

## **SPECTROSCOPIC AND THERMAL STUDIES OF MIXED LIGAND COMPLEXES OF TRANSITION METAL ION WITH ETHYL- $\alpha$ -ISONITROSOACETOACTATE AND PHENYL DIAMINE**

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A series of new mixed ligand complexes of Co(II), Ni(II), Cu(II), Mn(II) has been synthesized with Ethyl- $\alpha$ -isonitrosoacetoacetate (HEINA) and para-phenyl diamine (PPD). Ethyl- $\alpha$ -isonitrosoacetoacetate as primary ligand and para-phenyl diamine as secondary ligand. Structural investigation of the ligands and their complexes has been made based on elemental analysis, molar conductivity, UV-Vis, FT-IR and  $^1\text{H}$ NMR spectroscopy and magnetic moment measurements as well as thermal analysis (TGA and DTA). The investigated ligands acts as bidentate ligands bonded to the metal ion through the two oxygen atom of the carboxyl and nitroso group the isolated complexes behave as non-electrolyte in DMF solution. The  $\text{Mn}^{+2}$ ,  $\text{Co}^{+3}$ ,  $\text{Ni}^{+2}$ , and  $\text{Cu}^{+2}$  complexes exhibit an octahedral coordination with ligands.

**KEY WORDS** : Mixed ligand complexes, Ethyl- $\alpha$ -isonitrosoacetoacetate, TGA, DTA.

## **INTRODUCTION**

**S**ignificant progress in utilization of transition metal complexes as drugs to treat several human diseases has known like carcinomas, infection control, anti inflammatory, diabetes and neurological disorders [1]. The geometry, number of ligands, donor groups, nature of binding i.e. microcoordination environment is the key to the understanding specific physiological function [2]. Ethyl- $\alpha$ -isonitrosoacetoacetate is a bidentate ligand that has nitroso and carboxylate group as metal ion binding sites, but only a metal ion with an octahedral coordination sphere can form a tridentate chelate [3]. Mixed ligand amino acid complexes are also of relevance in enzyme inhibition [4].

The study of mixed ligand complexes of transitions and non transition metals [5-8] is of great interest due to their important role in biological processes [9].

The present study deals with the preparation  $\text{Mn}^{+2}$ ,  $\text{Co}^{+3}$ ,  $\text{Ni}^{+2}$ , and  $\text{Cu}^{+2}$  complexes with ligands HEINA and PPD. The complexes obtained were subjected to many analytical tools

such as elemental analysis, infrared (FT-IR), thermogravimetric (TG) and derivative thermogravimetric analysis (DTA), molar conductance and electronic spectra to throw some light on their structure.

## EXPERIMENTAL

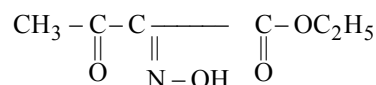
All chemicals used in this work were chemically pure, obtained from BDH chemicals. They include Manganese chloride, cobalt acetate nickel acetate, copper nitrate, sodium nitrite, ethyl acetoacetate para-phenyldiamine. The solvents used were ethanol, toluene deuterated dimethyl sulfoxide (d6-DMSO), dimethyl formamide (DMF), chloroform.

### Synthesis of Ethyl- $\alpha$ - isonitrosoacetoacetate (HEINA)

Ethyl- $\alpha$ - isonitrosoacetoacetate (HEINA) is synthesized by the following procedure [10, 11].

Ethyl acetoacetate 1.4 moles and 3.5 mole of glacial acetic acid were taken in three naked round bottom flask fitted with thermometer, reflux condenser and mechanical stirrer and cooled in ice bath at 0° C and a solution of 95 % sodium nitrite was added over a period of one hour and temperature being kept between 5°C to 10°C. This mixture mixed with double distilled water, stirring for two hour and extracted with ether. After drying ether solution with sodium sulphate, the solvent was distilled off on a steam bath the crude product was dissolved in toluene and cooled to -13°C to -15°C. The separated white crystals were filtered, washed. The purity of the compounds was determined from the results of elemental analysis are summarized in Table 1. IR and <sup>1</sup>H NMR are analyzed.

