

Formation of ZnS and CdS by Thermolysis of Homoleptic Thiolato Compounds $[M(SMe)_2]_n$ ($M = Zn, Cd$)

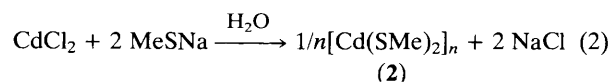
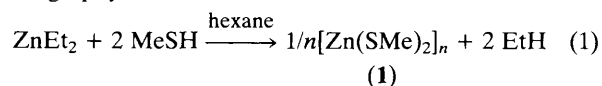
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Thermolysis of the Zn and Cd thiolato compounds $[M(SMe)_2]_n$ ($M = Zn, Cd$) gave the metal sulphide, MS, with evolution of MeSMe.

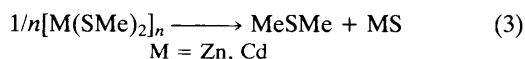
It is known that thiolato groups co-ordinated to transition metals will undergo desulphurization promoted by the metal centre.¹⁻³ Recently we reported that thermolysis of nickel thiolato complexes with auxiliary ligands, $Ni(SPh)_2L_2$ ($L = PEt_3, 2,2'$ -bipyridyl), gave PhSPh through desulphurization of a thiolato ligand.⁴ Analogous reaction of homoleptic thiolato compounds of bivalent metal centres, $M(SR)_2$, was thus expected to give metal sulphide, MS, accompanied by evolution of RSR, and we have attempted to apply this reaction to the preparation of metal sulphides, which are often utilized as electric and photoelectric materials. Recently it was reported that ZnS was formed *in situ* by u.v. irradiation of the tetrabutylammonium salt of bis(*cis*-1,2-dicyanoethylene-1,2-dithiolato)zinc, although the reaction details are not clear.⁵ In this paper we report that thermolysis of $[Zn(SMe)_2]_n$ (**1**) and $[Cd(SMe)_2]_n$ (**2**), which are known compounds⁶ whose properties have not been studied, cleanly gives ZnS and CdS, respectively, with evolution of MeSMe.

Compounds (**1**) and (**2**) were prepared by reactions (1) and (2),⁷ and gave satisfactory elemental analyses (C, H, Zn, Cd). Both compounds are insoluble in common organic solvents, probably owing to their polymeric structures with bridged thiolato ligands similar to $[Zn(SPh)_2]_n$ (**3**) and $[Cd(SPh)_2]_n$ (**4**), the structures of which have been established by X-ray crystallography.⁸



Heating of (**1**) and (**2**) at 260–280 °C under vacuum or under argon atmosphere gives quantitative yields of MeSMe, identified by g.c.–mass spectroscopy and ¹H n.m.r. spectro-

scopy. No other organic compounds such as CH_4 , C_2H_6 , MeSH , or MeSSMe are found in the reaction mixture. Residual solid materials in the reaction mixtures are almost free from C and H, and give satisfactory analytical values for Zn and Cd as bivalent sulphides. X-Ray diffraction patterns of the solids agree well with those of β -ZnS and CdS, respectively. These observations indicate that the thiolato compounds (1) and (2) undergo thermal degradation represented by reaction (3). Thermogravimetric analyses of (1) and (2)



also indicate weight loss corresponding to evolution of MeSMe from $\text{M}(\text{SMe})_2$ in the vicinity of 230 to 270 °C. Evolution of MeSMe from (1) and (2) at constant temperature is followed by a change of weight of the compound to reveal that the thermolysis obeys first-order kinetics. The activation energies of thermolysis of (1) and (2) were determined as 143.0 and 190.8 kJ mol^{-1} , respectively, from Arrhenius plots.

Mixed metal sulphides $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ ($x = 0.25, 0.52, 0.78$) were similarly obtained by thermolysis of $[\text{Cd}_x\text{Zn}_{1-x}(\text{SMe})_2]_n$, prepared by the reaction of an aqueous solution containing both ZnCl_2 and CdCl_2 with MeSNa. The X-ray diffraction pattern of the $\text{Cd}_{0.52}\text{Zn}_{0.48}\text{S}$ thus obtained shows new peaks at the positions between those due to β -ZnS and β -CdS, and shows no peaks due to ZnS and CdS, indicating that the solid obtained is a mixed sulphide rather than a physical mixture of ZnS and CdS.

Thermolysis of the benzenethiolato compounds (3) and (4),

prepared similarly to the methyl derivatives, gave solids showing appropriate X-ray diffraction patterns for β -ZnS and CdS, respectively. As these benzenethiolato compounds dissolve in acetone and *N,N*-dimethylformamide to some extent, their thermolysis may provide a new method for the preparation of thin films of ZnS and CdS.

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