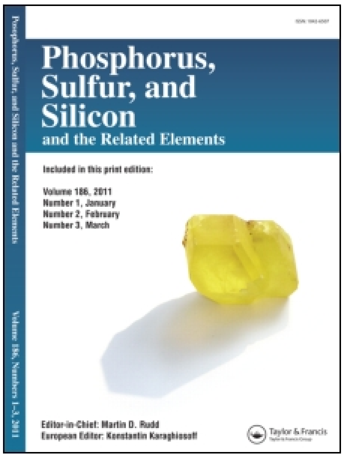

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Intra-Ring Differentiation Between MS and MX in the Preparation of Electronic Materials from Metal Thiolate Precursors

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INTRA-RING DIFFERENTIATION BETWEEN MS AND MX IN THE PREPARATION OF ELECTRONIC MATERIALS FROM METAL THIOLATE PRECURSORS

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Abstract Chloromercurythiolate compounds of the general formula RSHgCl (R = *neo*Pent, *iso*Pr, Bz) have been prepared and characterized by single crystal X-ray diffraction. The solid state decompositions of the chloromercurythiolate compounds have been studied. The volatile and involatile decomposition products have been isolated and characterized by GC/MS and XRPD, respectively. The decomposition pathways were found to be dependent greatly on the identity of the organic group present in the molecular precursor. The influence of the structure of the starting reactants on the structure of the solid state material obtained by the thermolyses of these species is discussed. The decomposition pathways found are compared to the decomposition mechanism observed for lead *bis*(butylthiolate) compounds.

INTRODUCTION

Many metal chalcogenides display interesting electrical and optical properties such as semiconductivity, photoconductivity and luminesence. These compounds can be prepared by the thermolyses of molecular precursors of the general formula $M(ER)_x$ (E = S, Se, Te). The molecular precursor method offers several advantages including simplified processing equipment due to single source processing,[1] mild decomposition conditions, and, even more importantly, the possibility of the fabrication of unusual phases,[2] the achievement of site-selective doping[3] and unexpected growth morphologies of the final materials.

Recently, the employment of metal *bis*(thiolate) compounds, $M(SR)_2$ (M = Zn, Cd, Pb), as precursors for the preparation of binary metal sulfides has been investigated.[4-11] These compounds decompose under mild conditions to yield pure binary metal sulfides. Phase control can be achieved in the case of cadmium thiolate compounds, which decompose to form either the hexagonal or the cubic phase of cadmium sulfide, depending on the organic group present in the precursor.[9] This report now adds an examination of the decomposition of mercury thiolato complexes of the general formula RSHgCl among these studies. Unlike most metal thiolates, chloromercurythiolate compounds are crystalline solids which are soluble in polar organic solvents.[12-13] Thus, characterization of these compounds via single crystal X-ray diffraction is possible. These compounds, therefore, are promising canditates for investigations concerning the issue of influence over the structure of a solid state material being exerted by the molecular structure of the precursor used for its preparation.

RESULTS AND DISCUSSION

Chloromercurythiolate compounds can be obtained readily by the reaction of mercury dichloride with the appropriate thiol in ethanol (equation 1). The *iso*-propyl derivative crystallizes solvent-free from ethanol. It forms a polymeric chain $(Hg_2Cl_2)_n$ which is surounded by thiolate ligands.[14] The *neo*-pentyl analog crystallizes as an adduct from pyridine and displays a polymeric $(Hg_2Cl_2)_n$ two-dimensional sheet, similar to the analogous *iso*-propyl compound. Chloromercurybenzylthiolate dissolves in tetramethylethylenediamine (TMEDA) and crystallizes as a TMEDA adduct, which is monomeric in the solid state.

$$HgCl_2 + RSH \longrightarrow ClHgSR + HCl \qquad (1)$$

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

If the solvent-free compounds are heated (220°C for 4h at 0.1 Torr) they decompose yielding Hg_2Cl_2 and organosulfur compounds in the case of the *iso*propyl and the *neo*pentyl derivative and HgS and benzylchloride in the case of the benzyl compound. This observation lends some credence to the assumption that the molecular structure of the precursor influences the decomposition pathway and thus, the identity of the final product.