The resulting ligands have the following formula:



**Table 1. Elemental analysis and Magnetic moments for Mn<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> complexes**

Ligand Complexes	% calculated (found)					
	M : L	C	H	N	M	$\mu_{\text{eff}}$
HEINA	---	45.30(45.28)	5.70(5.66)	8.78(8.80)	--	--
Mn(EINA)2PPD	1 : 2 : 1	44.91(45.02)	6.25(6.31)	11.64(11.88)	11.42(11.22)	10.7
Co(EINA)2PPD	1 : 2 : 1	44.72(44.80)	6.21(6.28)	11.59(11.99)	12.20(12.25)	10.5
Cu(EINA)2PPD	1 : 2 : 1	44.12(43.96)	6.12(6.20)	11.43(11.79)	12.97(12.36)	5.35
Ni(EINA)2PPD	1 : 2 : 1	44.56(44.54)	6.18(6.30)	11.56(11.64)	12.10(12.16)	3.2

### Synthesis of the complexes

The 1 : 2 : 1 complexes were prepared by mixing a hot alcoholic solution of the HEINA (0.2 mol) and para-phenyldiamine (0.1 mol) with the calculated (0.1 mol) of metal salt solution. The reaction mixture was refluxed for 4h. The pH of the solution was maintained at a value of 5.0-6.0 by the addition of dil. NH<sub>4</sub>OH/dil HCl. The solid complexes were dried on a steam bath with stirring, then filtered off and washed several times with alcohol. The solid complexes were dried and analyzed.

### Physical Measurements

The FT-IR spectra recorded in the range 4000-400  $\text{cm}^{-1}$  on a FT-IR spectrophotometer as KBR discs. The NMR spectra were measured using Varian Gemini 200-200 MHz spectrophotometer and the spectra were recorded from 0-15 ppm using TMS as an internal standard in dimethylsulfoxide (d6-DMSO) as the solvent. Thermal analysis (TG and DTG) were obtained in a nitrogen atmosphere using a type TGA 50 of Shimadzu deviatograph thermal analyzer. The molar conductivities were carried out using a Jenway 4310 conductivity meter. Electronic spectra were recorded in the range 200-800nm, on jasco V-530 UV-Vis, spectrophotometer.

## RESULT AND DISCUSSION

### Characterization of the Ligand

The structures of the complexes were established by the use of elemental analysis in Table 1, IR UV-Vis and  $^1\text{H}$  NMR spectra. The infrared spectra of the ligand and the most important IR band assignments that affect the structural features are listed in Table 2. The different types of protons in EtOD of the complexes were obtained. The spectra of the ligand exhibit a sharp singlet signal at 8.651 ppm. The sharp singlet is observed at 2.330 ppm, 4.292 ppm and 1.296 ppm respectively. This signal is assigned to the aliphatic proton [12, 13] as shown in figure.

The electronic spectral band of the ligand scanned in different organic solvents is depicted in Ligand show three bands the first one at 206 nm referred to  $\pi$ - $\pi^*$  transition. It splits into two strong bands 240 nm and 248 nm. This can be explained by presuming that the symmetric  $\pi$  electron system cloud of ligand becomes asymmetric by the dissociation of a proton.

### Characterization of the Complexes

The solid complexes were subjected to elemental analysis and metal content, infrared (FTIR), ultraviolet and visible spectra (UV-Vis), magnetic susceptibility ( $\mu_{\text{eff}}$ ) and thermal analysis. The result of elemental analysis are given in Table 1 and are in good agreement with those calculated by the proposed formulae for 1 : 2 : 1 ( $M : L_1 : L_2$ ) solid complexes.

