

AD-A277 055



94-08226



REPORT DOCUMENTATION PAGE

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OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 08 March 1994		3. REPORT TYPE AND DATES COVERED interim, 1 July 1992 - 1 March 1994	
4. TITLE AND SUBTITLE Group 12 Thiolates: Syntheses, Characterization and Decomposition Pathways				5. FUNDING NUMBERS G: N00014-92-J-1828 R&T PR: 44135035-01	
6. AUTHOR(S) Gertrud Kräuter, Virgil L. Goedken, Bernhard Neumüller, and William S. Rees, Jr.					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) School of Chemistry and Biochemistry and School of Materials Science and Engineering Georgia Institute of Technology Atlanta, Georgia 30332-0400				8. PERFORMING ORGANIZATION REPORT NUMBER TR No. 5	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of the Chief of Naval Research Arlington, Virginia 22217-500				10. SPONSORING / MONITORING AGENCY REPORT NUMBER unknown	
11. SUPPLEMENTARY NOTES Accepted for Publication in: <i>Materials Research Society Proceedings</i> .					
12a. DISTRIBUTION / AVAILABILITY STATEMENT This document has been approved for public release and sale; its distribution is unlimited.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Zinc- and cadmium bis(alkylthiolate) compounds have been prepared and converted into the appropriate binary metal sulfides by thermal treatment. Several mercury chlorothiolates have been synthesized and characterized by single crystal X-ray diffraction. Their decomposition pathways are discussed. The prepared binary metal sulfides have been studied by XRPD and - in selected cases - by particle size determination. The volatile co-products have been isolated and characterized by GC/MS.					
14. SUBJECT TERMS group 12 thiolates, metal sulfides, decomposition pathways				15. NUMBER OF PAGES 10	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL		

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OFFICE OF NAVAL RESEARCH

GRANT N00014-92-J-1820

R&T Code 4135035---01

Technical Report No. 5

Group 12 Thiolates: Synthesis, Characterization and Decomposition Pathways

by

Gertrud Kräuter, Virgil L. Goedken, Bernhard Neumüller, and William S. Rees, Jr.

Accepted for Publication
in

Materials Research Society Proceedings

School of Chemistry and Biochemistry and
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332-0400

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**GROUP 12 THIOLATES: SYNTHESSES, CHARACTERIZATION
AND DECOMPOSITION PATHWAYS**

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SUBMITTED FOR PUBLICATION IN

MATERIALS RESEARCH SOCIETY PROCEEDINGS

FALL MEETING 1993

BOSTON, MA

MANUSCRIPT NUMBER: N 4.7

GROUP 12 THIOLATES: SYNTHESSES, CHARACTERIZATION AND DECOMPOSITION PATHWAYS

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ABSTRACT

Zinc- and cadmium *bis*(alkylthiolate) compounds have been prepared and converted into the appropriate binary metal sulfides by thermal treatment. Several mercury chlorothiolates have been synthesized and characterized by single crystal X-ray diffraction. Their decomposition pathways are discussed. The prepared binary metal sulfides have been studied by XRPD and - in selected cases - by particle size determination. The volatile co-products have been isolated and characterized by GC/MS.

BACKGROUND

Group 12 element sulfides show interesting electrical and optical properties. Zinc sulfide is a piezoelectric material, undergoing distortion of the crystallographic tetrahedron upon application of a shearing stress. Cadmium sulfide is highly photosensitive and is employed widely in photoconducting cells. The conventional method for the preparation of binary group 12 sulfides involves the decomposition of two-component mixtures of volatile organometallic precursors, typically metal alkyls and H₂S. Although the use of unimolecular precursors, containing both the metal and non-metal in one compound, offers obvious advantages compared with multiple source processing,[1] only a few single source precursors to 12 - 16 electronic materials have been reported to date.[2-6] Metal thiolates are promising precursors to metal sulfides, as that they are readily available for many metals [7] and may decompose to potentially form metal sulfides upon heating.[10-13]

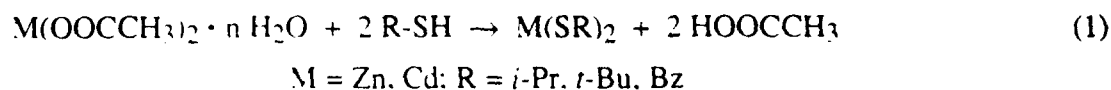
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We have studied the decomposition pathways of zinc- and cadmium *bis*(alkylthiolate) compounds and mercury chlorothiolate and have isolated and characterized the binary metal sulfides thermolytically produced as well as the volatile co-products of the preparation of MS.

