# Synthesis Andcharacterization of Zinc Sulfide and Zinc-Iron Sulfide Nanoparticles from Zinc (II) Dithiocarbamate Complexes

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#### ABSTRACT

Bis(N-(pyrrol-2-ylmethyl)-N-(2-phenylethyl)dithiocarbamato-S, S') zinc(II) (1) and bis(N-methylferrocenyl-N-

(2-phenylethyl) dithiocarbamato-S, S') zinc(II) (2) have been synthesized and characterized by elemental analysis and spectroscopy (IR and UV-vis). Complexes 1 and 2 have been used as precursors for the preparation of zinc sulfide and zinc-iron sulfide nanoparticles. Morphological characterization of nanoparticles was carried out using TEM.

#### Keywords:

Zinc(II) dithiocarbamate; zinc sulfide; zinc-iron sulfide; nanoparticles; single source precursors

#### 1. Introduction

A wide range of metal-dithiocarbamate complexes is known with examples finding use in applications as diverse as industry, agriculture, medicine and material science <sup>[1-3]</sup>. Metal sulfide nanoparticles have shown vital applications in many fields as an advanced material such as IR detectors <sup>[6]</sup>, photocapacitors for energy conversion and storage <sup>[4]</sup>, sensors <sup>[5]</sup>, photonic materials <sup>[6]</sup> and advanced optoelectronic devices <sup>[7]</sup>. In recent years, transition metal dithiocarbamate complexes have received a great deal of attention because of their importance as single source precursors for the preparation of metal sulfide nanoparticles <sup>[8,9]</sup>. The N-bound organic moieties in dithiocarbamate ligands in metal complexes affect the morphology and size of the metal sulfide nanoparticles <sup>[10,11]</sup>. The photocatalytic activity of the metal sulfide nanoparticles depends on the morphology and size of the nanoparticles <sup>[13]</sup>.

#### 2. Experimental

### 2.1. Materials and techniques

All reagents and solvents were commercially available high-grade materials (Merck/ Sd fine/Sigma Aldrich) and used as received. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer (range:  $4000-400 \text{ cm}^{-1}$ ) as KBr pellets. EM images were recorded using TECNAI T2 G2 make-FEI, respectively. EDS were performed by SUPRA 55VP CARL. Photoluminescence spectra were recorded using Perkin Elmer 1555 fluorescence spectrophotometer at room temperature.

### **2.2. Preparation of complexes**

Bis(N-(pyrrol-2-ylmethyl)-N-(2-phenylethyl) dithiocarbamato-S, S') zinc(II) (1) and bis(N-methylferrocenyl-N-(2-phenylethyl) dithiocarbamato-S, S') zinc(II) (2) were prepared by general methods reported earlier<sup>[9]</sup>.

# 2.3 Preparation of zinc sulfide and zinc-iron sulfide

0.5 g of **2**was mixed in 15 ml triethylenetetra amine in a round bottom flask and then the content of the flask was refluxed for 15 minutes. The black precipitate obtained was filtered off and washed with methanol. Similar procedure was adopted for the preparation of zinc-iron sulfide from **2**.

#### **3.** Results And Discussion

# 3.1 Spectral studies of 1 and 2 3.1.1 IR spectral studies

IR spectra of complexes **1** and **2** show a distinct vibrational band in the region 1439–1499 cm<sup>-1</sup>, which is attributed to the  $v_{C-N}$  vibrations. The band is termediate between the stretching vibrations of the C–N single band at 1250-1350 cm<sup>-1</sup> and C=N band at



spectrum of complex 1 and 2

1640-1690 cm<sup>-1</sup>, suggesting partial double bond character and therefore, partial delocalization of  $\pi$ -electron density within NCS<sub>2</sub> moiety of the dithiocarbamate group. The v<sub>C-S</sub> bands appear around 1025 cm<sup>-1</sup> without any splitting. This is an indication of the bidentate character of the dithiocarbamate ligands.

### 4. characterization of nanoparticles

### 4.1. Powder X-ray diffraction analysis

The phase and structure of the samples were examined by powder X-ray diffraction. Nanoparticles obtained from **1** and **2** are represented as zinc sulfide, zinc-iron sulfide. The powder X-ray diffraction patterns for the nanoparticles are shown in Figs.2. Zinc sulfide displays peaks (Fig. 2.) which can be indexed to single phase rhombohedral with lattice constant comparable to the values of JCPDS file No. 89-2426. The peaks observed in the PXRD pattern of zinc-iron sulfide are due to cubic which are close to the data in JCPDS card No. 65-4384.



Fig.2. Powder X-ray diffraction pattern of zinc sulfide and zinc-iron sulfide

### 4.2. Morphological Characterization

The dimensions and morphologies of zinc sulfide and zinc-iron sulfide were studied by TEM measurements. The TEM images for the three samples are shown in Fig.3.indicates that the zinc sulfide particles are spherical. The average particle diameter as determined from the TEM images is around 40 nm. Nearly spherical zinc-iron sulfide particles can be seen in the TEM image (Fig.3) of the sample prepared from complex **2**.



Fig.3. TEM image of zinc sulfide and zinc-iron sulfide

# 4.3. Energy dispersive X-ray spectral (EDS) analysis

The energy dispersive X-ray spectra of zinc sulfide and zinc-iron sulfides are shown in Figs.4. Energy dispersive X- ray spectroscopy analysis was performed to confirm the formation of zinc sulfide and zinc-iron sulfides. The atomic ratio of Zn/S of the products obtained from 1 calculated from the EDS is 1: 1.09. The excess sulfur comes from the S impurities. Zn, Fe and S elements are found to present in the EDAX of zinc-iron sulfide the atomic ratio of Zn, Fe and S is 3.0:2.05: 4.95 respectively. This provides the evidence for the formation bimetallic sulfides <sup>[14]</sup>. Fig.4. EDS spectrum of zinc sulfide and zinc-iron sulfide

### 5. Conclusion

In this contribution two new zinc(II) dithiocarbamate complexes have been synthesized and characterized by spectroscopic techniques. These complexes have been exploited as single source precursors for the preparation of zinc sulfide and zinc-iron sulfide nanoparticles. Zinc sulfide and zinc-iron sulfide nanoparticles were characterized using pXRD, TEM and EDS



spectroscopy. TEM image of zinc-iron sulfide nanoparticles demonstrated that the particles are nearly spherical shapes. We expect this simple approach can be used for the synthesis of monometallic and bimetallic sulfide semiconductor nanoparticles with different morphologies, compositions and properties from single source precursors.

# **Conflict Of Interest**

The authors declare no conflict of interest.

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