Infrared spectral data of the complexes display interesting changes which may give a reasonable idea about these complexes. However, if these changes were interpreted in relation to elemental analysis, also the thermogravimetric analysis, molar conductance, electronic spectra and magnetic susceptibility measurements, the structure of the solid complexes may be clarified.

In the spectra of the complexes (Table 2) the band observed within the range 3441 $\text{cm}^{-1}$  assigned to N-OH in the free ligand shifts to lower wave number in the complex indicating the coordination of N-OH to metal ion. The band observed within the range 1705-1678  $\text{cm}^{-1}$  assigned to  $\nu\text{C}=\text{O}$  in the free ligand shifts to lower wave number (1690  $\text{cm}^{-1}$ ) indicating the involvement of the C=O group in chelation [14] Pathak and Haldar [15] have reported the C-N vibration in tris (isonitrosoacetophenato) CO(III) at 620  $\text{cm}^{-1}$ . Taylor and Talwar [16] have suggested that the band at 613  $\text{cm}^{-1}$  in Pd(INA)<sub>2</sub> may be attributed to the Pd-N vibration. It is therefore likely that the M-N vibrations in metal complexes of ligand would occur in the region 700-550  $\text{cm}^{-1}$ .

**Table 2. IR band assignment**

Ligand and Complexes	M : L	$\nu(\text{OH})$	$\nu(\text{Ester C=O})$	$\nu(\text{Ketone C=O})$	$\nu(\text{C=N})$	$\text{CH}_3$	$\text{COOC}_2\text{H}_5$
HEINA	---	3441	1760	1745	1620	1418	1230
Mn(EINA) <sub>2</sub> PPD	1 : 2 : 1	3457	1690	1660	1610	1318	1258
Co(EINA) <sub>2</sub> PPD	1 : 2 : 1	3348	1690	1660	1606	1418	1218
Cu(EINA) <sub>2</sub> PPD	1 : 2 : 1	3444	1690	1660	1610	1410	1217
Ni(EINA) <sub>2</sub> PPD	1 : 2 : 1	3441	1690	1665	1606	1418	1216

### Thermal Analysis

TG analyses are very useful method for investigating the thermal decomposition of solid substances involving simple metal salts [17] as well as for complex compounds [18, 19]. The thermogram follows the decrease in sample weight with the linear increase in heat treatment temperature ( $10^\circ\text{C min}^{-1}$ ) up to  $800^\circ\text{C}$ . The aim of the thermal analysis is to obtain information concerning the thermal stability of complexes as seen in Table 3. For Mn(EINA)<sub>2</sub>PPD complex a mass loss occurred within the temperature range  $200^\circ\text{C}$  corresponding to the loss of moisture. The significant weight loss is observed in between  $259.97^\circ\text{C}$  to  $338.31^\circ\text{C}$  -57.23 %. At the end of the thermogram at higher temperature the metal oxide are formed as final product. For Ni (EINA)<sub>2</sub>PPD complex, a mass loss occurred within the temperature range  $476.41^\circ\text{C}$  - $672.10^\circ\text{C}$ . This significant loss in weight may be due to decomposition of compound which is also supported by DTA curve. The TGA curves of Cu (EINA)<sub>2</sub>PPD shows a significant reduction in weight (12%) due to decomposition of compound at lower temperatures. The results of DTA curve show an endothermic peak at  $222.31^\circ\text{C}$  which indicates the formation of stable compound from the decomposition of compound Cu (EINA)<sub>2</sub>PPD. The complex of CO(II) with HINA and PPD undergo decomposition in between  $150^\circ\text{C}$ - $200^\circ\text{C}$ , which is confirmed from the TGA and DTA curve that shows significant loss in weight.