RESULTS AND DISCUSSION

Zinc- and cadmium *bis*(alkyl) thiolate compounds are available readily by the reaction of the appropriate metal acetate with the desired thiol in ethanol (equation 1).



These compounds decompose when heated to a temperature of about 200°C. The weight loss determined by thermogravimetric analysis corresponds to the formation of metal sulfide (Table I).

Table I. Thermogravimetric analyses of zinc- and cadmium *bis*(thiolate) compounds

Compound	Weight Residue	
	Observed	Calculated
Zn(<i>Si</i> -Pr) ₂	46.8%	45.2%
Zn(<i>St</i> -Bu) ₂	42.4%	40.0%
Cd(<i>Si</i> -Pr) ₂	55.5%	54.9%
Cd(<i>St</i> -Bu) ₂	49.2%	49.6%
Cd(SBz) ₂	40.5%	40.2%

The decomposition of zinc- and cadmium *bis*(thiolate) compounds in the solid state at 250°C under vacuum affords cubic zinc sulfide (Sphalerite) and hexagonal cadmium sulfide (Greenockite). Surprisingly, the rather uncommon cubic phase of cadmium sulfide (Hawleyite) is formed during the decomposition of Cd(SBz)₂. The *t*-butyl derivatives can be converted into metal sulfides at temperatures as low as 190°C. This was achieved by heating a suspension of Zn(*St*-Bu)₂ or Cd(*St*-Bu)₂ in boiling decalin. The XRPD pattern of the obtained metal sulfides (Figures 1 and 2) resemble those of the metal sulfides obtained by the solid state decomposition.

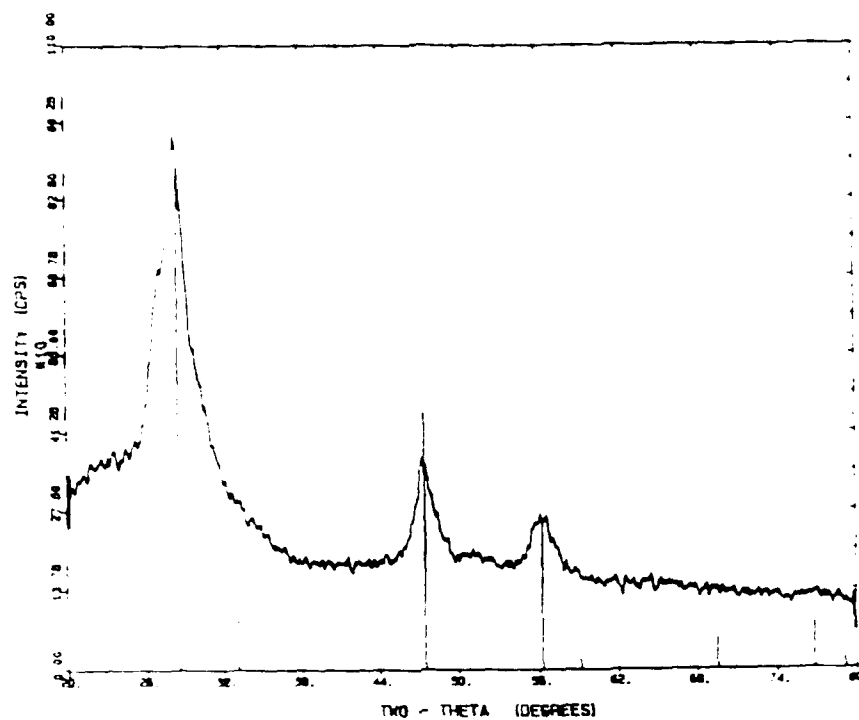


Figure 1. XRPD pattern of ZnS obtained by the decomposition of $\text{Zn}(\text{SrBu})_2$ in decalin (190°C, 3d)

