

Syntheses of Ni_3S_2 , Co_9S_8 , and ZnS by the Decomposition of Diethyldithiocarbamate Complexes

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Received March 23, 1992; accepted April 20, 1992

Three useful sulfides, Ni_3S_2 , Co_9S_8 , and ZnS , have been prepared by the decomposition of their respective diethyldithiocarbamate complexes. The products were characterized by X-ray diffraction analysis, crystallite size determination, and magnetic susceptibility measurements. The problems associated with organometallic precursors for the synthesis of metal sulfides are discussed and the method is compared with the direct conversion of sulfate salts to sulfides in a controlled $\text{H}_2/\text{H}_2\text{S}$ environment. © 1992 Academic Press, Inc.

Introduction

The preparation of metal sulfides from organometallic precursors is an attractive and relatively new technique. It is advantageous to use precursors which have preformed metal–sulfur bonds and whose decomposition by-products are volatile. However, the presence of undesirable carbon impurities is difficult to avoid (*1*).

The sulfides of nickel and cobalt are of interest as promoters of hydrodesulfurization catalysts. Zinc sulfide has many uses because of its optical and electronic properties. The traditional method used to prepare ZnS , Ni_3S_2 , and Co_9S_8 involves the direct combination of the elements in sealed, evacuated silica tubes. In order to achieve complete reaction, long periods of heating are required. The preparative procedures are tedious and the products may appear to be single-phase as determined by X-ray analy-

sis and yet not be pure enough for certain applications.

D. M. Pasquariello *et al.* (*2*) have reported the preparation of Co_9S_8 and Ni_3S_2 by heating anhydrous sulfates in a stream of $\text{H}_2/\text{H}_2\text{S}$. In this study, the procedure has been applied to the synthesis of hexagonal ZnS from the sulfate salt. In addition, ZnS , Ni_3S_2 , and Co_9S_8 have been prepared by the decomposition of their respective diethyldithiocarbamate complexes. A comparison is made between the purity of these products with those obtained from the sulfates.

Experimental

Preparation of ZnS from $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

Zinc sulfide was prepared by heating predried zinc sulfate in a vertical reactor according to the following procedure: the zinc sulfate was first predried for 4 hr at 135°C . The dried product was then placed into a

silica reactor tube and the entire system purged with argon. The temperature of the reactor was raised from room temperature to 250°C at a rate of 15°/min and maintained at that temperature for 1 hr. The gas was then changed from argon to a H₂/H₂S mixture (250 : 1) and the temperature was raised to 660°C at a rate of 15°/min. This temperature was maintained for 4 hr; the gas was changed to pure H₂S and the temperature maintained for an additional 4 hr at 660°C. The reactor tube was removed from the furnace and rapidly quenched to room temperature. The system was then purged with argon and the product removed. Annealing of the ZnS was carried out in a sealed, evacuated silica tube for 1 hr at 750, 850, 950, 1050, and finally 1075°C. The sealed tubes were air-quenched to room temperature after each annealing and the product was X-rayed.

Preparation of the Dithiocarbamates

Diethyldithiocarbamate complexes of nickel(II) and cobalt(III) were prepared by the following procedure: the appropriate amounts of CoSO₄ · 7H₂O and sodium diethyldithiocarbamate trihydrate were dissolved separately in water. Aqueous solutions of cobalt(II) were oxidized to cobalt(III) during the reactions with aqueous (C₂H₅)₂NCS₂Na · 3H₂O (3), producing a green product, Co(Et₂dtc)₃. The solution was filtered and the green precipitate was dried at 110°C overnight. The dried precipitate was Soxhlet extracted with methylene chloride and then hexane was added to the solution. A deep green product, Co(Et₂dtc)₃, was crystallized slowly at 5°C.