**Table 3. Thermal Studies for Mn<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup> complexes**

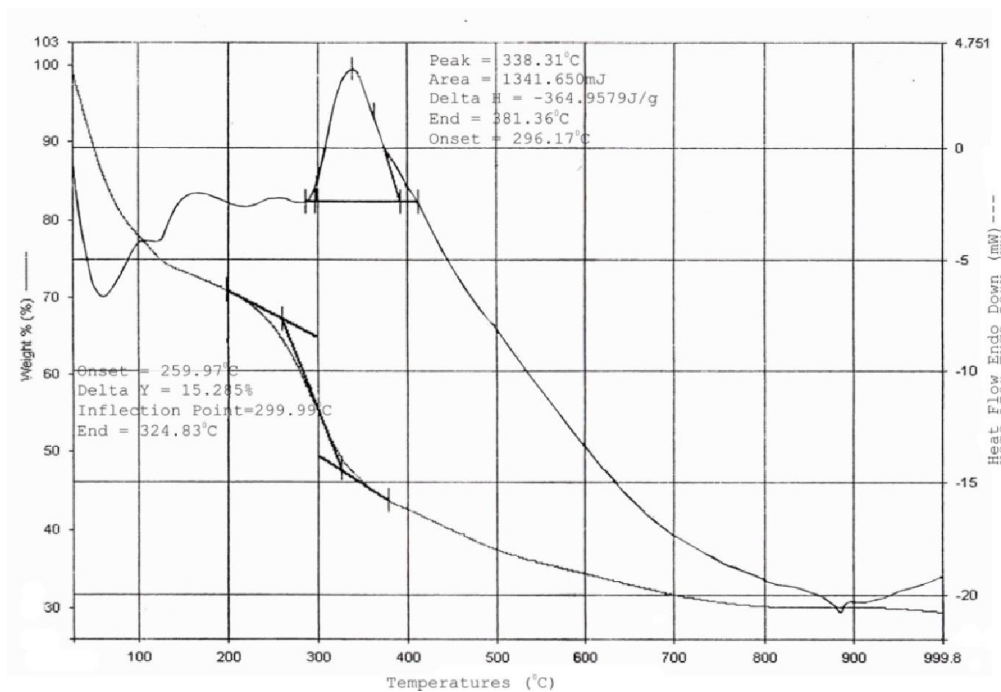
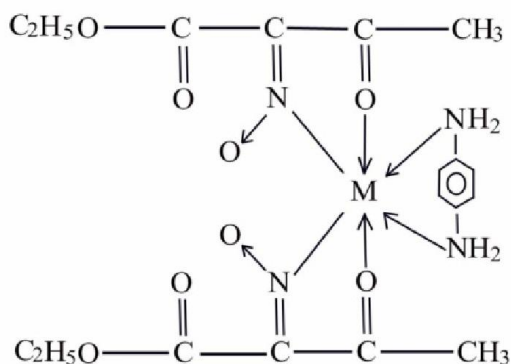
Complexes	mol. wt.	Temp. °C	weight loss		Probable Composition
			Found	Calculated	
Mn(EINA) <sub>2</sub> PPD	480.93	200	58.01	57.23	Mn(EINA) <sub>2</sub> PPD
		500	68.78	67.12	MnO
Co(EINA) <sub>2</sub> PPD	482.93	200	68.00	20.23	-----
		500	90.98	91.41	Co <sub>3</sub> O <sub>4</sub>
Cu(EINA) <sub>2</sub> PPD	489.54	200	12.06	11.4	Cu(EINA) <sub>2</sub> PPD
		500	75.05	74.21	CuO
Ni(EINA) <sub>2</sub> PPD	484.69	200	7.5	8.5	Ni(EINA) <sub>2</sub> PPD
		500	75.64	74.26	NiO

