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Synthesis of *d* Transition Metal Sulfides from Amorphous Dithiooxamide Complexes

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Sulfides of six transition or post-transition metals have been prepared by decomposition of amorphous dithiooxamide complexes. The best procedure of pyrolysis corresponds to a heating at 680°C under a dynamic vacuum during 4 hr. This preparation, without any added sulfurizing atmosphere, leads to carbon-free sulfides.

INTRODUCTION

Sulfides of many transition or post-transition metals show interesting electrical and optical properties such as semiconductivity or photoconductivity (1). Particularly, zinc sulfide is an interesting infrared optical material and cadmium sulfide can be used for photoresists and solar cells (2, 3). Sulfides of nickel and cobalt can be used in hydrodesulfurization processes. A wide variety of techniques, including precipitation at room temperature, electrolysis of thiosulfate solution, gas-phase reaction with H_2S, and solid-state reactions, have been used for the preparation of these sulfides (4–6).

Thermal degradation of metal complexes with sulfur-containing ligands seems to be an attractive method. Several works have been reported with thiolato (7–9), dithiocarbamato (10), and thiourea complexes (6, 11). But these syntheses are made in a stream of H_2S or H_2/H_2S. On the contrary, dithiooxamide complexes have been reported to give sulfides, without any added sulfurizing atmosphere, in the case of nickel and cadmium (12); however, this paper gave no details on the phase purity.

Continuing our interest in the structural chemistry of dithiooxamide complexes (13–15), we have studied the thermal behavior of several 3*d* transition metal and cadmium complexes in order to optimize the preparation of the corresponding sulfides.

EXPERIMENTAL

General Procedures

The following reagents were used as received: metal acetates (Aldrich), dithiooxamide (Aldrich), methanol (Aldrich, 99.8%), and ammonium hydroxide solution (Prolabo).

Pyrolysis experiments were conducted within a Thermolyne type 21100 tube furnace. Samples were placed in an alumina boat, inside a quartz tube which can be connected to a vacuum pump. Elemental analyses were carried out at Laboratoire Central de Microanalyse du CNRS (Lyon, France). XRD patterns were obtained on a Seifert XRD3000 diffractometer using Cu$K\alpha$ radiation over the range $5 < 2\theta < 120°$ with a scan rate of 1° 2θ/min. Scanning electron microscopy (SEM) micrographs were obtained on a Cambridge 250MK3 instrument.

Preparation of the Dithiooxamide Complexes

Two solutions of dithiooxamide and metal acetate in methanol (10^{-3} mol in 100 ml in both cases) were prepared. The dithiooxamide solution was slowly added to the metal salt solution under stirring. Twenty-five ml of ammonium hydroxide solution was added in order to get a complete precipitation of the complex. Ammonium hydroxide was preferred to alkali hydroxide to avoid the presence of alkali ions in the final product. Stirring was continued for 2 hr. The precipitate was then collected by filtration, washed with methanol and distilled water, and dried at 50°C.

Other metal salts, like nitrate or chloride, were tested. But, in all cases as previously shown (13), the precipitation was not complete.

Pyrolysis of the Dithiooxamide Complexes

Two procedures of pyrolysis were tested : at 480°C in air or at a temperature between 480 and 680°C under a dynamic vacuum. In both cases, the heating rate was 8°/min and the product was held at the final temperature for

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TABLE 1

Elemental Analysis of Dithiooxamide Complexes

Complexes	*M*	S	N	C	H
Mn exp./calc. for	21.6	35.0	13.4	12.6	1.7
$MnL_{1.4}(H_2O)_{2.5}$	20.7	33.8	14.4	12.7	2.6
Co exp./calc. for	20.3	29.9	14.6	14.0	3.5
$CoL_{1.4}(H_2O)_{3.75}$	20.2	30.7	13.4	11.5	3.9
Ni exp./calc. for	29.4	30.9	13.4	12.3	2.2
$NiL(H_2O)_{1.5}$	28.8	31.4	13.7	11.8	2.4
Cu exp./calc. for	31.6	30.8	13.5	12.2	2.1
$CuL(H_2O)_{1.25}$	31.1	31.4	13.7	11.8	2.2
Zn exp./calc. for	34.6	34.2	14.4	15.8	1.7
Zn*L*	35.6	34.9	15.3	13.1	1.1
Cd exp./calc. for	40.6	29.3	12.2	11.7	1.5
$Cd_4L_5(H_2O)_{3.2}$	40.9	29.2	12.8	10.9	1.6

Note. exp. values on first line and calc. values on second line for each metal atom.