The preparation of Ni(Et₂dtc)₂ was similar to that of Co(Et₂dtc)₃. However, aqueous solutions of nickel(II) are stable toward oxidation when mixed with an aqueous solution of sodium diethyldithiocarbamate. The green product corresponded to the composition Ni(Et₂dtc)₂. Zn(Et₂dtc)₂ was purchased from Aldrich Chemical Co. and was recryst-

tallized at 5°C from a 9 : 1 toluene : hexane solution before using.

Preparation of Ni₃S_{2.04}, Co₉S_{8.3}, and ZnS from Ni(Et₂dtc)₂, Co(Et₂dtc)₃, and Zn(Et₂dtc)₂

Ni(Et₂dtc)₂ was placed in the reactor tube and the system was purged with pure H₂S and heated at a rate of 1.33°C/min from room temperature to 200°C. The temperature was maintained at 200°C, in an atmosphere of pure H₂S, for 1.5 hr. The desired flow rates for H₂ and H₂S were then adjusted to 125 : 1 and the temperature of the reactor was raised from 200 to 525°C at a rate of 1.33°C/min. This temperature was maintained for 3 hr in order to ensure complete reaction. The reactor tube was then removed from the furnace and the sample rapidly quenched to room temperature. The system was then purged with argon before removal of the sample. Free sulfur was extracted from the product with CS₂ in a Soxhlet extractor. The procedures for the preparation of Co₉S_{8.3} and ZnS are similar to that for Ni₃S_{2.04}.

Characterization of Samples

X-ray powder diffraction patterns of the samples were obtained using a Philips diffractometer with monochromated high intensity CuKα₁ radiation (λ = 1.5405 Å). For qualitative phase identification, diffraction patterns were taken over the range 12° < 2θ < 72° with a scan rate of 1° 2θ/min, while cell parameters were determined from scans taken at 0.25° 2θ/min. Precise lattice parameters were obtained from the diffraction peaks using a least-squares refinement program which corrects for the systematic errors of the diffractometer.

The crystallite sizes were determined by the Scherrer method, and a shape factor of 0.9 was applied (4). A computer program was used to digitize the selected X-ray peaks (slow scan, 0.25° 2θ/min) and determine their widths.

TABLE I
 CONDITIONS FOR THE PREPARATION OF Ni₃S_{2.04}, Co₉S_{8.3}, AND ZnS FROM
 THE DIETHYLDITHIOCARBAMATES

Compound	Source	Conditions
Ni ₃ S _{2.04}	Ni(Et ₂ dtc) ₂	(a) R.T. → 200°C in pure H ₂ S ^a
		(b) 1.5 hr 200°C in pure H ₂ S
		(c) H ₂ /H ₂ S 125 : 1; 200 → 525°C; 3 hr 525°C
		(d) Quench
Co ₉ S _{8.3}	Co(Et ₂ dtc) ₃	(a) R.T. → 250°C in pure H ₂ S
		(b) 3 hr 250°C in pure H ₂ S
		(c) H ₂ /H ₂ S 350 : 1; 250 → 600°C; 3 hr 600°C
		(d) Quench
ZnS	Zn(Et ₂ dtc) ₂	(a) R.T. → 165°C in pure H ₂ S
		(b) 3 hr 165°C in pure H ₂ S
		(c) H ₂ /H ₂ S 125 : 1; 165 → 650°C; 3 hr 650°C
		(d) Quench

^a Temperature increases were always made at 1.33°C/min.

The thermogravimetric analyses were performed with a Cahn electrobalance (Model RG). Each sulfide was first heated in a stream of oxygen to 800°C and then reduced to the metal in a stream of 85% Ar/15% H₂. Magnetic data were obtained at liquid nitrogen and room temperature with a Faraday balance equipped with a Cahn electrobalance (Model RG). Measurements were performed at field strengths between 6.2 and 10.4 kOe. The core diamagnetic correction was not applied to these measurements because of the large uncertainty in the magnitude of the correction relative to the susceptibility of the materials studied.