The chloromercurythiolates containing Hg-Cl-chains decompose to yield Hg_2Cl_2, thereby preserving the main element of the precursor structure (Figure 1), while the monomeric benzyl compound yields Metacinnabar (Figure 2). Another difference

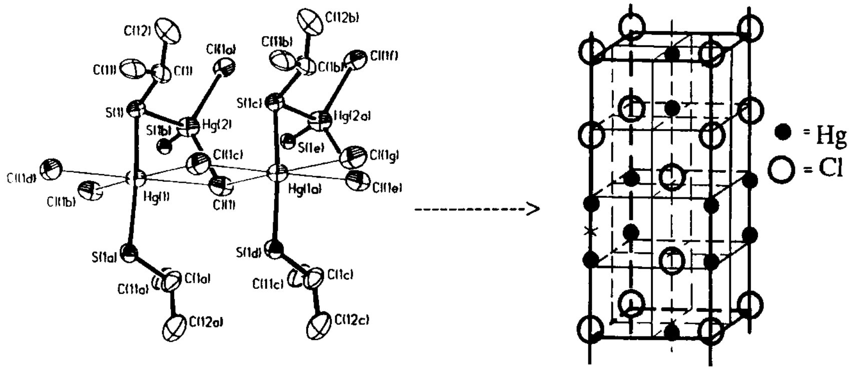


FIGURE 1 ORTEP representation of one segment of the extended two-dimensional chain structure of [*i*-PrSHgCl]$_n$

Drawing of the unit cell of Hg_2Cl_2[15]

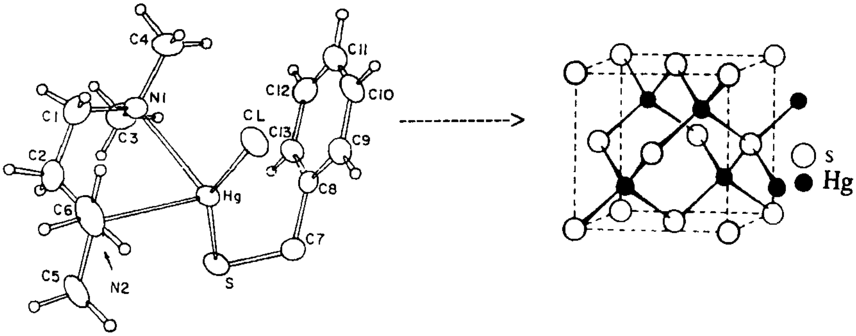
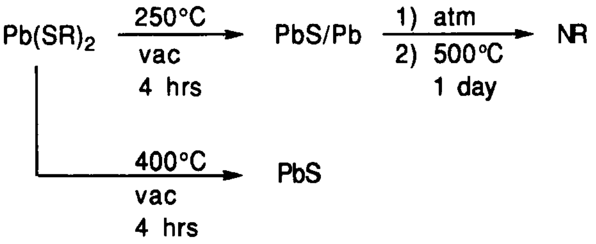


FIGURE 2 ORTEP representation of the molecular structure of BzSHgCl·TMEDA

Drawing of the unit cell of black HgS (Metacinnabar)[16]