4 hr. The as-prepared sulfide was then air-quenched to room temperature.

RESULTS AND DISCUSSION

Table 1 gives the results of elemental analysis obtained for the dithiooxamide complexes. Although the starting ligand/metal ratio is always equal to one, this ratio is only kept in the final product for nickel, copper, and zinc. In all other cases, the ratio is greater. It means that, for nickel, copper, and zinc, the precipitation is complete and the amorphous solids are formed with infinite ---*M-L-M*--- ribbons. This structural feature was proved by large angle x-ray scattering studies (15). For the cadmium complex, the ratio is coherent with a M_4L_5 formula corresponding to the presence of finite oligomers in the amorphous solid. The same conclusion can be drawn for cobalt and manganese. However, the ligand/metal ratio is equal to 1.4; this value can be explained by a mixture of oligomers with different lengths. These mean raw formulae are fully reproducible.

TABLE 2

Sulfide Compounds Obtained with the Two Pyrolysis Procedures

Starting complexes	1st procedure (Air–480°C–4H)	2nd procedure (Vacuum–680°C–4H)
$MnL_{1.4}(H_2O)_{2.5}$	Mixture	MnS + amorphous oxides
$CoL_{1.4}(H_2O)_{3.75}$	CoS_2 + β-$CoS_{1.097}$	Co_9S_8 (94%) + $CoS_{1.097}$ (6%)
$NiL(H_2O)_{1.5}$	NiS_2	Ni_3S_2 (88%) + α-Ni_7S_6 (12%)
$CuL(H_2O)_{1.25}$	CuO + $CuSO_4$	$Cu_{1.96}S$ + β-Cu_2S
Zn*L*	Cubic ZnS	Hexagonal (+cubic) ZnS
$Cd_4L_5(H_2O)_{3.2}$	Cubic CdS	Hexagonal CdS
$Cd_4L_5(H_2O)_{3.2}$ + Zn*L*	Cubic $Cd_{0.57}Zn_{0.43}S$	Hexagonal $Cd_{0.38}Zn_{0.62}S$

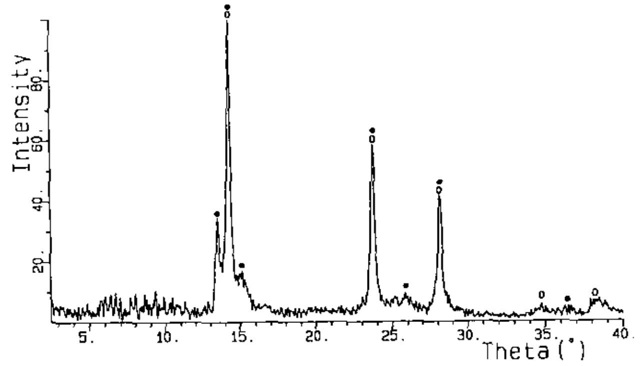

FIG. 1. XRD pattern for ZnS obtained with the vacuum procedure. ○, cubic form (JCPDS file 5-566); ● hexagonal form (JCPDS file 36-1450).

First attempts of pyrolysis were done in air. TG curves show a rather continuous loss of weight which ends at a temperature ranging from 360°C for copper to 560°C for cadmium. The weight loss is not large enough to correspond to the formation of pure sulfides. But it is not possible to proceed at higher temperatures because of oxidation phenomena leading to carbonates or sulfates and eventually oxides. So, the first pyrolysis procedure was the following : 480°C in air for 4 hr. As-prepared products were characterized by elemental analysis and XRD. A pure crystallized sulfide is obtained for Ni, Zn, and Cd, and a mixture of phases is obtained for Mn, Cu, and Co (Table 2). But in all cases, the powder contains a rather great amount (10–15%) of residual organics.

