

PREPARATION AND CHARACTERIZATION OF ZINC(II) AND NICKEL(II) PHENYLETHANOLDITHIOCARBAMATE

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ABSTRACT

Dithiocarbamate compounds have been found to be biologically active. A new series of Zinc(II) and nickel(II) phenylethanoldithiocarbamate [Zn(Phe-EtoH-Dtc)₂ and Ni(Phe-EtoH-Dtc)₂] complexes were synthesized from 2-(hydroxyethyl)aniline, carbon disulfide and metal salts by using the in-situ method. The resulting new complexes have been characterized by CHNS-O analysis, melting point, gravimetric analysis as well as FTIR spectral study. The presence of $\nu(\text{CN})$ and $\nu(\text{CS})$ band in the infrared spectra confirmed the presence of dithiocarbamate ligand in the compound.

Keywords: zinc(II); nickel(II); dithiocarbamate; in situ method

1. INTRODUCTION

Dithiocarbamate ligands, [S₂CNR₁R₂]-, have found extensive use in coordination chemistry (de Lima et al., 2010). Their wide range of applications, e.g. in industry, agriculture and medicine, has generated a large collection of crystallographic data for their metal complexes (Allen, 2002; de Lima et al., 2010). In addition, the applications of dithiocarbamate ligands have been demonstrated in the construction of new supramolecular structural motifs including polymetallic nanosized macrocycles, cryptands and catenane (Allen, 2002). The majority of the complexes studied have simple R₁ and R₂ groups, such as methyl, ethyl and phenyl but very limited reports have been made on C₆H₅OH (de Lima et al., 2010). In this work, Zinc(II) and nickel(II) phenylethanoldithiocarbamate [Zn(Phe-EtoH-Dtc)₂ and Ni(Phe-EtoH-Dtc)₂] complexes were synthesized using 2-(hydroxyethyl) aniline, carbon disulfide and metal salts by corresponding the *in situ* method. The complexes have been characterized by CHNS-O analysis, melting point, gravimetric analysis and as well as FTIR spectra study.

2. EXPERIMENTAL

2.1 Materials and Methods

All starting materials were purchased from Fluka Chemica, System, BDH Chemicals Ltd, Ajax Chemicals, QP Panreac, or Fisher Chemicals and were used as received. Infrared spectra

were recorded in the range of 4000-370 cm^{-1} from KBr pellets using a Perkin-Elmer Spectrum GX spectrometer. Carbon, hydrogen, nitrogen, sulfur and oxygen (CHNS-O) analyses were performed on a Fison EA 1108 CHNS-O analyser - analysis using tin sample-tubes. Gravimetric analysis and melting point were determined using Lindberg/Blue M and Electrothermal 9100 respectively.

2.2 Synthesis Zinc(II) Phenylethanoldithiocarbamate Complexes, $\text{Zn}(\text{Phe-EtoH-Dtc})_2$

Metal dithiocarbamate complexes were prepared by using *in situ* method (Nomura, Fujii, Takabe, & Matsuda, 1989). 5 mL ammonia 30% solution was added to 0.2 mol of excess N-(2-hydroxyethyl) aniline without solvent. The mixture was continuously stirred for 15 min in cold water with control temperature of less than 10 $^{\circ}\text{C}$. 0.16 mol of carbon disulfide in 20 mL methanol was slowly dropped into the solution. The reaction was carried out in low temperature to prevent decomposition and polymerization of the compound. Then 0.08 mol of Zinc (II) chloride in 20 ml distilled water was slowly dropped into the solution. The mixture was continuously stirred for 4 hours. After stirring for 4 hours the solid product was collected and re-crystallized.

2.3 Synthesis Nickle(II) Phenylethanoldithiocarbamate Complexes, $\text{Ni}(\text{Phe-EtoH-Dtc})_2$

0.1 mol N-(2-hydroxyethyl) aniline was dissolved in 30 mL methanol and 5 mL ammonia 30% solution was added to it. The mixture was continuously stirred for 15 min at room temperature. 0.1 mol of carbon disulfide dissolved in 10 mL methanol was dropped slowly into the solution. The reaction was carried out in higher temperature using hot plate to increase the reaction rate. The temperature was controlled not to exceed 40 $^{\circ}\text{C}$ to prevent decomposition and polymerization of the compound. Then, 0.05 mol Nickle(II) chloride dissolved in 20 mL methanol was slowly dropped into the solution. The mixture was continuously stirred for 3 hours. After stirring for 3 hours, the solid product was collected. The dark green residue was re-crystallized and dried in a decicator.