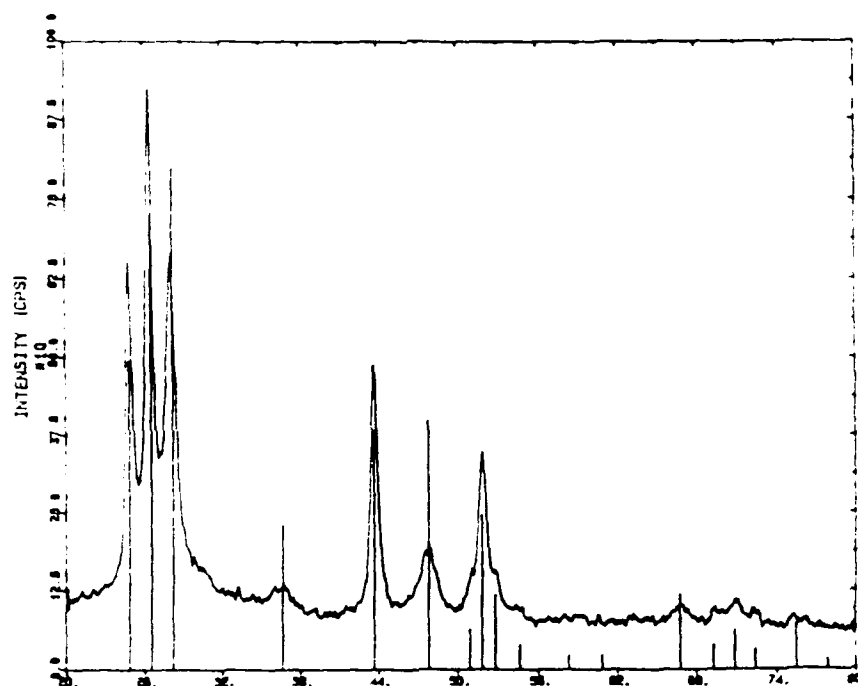


Figure 2. XRPD pattern of CdS obtained by the decomposition of $\text{Cd}(\text{SrBu})_2$ in decalin (190°C, 3d)

The size of the formed metal sulfide particles was determined. The zinc sulfide particles were found to have an average diameter of 0.74μ (Figure 3), while the cadmium sulfide particles displayed an average size of 0.90μ .

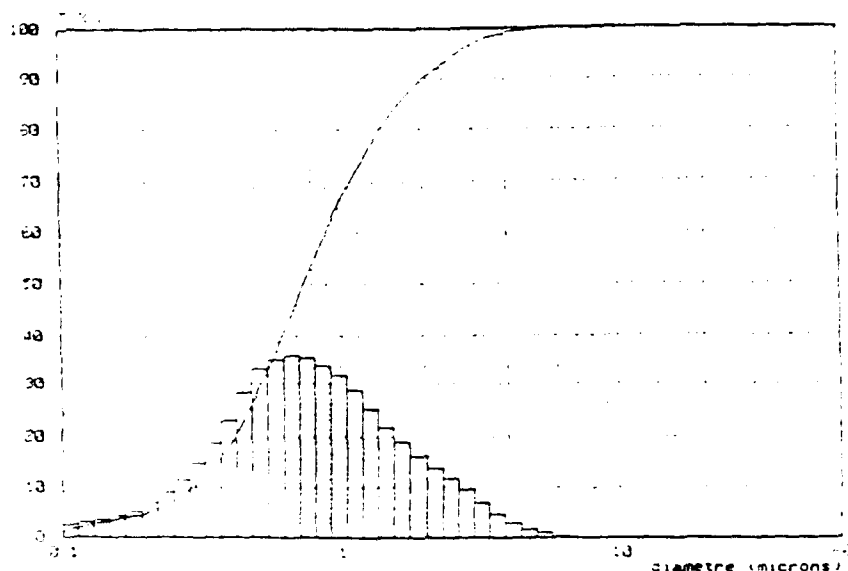
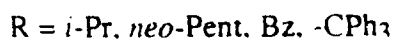
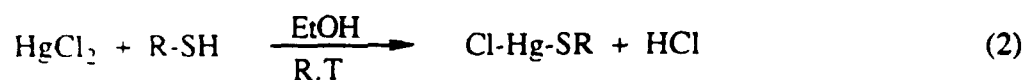


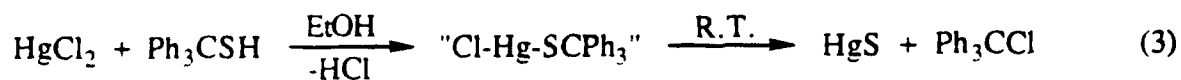
Figure 3. Particle size distribution in ZnS obtained by the decomposition of $\text{Zn}(\text{S}t\text{Bu})_2$ in decalin

Mercury chlorothiolate compound can be obtained by the reaction of mercury dichloride and the appropriate thiol in ethanol (equation 2).