Results and Discussion

Polycrystalline samples of ZnS, Ni₃S₂, and Co₉S₈ were prepared by the decomposition of the corresponding diethyldithiocarbamate complexes. The conditions for the preparation of these sulfides are summarized in Table I. The dithiocarbamates are well-known coordination complexes (5) and are easily prepared. They decompose in a hydrogen sulfide atmosphere below their melting points. Further heating in an atmo-

sphere of H₂/H₂S in the range of 400–650°C produces metal sulfide phases which correspond to those obtained by direct combination of the elements at higher temperatures.

This study has confirmed the earlier work of Pasquariello *et al.* (2) on the preparation of Ni₃S₂ and Co₉S₈ by heating their sulfates in a stream of H₂/H₂S. When zinc sulfate is heated in an atmosphere of H₂/H₂S at 660°C, there was a substantial conversion to a mixture of cubic and hexagonal ZnS. Continued treatment of the product at 660°C in pure H₂S resulted in complete conversion of the sulfate to a mixture of the sulfides. Complete conversion to hexagonal ZnS occurred when the product was heated in a sealed, evacuated silica tube at 1075°C for 1 hr. The three sulfides, ZnS, Ni₃S₂, and Co₉S₈, were also obtained by decomposing the diethyldithiocarbamate complexes. The decomposition proceeds in a complex manner and carbon is an undesired impurity in the final products. However, X-ray analysis of these sulfides indicate the formation of single-phase materials. The presence of carbon in the hexagonal ZnS was verified by its dark gray color. In contrast, the hexagonal ZnS prepared by conversion of the sulfate was pale yellow.

TABLE II
CHARACTERIZATION OF ZnS, Ni₃S₂, AND Co₉S₈

Compound source	Cell parameters	Crystallite size (Å)	% metal	
			Obsd	Calcd
ZnS (ZnSO ₄ · 7H ₂ O)	<i>a</i> = 3.817(3) <i>c</i> = 6.256(4)	160	—	—
ZnS(Zn(Et ₂ dte) ₂)	<i>a</i> = 3.821(1) <i>c</i> = 6.262(2)	87	—	—
Ni ₃ S _{2,02} (NiSO ₄ · 6H ₂ O)	<i>a</i> = 5.745(4) <i>c</i> = 7.138(1)	395	73.1	73.3
Ni ₃ S _{2,04} (Ni(Et ₂ dte) ₂)	<i>a</i> = 5.746(5) <i>c</i> = 7.138(1)	345	72.9	73.3
Co ₉ S _{8,2} (CoSO ₄ · 7H ₂ O)	<i>a</i> = 9.922(10)	300	66.9	67.4
Co ₉ S _{8,3} (Co(Et ₂ dte) ₃)	<i>a</i> = 9.921(11)	263	66.5	67.4

Cell parameters, crystallite sizes, and percentage metal analysis for ZnS, Ni₃S₂, and Co₉S₈ are given in Table II. The sulfides prepared from both sources have similar cell parameters, but the crystallite sizes of the sulfides from the sulfates were larger than those from the dithiocarbamate complexes.

Magnetic susceptibility measurements for the nickel and cobalt sulfides gave values of 1.04×10^{-6} emu/g for Ni₃S_{2,04} and 2.1×10^{-6} emu/g for Co₉S_{8,3}. These results were independent of both field and temperature and indicate Pauli paramagnetic behavior as well as the absence of ferromagnetic impurities.

Conclusions

Ni₃S₂, Co₉S₈, and ZnS have been prepared by the decomposition of their diethyldithiocarbamate complexes. They have been characterized by X-ray crystallography and magnetic susceptibility measurements. This

preparative technique has been compared to the conversion of the sulfate salts to the sulfide in a H₂/H₂S atmosphere. Whereas decomposition of the dithiocarbamates results in single-phase products as determined by X-ray diffraction, the problem of undesirable carbon impurity has yet to be resolved.

Acknowledgments

This research was supported by the National Science Foundation Contract No. DMR 9016302.

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