2.4 Instrumentation

Elemental analyses of carbon, hydrogen, nitrogen and sulfur were carried out on Fison EA 1108 CHNS-O analyser. Gravimetric analysis and melting point was determined using Lindberg/Blue M and Electrothermal 9100 respectively. The infrared spectra were recorded on a Perkin Elmer FT-IR Model GX spectrophotometer using KBr discs from the range 4000 – 370 cm^{-1} and nujol in polyethylene for the wave number range between 200 to 370 cm^{-1} .

3. RESULT AND DISCUSSION

3.1 General

A stable white-gray-coloured solids ($\text{Zn}(\text{Phe-EtoH-Dtc})_2$) and dark-green-coloured solid ($\text{Ni}(\text{Phe-EtoH-Dtc})_2$) were obtained from the reaction between N-(2hydroxyethyl) aniline, carbon disulfide and metal salts by applying the *in situ* method. The complexes formed were readily soluble in polar solvents such as ethanol, methanol and acetone. The elemental analysis data showed good agreement between the experimental and theoretical values based on the predicted general formula. An outline of the proposed structure the formation of $\text{Zn}(\text{Phe-EtoH-Dtc})_2$ and $\text{Ni}(\text{Phe-EtoH-Dtc})_2$ are depicted in Figure 1 and 2, respectively. The

complexes produced (71% for $Zn(Phe-EtoH-Dtc)_2$ and 69% for $Ni(Phe-EtoH-Dtc)_2$) obtained was purified by re-crystallization from ethanol. The physical properties and elemental analysis of $Zn(Phe-EtoH-Dtc)_2$ and $Ni(Phe-EtoH-Dtc)_2$ were shown in Table 1.

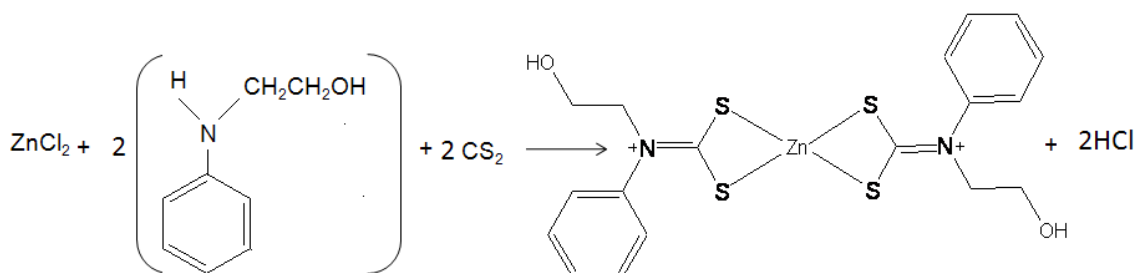


Figure 1: The Synthetic Route of $Zn(Phe-EtoH-Dtc)_2$

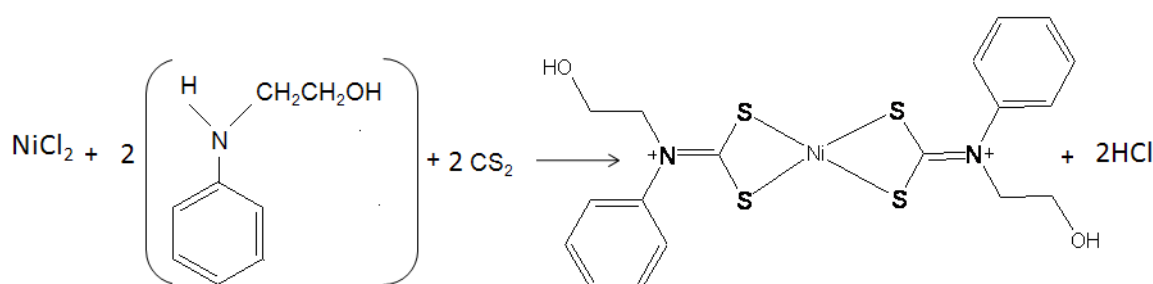


Figure 2: The Synthetic Route of $Ni(Phe-EtoH-Dtc)_2$

Table 1: Physical Properties and Elemental Analysis Data of $Zn(Phe-EtoH-Dtc)_2$ and $Ni(Phe-EtoH-Dtc)_2$