## CONCLUSIONS

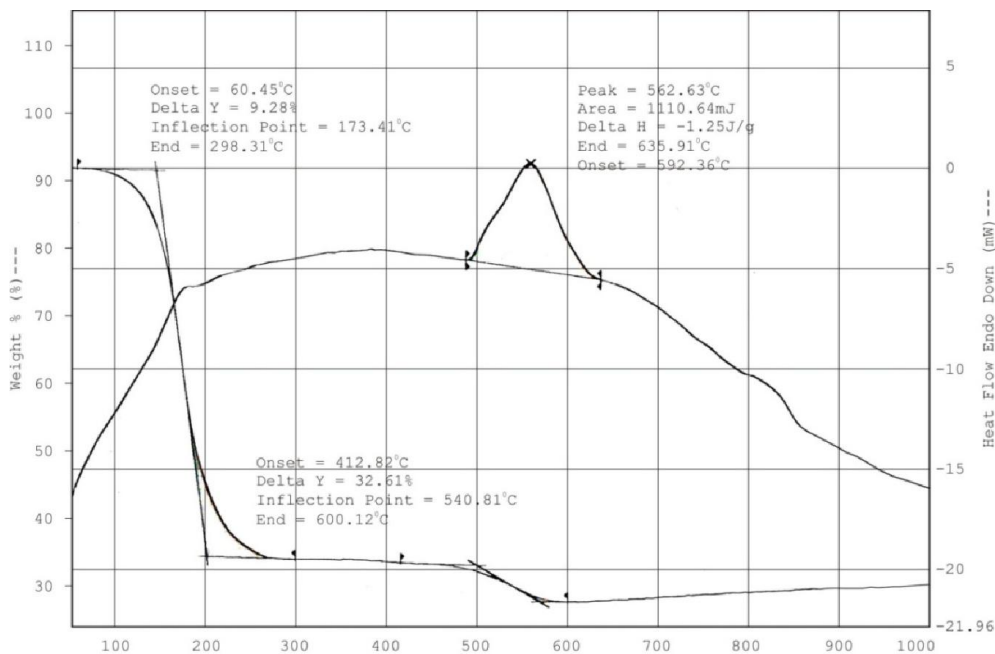
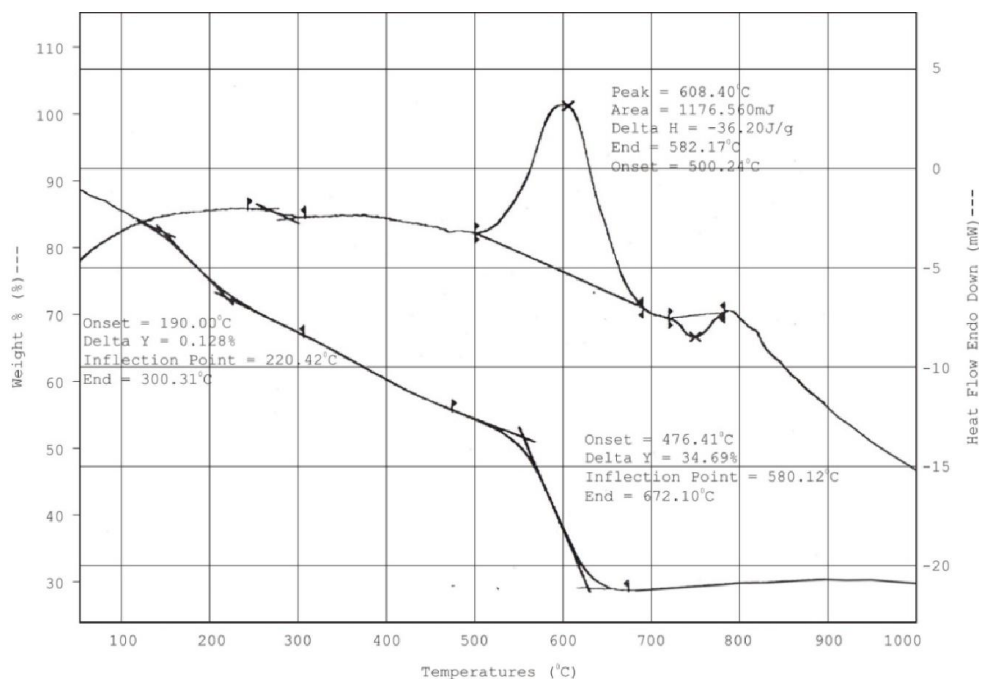
In the present paper, the data obtained from elemental analysis, FT-IR, electronic absorption spectra, Thermal analyses, molar conductivities and magnetic susceptibility measurements show that the complexes of Mn, Co, Ni, and Co metal ions with ligand may be formulated as  $\text{M}(\text{EINA})_2\text{PPD}$ , where bonding in case of 1 : 2 : 1 complexes are formed through