While the *i*-Pr-, *neo*-Pent- and Bz- derivatives have been isolated and characterized by single crystal X-ray diffraction, the triphenylmethyl derivative is not stable and decomposes in a periode of minutes to form a black precipitate. The XRPD pattern of the black solid is discussed elsewhere.[10]

The decomposition affords crystalline mercury sulfide (Metacinnabar) at room temperature (equation 3). This is surprising, considering that usually temperatures of several hundred degrees are required to obtain crystalline metal sulfides. The co-product of the reaction is triphenylmethylchloride as determined by GC/MS.



Temperatures of about 200°C are required to thermally degrade Cl-Hg-SR (R = *i*-Pr, *t*-Bu, Bz). Only the benzyl derivative forms the desired mercury sulfide, as determined by XRPD (Figure 4), while the *i*-propyl- and *t*-butyl derivatives decompose to form mercury(I) chloride.

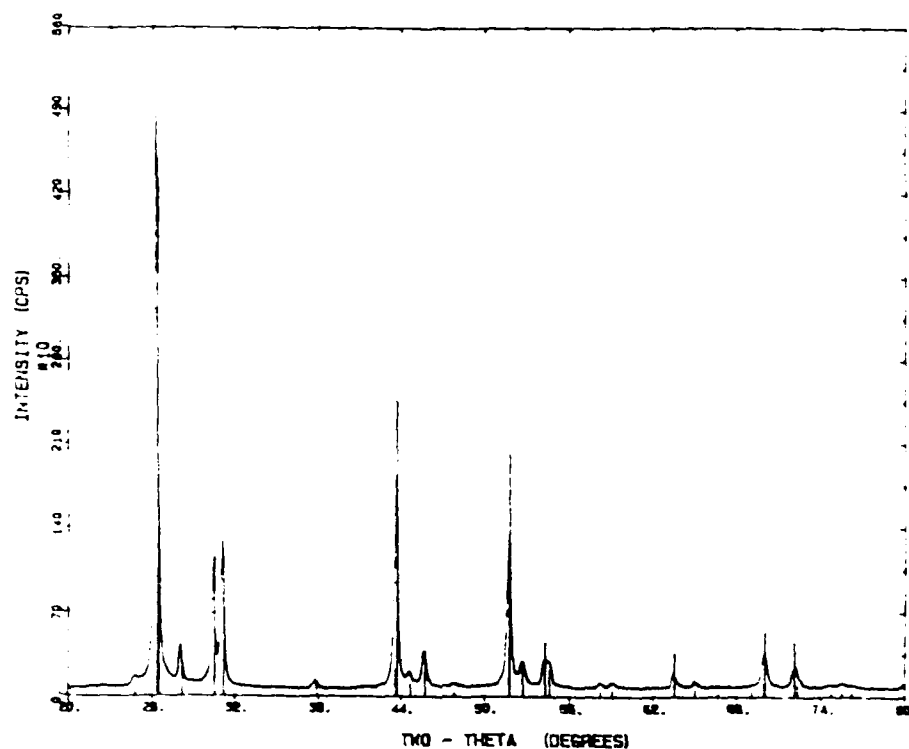


Figure 4. XRPD pattern of HgS obtained by the decomposition of ClHgSBz (200°C, 2h)

The solid state structures of Cl-Hg-Si-Pr [8,9,12] and Cl-Hg-SBz · TMEDA [9,12] have been described elsewhere. The *neo*-pentyl derivative crystallizes from pyridine as a pyridine adduct and forms a chain-like polymer.

At the present time we attribute the different decomposition behavior of the benzyl- and triphenylmethyl compound compared with that of the *i*-propyl- and *neo*-pentyl derivative to the different stability of the radicals of the alkyl groups present in the prepared compounds. Apparently, only compounds containing organic groups which form relatively stable radicals form the desired mercury sulfide.

SUMMARY

Zinc- and cadmium *bis*(alkylthiolate) compounds can be converted into metal sulfides at temperatures as low as 190°C. The binary metal sulfides produced are highly crystalline materials of relatively uniform particle size distribution. Mercury chlorothiolate compounds decompose to form mercury sulfide if they contain organic groups which form stable radicals, otherwise, the

observation of Hg_2Cl_2 is found.

Mercury chlorotriphenylthiolate, having the potential to form the most stable radical among the presently prepared compounds, is instable at ambient temperature and is converted into crystalline mercury sulfide at 25°C.

ACKNOWLEDGEMENTS

We gratefully acknowledge Mr. Michael Carris for assistance with TGA measurements and Dr. Gerard Mignani (Rhône-Poulenc, France) for particle size determinations. Financial support was provided by the Deutsche Forschungsgemeinschaft (postdoctoral fellowship to G. K.) and the Office of Naval Research Chemistry Division.

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