Samples	Physical properties		Found (<i>calculated</i>) %			
	Colour	Melting point ($^{\circ}C$)	C	H	N	S
$Zn(Phe-EtoH-Dtc)_2$	White-gray	162.1 – 163.4	43.06 (44.13)	3.93 (4.08)	5.38 (5.72)	22.02 (26.19)
$Ni(Phe-EtoH-Dtc)_2$	Dark-green	217.6 – 218.4	44.35 (44.74)	4.33 (4.14)	5.57 (5.80)	27.20 (26.55)

3.2 IR Spectra

The important IR bands of the $Zn(Phe-EtoH-Dtc)_2$ and $Ni(Phe-EtoH-Dtc)_2$ were shown in Table 2. The type of bonding between the dithiocarbamate ligands and the Zinc or Nickel atoms were deduced using the ν_{C-N} and ν_{C-S} vibrations. Chatt, Ducanson and Venanzi (1956) suggested resonance structures on the basis of an intense band in the region $1550-1480\text{ cm}^{-1}$ due to a CN stretching vibration. Bradley and Gitlitz (1989) studied IR bands in several metal N,N-dialkyldithiocarbamates and reported the thioureide (CN) band near 1500 cm^{-1} as characteristic in the $(S_2)CNR'R''$ bond. We have observed $\nu(CN)$ in the region $1428-1452\text{ cm}^{-1}$ region, which matches well with the literature value. The observed ν_{C-N} vibrations lie between the ranges for C-N single bonds ($1250-1360\text{ cm}^{-1}$) and C=N double bonds ($1590-1690\text{ cm}^{-1}$). This suggests that the C-N bonds in the compound have some partial double bond

character. The bands at 968-975 cm^{-1} due to $\nu(\text{CS})$ are suggestive of the chelating character of the dithiocarbamate ligand in all cases. Besides this, Far-IR spectra of the compounds showed a new band in the region of 348-357 cm^{-1} which was assigned to $\nu(\text{Zn-S})$ and for $\nu(\text{Ni-S})$: however the band is very small and cannot be detected. The FTIR spectra for $\text{Zn}(\text{Phe-EtoH-Dtc})_2$ and $\text{Ni}(\text{Phe-EtoH-Dtc})_2$ were shown in Figure 3 and 4, respectively.

Table 2: Infrared Adsorption Bands of $\text{Zn}(\text{Phe-EtoH-Dtc})_2$ and $\text{Ni}(\text{Phe-EtoH-Dtc})_2$

Complexes' name	Frequency number (cm^{-1})					
	$\nu(\text{O-H})$	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{Aromatic})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$
$\text{Zn}(\text{Phe-EtoH-Dtc})_2$	3309	1452	968	1593	354	348
$\text{Ni}(\text{Phe-EtoH-Dtc})_2$	3470	1428	1002	1592	ND	ND