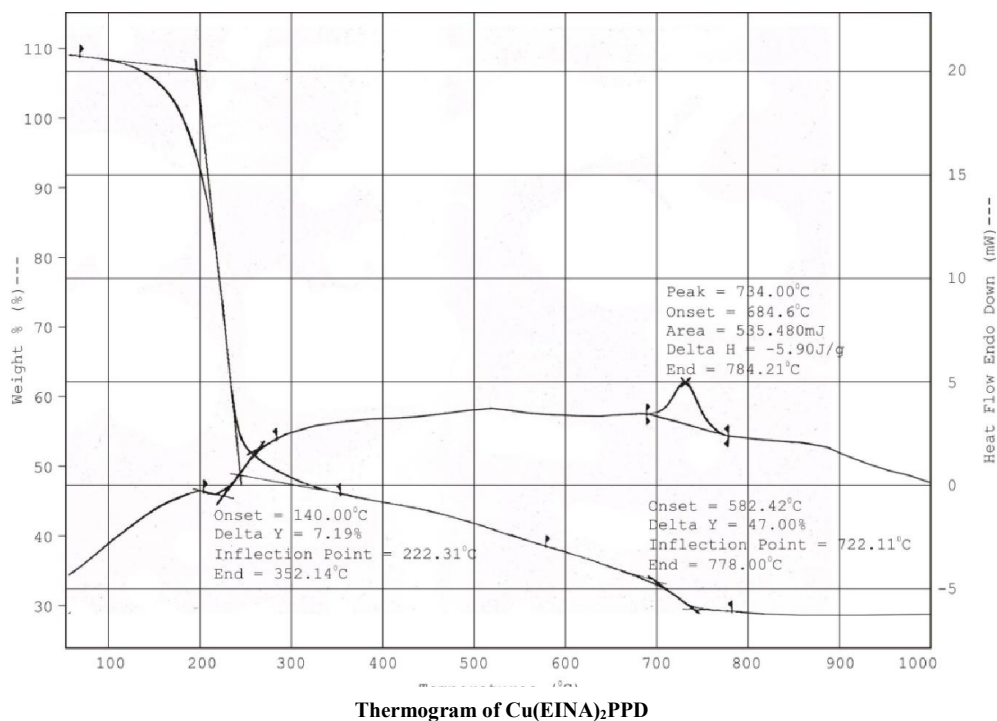
coordination with oxygen of the carboxyl group and nitroso group. The ligand HEINA acts as neutral bidentate ligand. The solid complexes prepared behave as non electrolytes in DMF solution. The electronic spectra of the ligands exhibits a CT band appears in the range 206-240-nm for the ligands. A shift to higher wavelength is observed on complex formation which may be attributed to  $M \rightarrow L$  charge transfer spectra. The band observed in the spectra of the free ligands which may be ascribed to d-d electronic transition within the metal ions. The complexes exhibit an octahedral coordination with the ligand HEINA and para-phenyldiamine.

General structure for the metal ligand complexes is as shown below :



Thermogram of  $Mn(EINA)_2PPD$

Thermogram of Co(EINA)<sub>2</sub>PPDThermogram of Ni(EINA)<sub>2</sub>PPD



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