed.*, **29**, 638 (1990).
6. J. G. Brennan, T. Siegrist, P. J. Carroll, S. M. Stuczynki, L. E. Brus and M. L. Steigerwald, *J. Am. Chem. Soc.*, **111**, 4141 (1989).
7. J. M. Berg, *Prog. Inorg. Chem.*, **37**, 143 (1988).
8. S. Dev, E. Ramli, T. B. Rauchfuss and C. L. Stern, *J. Am. Chem. Soc.*, **118**, 6385 (1990).
9. W. S. Rees, Jr., G. Kräuter and V. Goedken, *MRS Symposium Proceedings*, Volume 283, Materials Research Society, Pittsburgh, PA, 1993, p. 859.
10. G. Kräuter, V. L. Goedken, B. Neumüller and W. S. Rees, Jr., MRS, Abstract N.4.7, Fall Meeting, Boston, MA, Materials Research Society, Pittsburgh, PA, 1993.
11. W. S. Rees, Jr. and G. Kräuter, MRS, Abstract N 6.1, Fall Meeting, Boston, MA, Materials Research Society, Pittsburgh, PA, 1993.
12. G. Kräuter, P. Favreau, B. Nunnally and W. S. Rees, Jr., MRS, Abstract N 4.8, Fall Meeting, Boston, MA, Materials Research Society, Pittsburgh, PA, 1993.
13. R. A. Shaw and M. Woods, *J. Chem. Soc.*, 1569 (1971).
14. P. Biscarini, E. Foresti and G. Pandella, *J. Chem. Soc., Dalton Trans.*, 953 (1984).