To improve the preparation, we tried the same procedure under a dynamic vacuum at 480°C. The powders still contain a small percentage of organics. It is necessary to increase the temperature to 680°C to prepare carbon-free products. Powders have been characterized by elemental analysis and XRD spectra. Results are gathered in Table 2. The carbon percentage is always lower than 0.5.

For cadmium and zinc, a pure monosulfide is always obtained. But the pyrolysis procedure has a strong effect on the crystalline species : cubic at low temperature in air, hexagonal at higher temperature under vacuum. However, the transformation is not complete for ZnS (Fig. 1). In all cases for ZnS and CdS, powders present a narrow distribution of crystallite size with a mean value around 200 nm (Fig. 2). Solid solutions $Cd_{1-x}Zn_xS$ can also be prepared starting from a mixture of complexes, but it seems difficult to control the stoichiometry because of the sublimation of the cadmium complex.

In the case of manganese, the air procedure leads to a mixture of crystalline and amorphous phases. With the vacuum procedure, amorphous oxides are still formed together with MnS. For copper, sulfides are only prepared with the vacuum procedure which results in a mix-

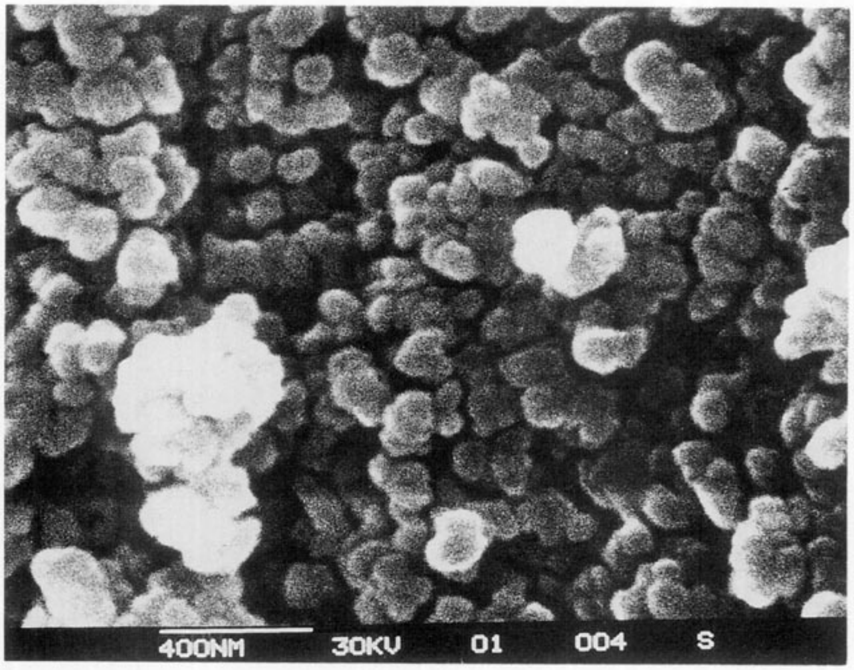

FIG. 2. SEM micrographs of ZnS powder.