SCHEME 1 Decomposition pathway observed for lead *bis*(butylthiolate) compounds

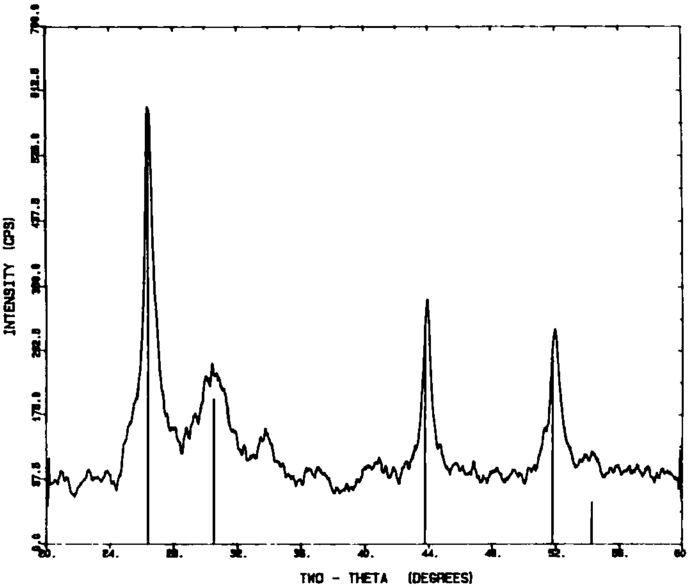


Figure 3 XRPD pattern of HgS (Metacinnabar) obtained from the reaction of $HgCl_2$ and Ph_3CSH (ethanol, ambient conditions, 1 day)

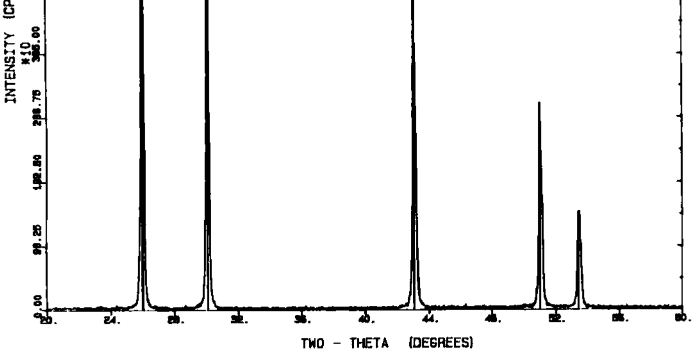


Figure 4 XRPD pattern of PbS obtained from the decomposition of Pb(S*t*Bu)$_2$ (refluxing decalin, 3 days)

between the *neo*pentyl and *iso*propyl derivatives on the one side and the benzyl compound on the other side is the relatively high degree of stability of the benzyl radical when compared to either the *neo*pentyl or *iso*propyl radical. To further investigate if the stability of the radical formed by the organic group present in the precursor influences the decompostion pathway, a chloromercurythiolate compound containing an organic group forming a very stable radical was prepared from the reaction of $HgCl_2$ with triphenylmethylthiol.[15] The reaction initially yields a white solid, presumably $ClHgSCPh_3$. However, this compound decomposes in a matter of minutes at ambient conditions to form mercury sulfide and triphenylmethylchloride, as determined by XRPD (Figure 3) and GC/MS, respectively. This observation supports the assumption that radicals are present during the decompostion of chloromercurythiolate compounds. At this juncture it is not possible to definitively assign a mechanism to this transformation; however, in view of the data available it likely is due to a combination of the influence of the factors of "molecular-solid state" design, coupled with a radical decomposition pathway.

The decomposition of lead *bis*(butylthiolate) compounds, which readily are available from the reaction of lead *bis*(acetate) trihydrate and the appropriate thiol, proceeds at temperatures as low as 190°C and results in the formation of highly crystalline lead sulfide (Figure 4). In general, such preparations result in Galena of exceptionally high purity, as determined by ESCA. However, under certain conditions, small amounts of elemental lead are isolated together with the main product lead sulfide. Apparently, the decomposition mechanism of these compounds involves an equilibrium between the lead *bis*(thiolate) on one hand and elemental lead possessing alkyldisulfide moieties attached to its surface (Scheme 1) on the other. If the alkyldisulfide units are removed from the equilibrium, the conversion to elemental lead becomes irreversible.

CONCLUSIONS

Chloromercurythiolates exhibiting strong Hg-Cl interactions in their molecular structures decompose to form Hg_2Cl_2 while an absence of such interactions encourages the formation of mercury sulfide. The identified compositions of the volatile decomposition products suggest that radicals are present during the decomposition. Although the molecular structures of the precursors seem to influence greatly the final products, the decomposition pathways also appear to be a function of the stability of the radicals produced during the decomposition. By introducing organic groups forming very stable radicals, the decomposition can be directed towards the formation of crystalline mercury sulfide at ambient conditions.

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