*ND: Not detected

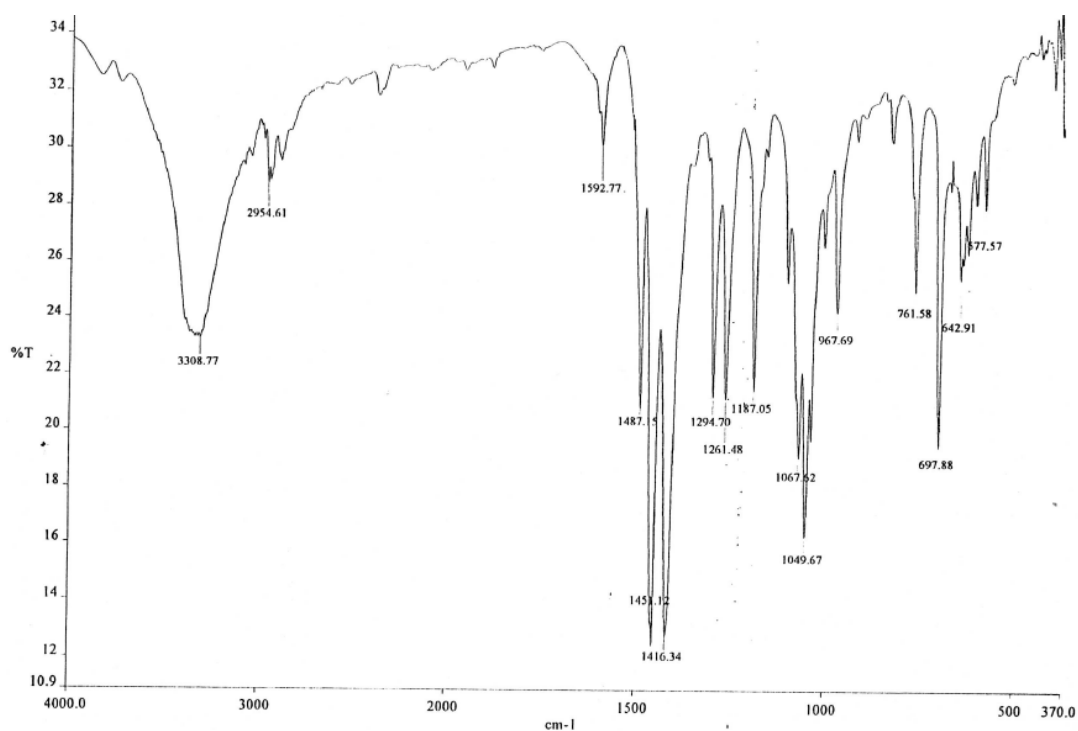


Figure 3(a): Infrared Spectra for $\text{Zn}(\text{Phe-EtoH-Dtc})_2$

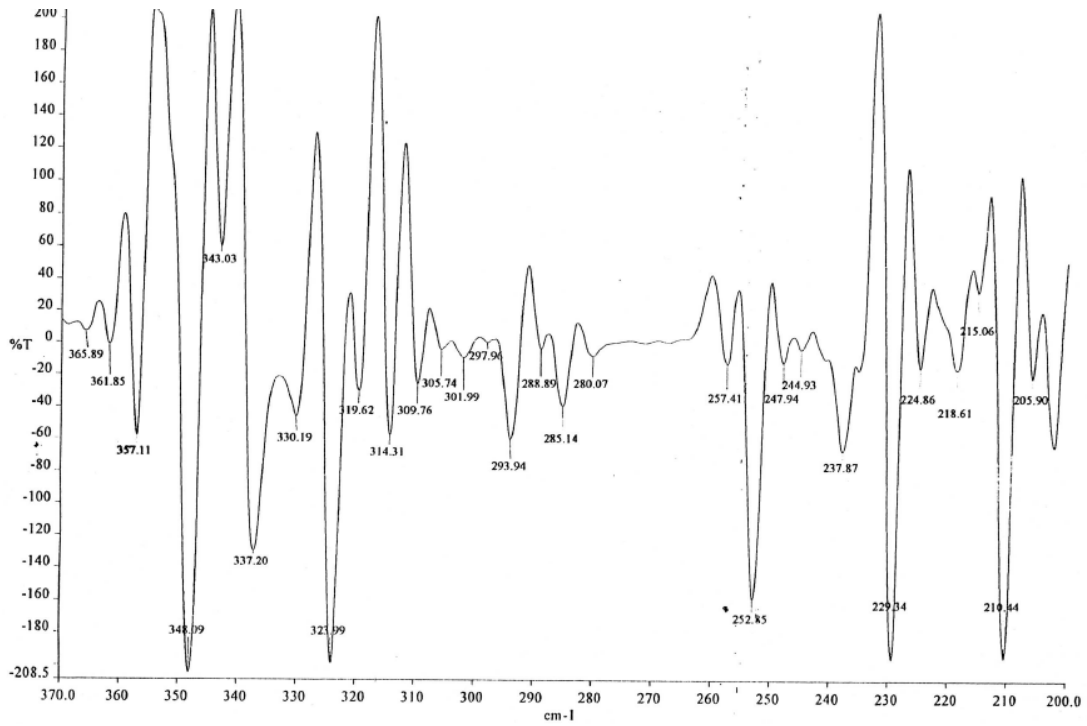


Figure 3(b): Far-Infrared Spectra for Zn(Phe-EtoH-Dtc)₂

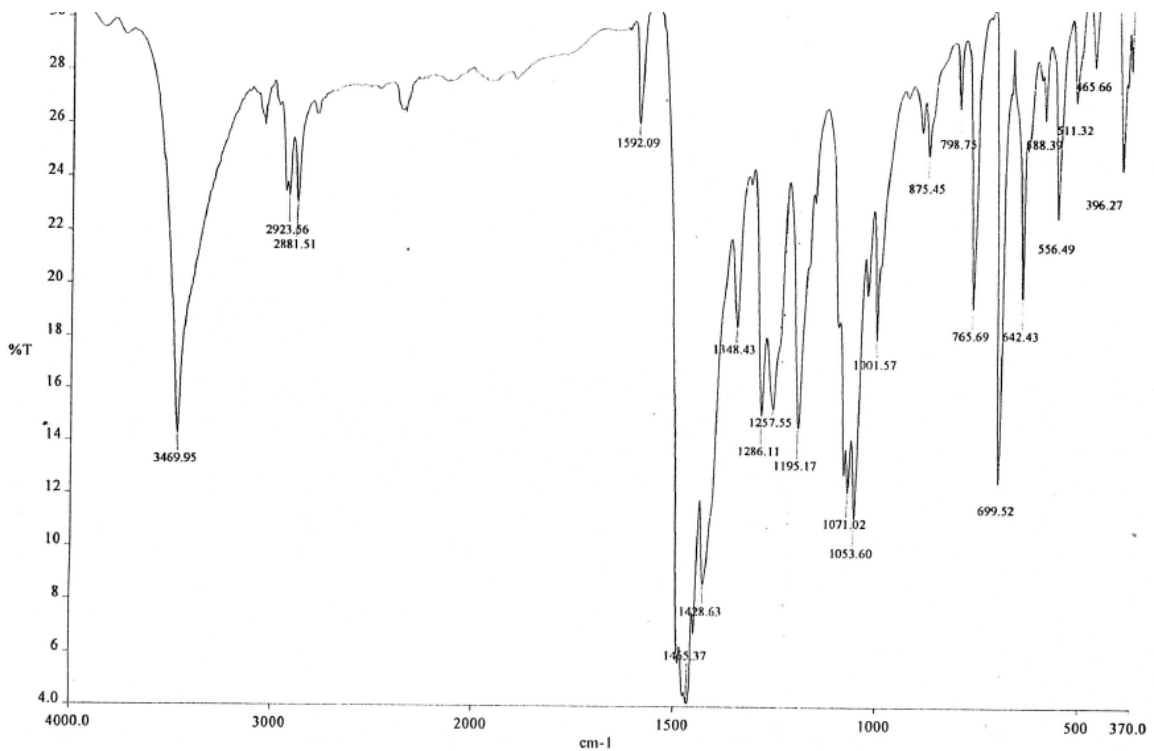


Figure 4(a): Infrared Spectra for Ni(Phe-EtoH-Dtc)₂

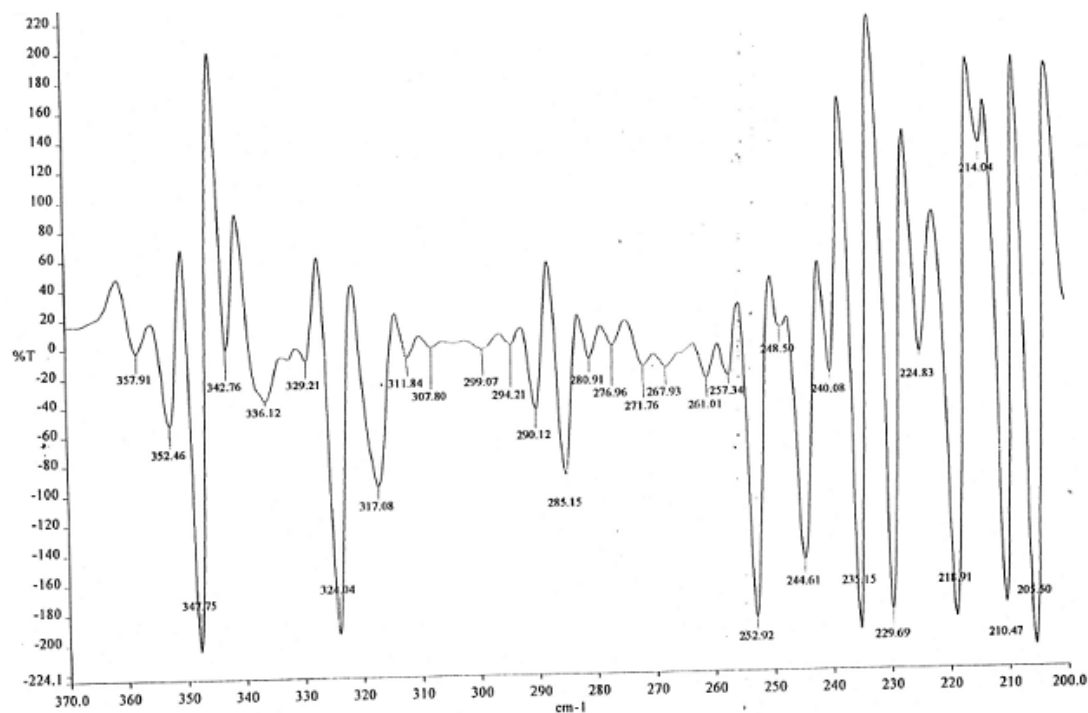
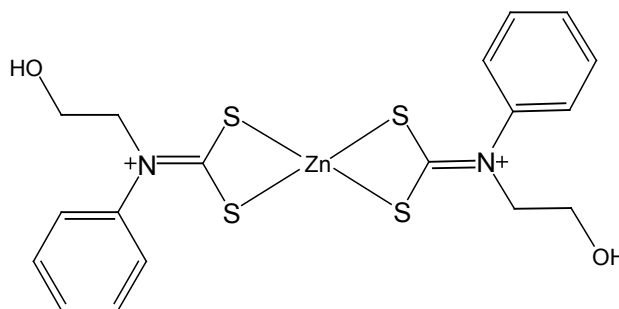


Figure 4(b): Far-Infrared Spectra for Ni(Phe-EtoH-Dtc)₂

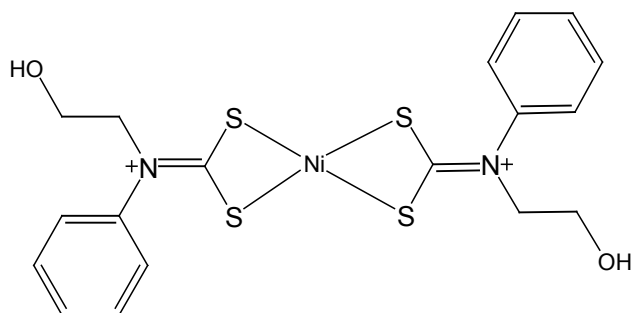
3.3 Structure

An outline of the proposed structure for zinc(II) phenylethanoldithiocarbamate and nickel(II) phenylethanoldithiocarbamate are depicted in Figure 5.



Mol. Wt.: 490.02
C, 44.12; H, 4.11; N, 5.72; O, 6.53; S, 26.18; Zn, 13.34

Figure 5(a): The Proposed Structure of Zn(Phe-EtoH-Dtc)₂



Mol. Wt.: 483.32
C, 44.73; H, 4.17; N, 5.80; Ni, 12.14; O, 6.62; S, 26.54

Figure 5(b): The Proposed Structure of Ni(Phe-EtoH-Dtc)₂

4. CONCLUSION

The new series of Zn(Phe-EtoH-Dtc)₂ and Ni(Phe-EtoH-Dtc)₂ were synthesized by reacting the secondary amine with corresponding zinc chloride and nickel(II) chloride at controlled temperature. The resulting new complexes were characterized by elemental analysis, gravimetric and melting point, as well as FTIR spectra study. The presence of $\nu(\text{CN})$ and $\nu(\text{CS})$ band in the infrared spectra confirmed the presence of dithiocarbamate ligand in that compound.

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