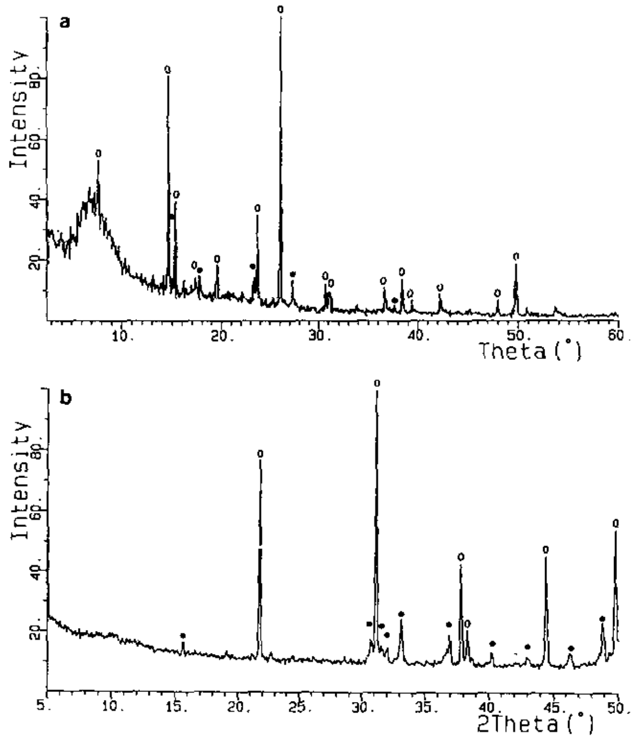

FIG. 3. XRD patterns for cobalt and nickel sulfides. (a) ○, Co_9S_8 (JCPDS file 19-364); ● β-$CoS_{1.097}$ (JCPDS file 19-366). (b) ○, Ni_3S_2 (JCPDS file 30-863); ●, α-Ni_7S_6 (JCPDS file 24-1021).

ture of large crystals of $Cu_{1.96}S$ and ill-crystallized powder of β-Cu_2S.

For cobalt and nickel, crystallized sulfides can be prepared with both procedures : sulfur-rich phases with the air procedure and metal-rich phases with the vacuum procedure. However, the high temperature products are not pure phases but mixtures of two sulfides with slightly different stoichiometry (Fig. 3). In the case of cobalt sulfides, SEM micrographs show crystallites with a mean size of 0.5 μm (Fig. 4).

CONCLUSIONS

Sulfides of manganese, cobalt, nickel, copper, zinc, and cadmium have been successfully prepared, free of residual organics, by pyrolysis of amorphous complexes of the ligand dithiooxamide. These precursors are very easy to prepare and are stable. The pyrolysis procedure did not necessitate any sulfur-enriched atmosphere. Powders have been characterized by elemental analysis and XRD spectra. They are free of residual organics. The decomposition procedure has a marked effect on the stoichiometry and the crystalline form of the sulfides prepared.

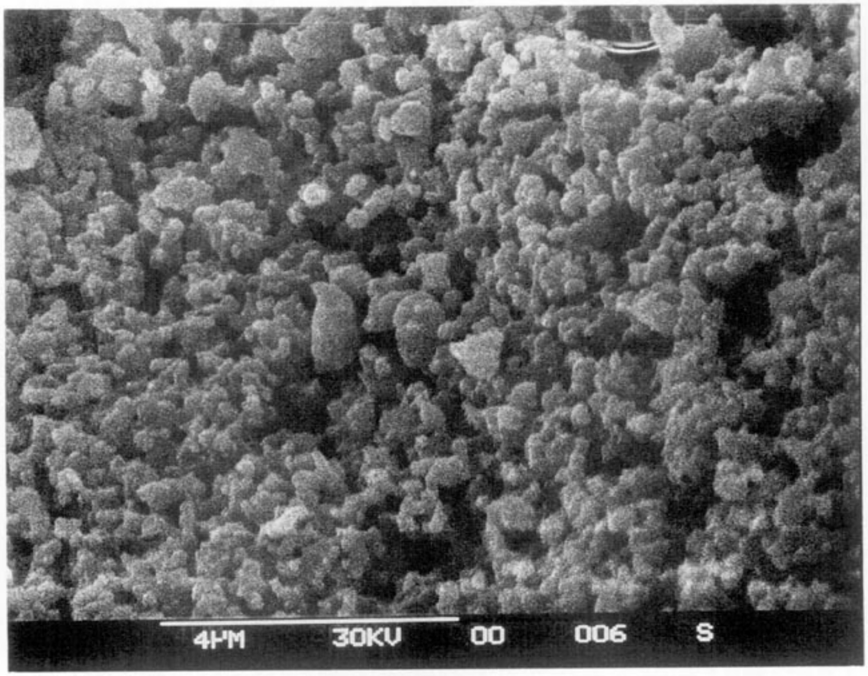

FIG. 4. SEM micrographs of cobalt sulfide.

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