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## Synthesis of 1-[N-(5-chloro-2-hydroxyphenyl)imino]methyl]-2-naphthol Schiff base: characterization and thermal behavior assessment of its complexes with some metal ions

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### ABSTRACT

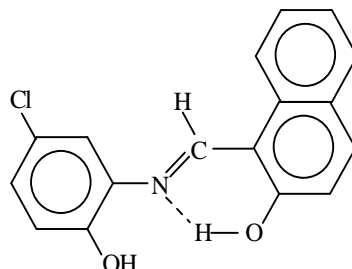
New Ni(II), Cu(II) and Zn(II) complexes have been synthesized by reaction of a terdentate Schiff base ligand 1-[N-(5-chloro-2-hydroxyphenyl)imino]methyl]-2-naphthol ( $H_2L$ ) with metal(II) acetates. The synthesized complexes have been characterized by elemental analyses, IR, UV-Vis and  $^1H$  NMR spectroscopy. The thermal behaviors of complexes have been investigated by TGA and DTA. In all complexes the Schiff base acts as a terdentate ligand and coordinates to the metal via two phenolic oxygen and azomethine nitrogen.

**Keywords :** Schiff base, Azomethine, Terdentate

### INTRODUCTION

In recent years there has been considerable interest in the chemistry of transition metal complexes of Schiff base ligand [1-4]. Also since the past few years the Schiff base complexes have become increasingly important as biochemical, analytical and antimicrobial reagents [5]. Synthesis, structural investigation and reaction of transition metal Schiff bases have received a special attention, because of their biological activities as antitumoral, antifungal and antiviral activities [6]. Since nickel compounds are present in the active sites of urease and are used extensively in the design and construction of new magnetic materials, study of nickel compounds is of great interest in various aspects of chemistry [7-9]. Over the past two decades, considerable attention has been paid to the chemistry of the transition metal complexes of Schiff bases containing nitrogen and other donors [10-14]. These ligand, derived by the condensation of a primary amin and an active carbonyl group, contain the azomethine (C=N) group [15-16]. Chelates in which one nitrogen atom of the azomethine group forms part of the coordination system can be called metalized azomethine dyes. Chelation of a chromphore can also result in a change in properties, including absorption spectra, brilliance, charge, solubility, and affinity for substrates. In general, metallization leads to a bathochromic shift and leads to a distinct improvement in lightfastness and in many cases an enhanced wetfastness compared to the metal-free compound. There has been considerable interest in ortho-hydroxy Schiff bases derived from salicylaldehyde and 2-hydroxy-1-naphtaldehyde, due to the possibility of finding them in the solid state and in solution as keto-amine or phenol-imine tautomers and their connections with photochromism and thermochromism [17]. Further more, metal complexes have gained importance as enzyme inhibitors [18]. We report here the Synthesis, characterization and spectroscopic studies as well as thermal investigation of new complexes with nickel

(II), copper (II) and zinc (II) metal ions, where H<sub>2</sub>L is an ortho – hydroxyl Schiff base ligand : 1-[N-(5-chloro-2-hydroxyphenyl)imino]methyl]-2-naphthol (scheme 1).



**Scheme 1.** The structure of Schiff bases (H<sub>2</sub>L)

These complexes are metallized azomethine compounds and They may also have potential applications as azomethine pigments and dyes.

## MATERIALS AND METHODS

### 2.1. Materials and physical measurements

All chemicals and solvents were purchased from Merck company.

Elemental analyses (carbon, hydrogen and nitrogen) of the ligand and complexes were performed using a Terkinpel limer Seri 2 2004 analyzer. IR spectra (KBr pellets) were recorded in the region 4000 – 400 Cm<sup>-1</sup> on a Perkin Elmer BX II FT- IR spectrophotometer. Electronic spectra of the complexes in DMSO solutions were recorded on a Perkin Elmer spectrophotometer, model Lambda 35. <sup>1</sup>H NMR spectra was recorded with a Bruker Advance Ultrashield spectrometer operating at 400 MHz using DMSO as a solvent. The thermal analyses (TGA – DTA) were recorded in the region 1300 – 25 °C. The thermal analyses were carried out on a Perkin Elmer model Pyris diamond S(II) thermal analyzer in a dynamic atmosphere of nitrogen. The samples were heated with rate of 10 °C min<sup>-1</sup>.

### 2.2. Preparation of Schiff base : 1-[N-(5-chloro-2-hydroxyphenyl)imino]methyl]-2-naphthol (H<sub>2</sub>L)

2-amino-4-chlorophenol (0.860 g, 0.005 mol) was dissolved in 15 mL ethanol, and a solution of 2-hydroxy naphthaldehyde (0.717 g, 0.005 mol) in 15 mL ethanol was added to it. The mixture was refluxed on a water bath for 2h. Then the intense orange precipitate was filtered and washed with ethanol (2×20 mL) and dried. Yield: 85 %, m.p. 240-241 °C (dec). Anal. Calc. for C<sub>17</sub>H<sub>12</sub>NO<sub>2</sub>Cl (%): C, 68.52; H, 4.03; N, 4.70. Found (%): C, 68.48; H, 4.07; N, 4.80. <sup>1</sup>H NMR (DMSO): C<sub>6</sub>H<sub>5</sub> multiplet at 6.66-7.87 δ range, (-OH) phenolic proton at 9.66 δ, enolic proton at 15.17 δ, and imine (CH=N) at 9.04 δ. IR (KBr, Cm<sup>-1</sup>): ν (C=N), 1636 Cm<sup>-1</sup>; ν (C=O), 1546 Cm<sup>-1</sup>; ν (OH), 3449 Cm<sup>-1</sup>.

### 2.3. Preparation of [Ni(L)(H<sub>2</sub>O)], [Cu(L)(H<sub>2</sub>O)] and [Zn(L)(H<sub>2</sub>O)] :

*General procedure for synthesis of complexes*

[Ni(L)(H<sub>2</sub>O)], [Cu(L)(H<sub>2</sub>O)] and [Zn(L)(H<sub>2</sub>O)] were prepared similarly. H<sub>2</sub>L (0.595 g, 0.002 mol) was dissolved in 15 mL ethanol, to this hot solution was added metal acetate (0.002 mol) dissolved in ethanol (15 mL). This solution was refluxed for 3h at 90-100 °C. The complexes were filtered, washed with ethanol and dried in air.

[Ni(L)(H<sub>2</sub>O)] (1): Green-brown, Yield: 81 %, m.p. > 300 °C

[Cu(L)(H<sub>2</sub>O)] (2): Green-yellow, Yield: 78 %, m.p. 260-263 °C

[Zn(L)(H<sub>2</sub>O)] (3): Orange, Yield: 74 %, m.p. > 300 °C

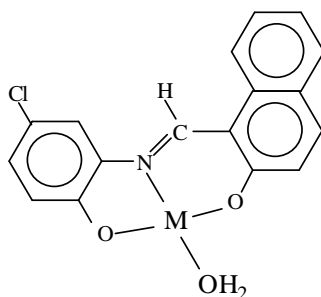
Anal. Calc. for C<sub>17</sub>H<sub>12</sub>NO<sub>3</sub> NiCl (%): C, 54.80; H, 3.76; N, 3.96; Ni, 15.71. Found (%): C, 54.69; H, 3.81; N, 3.89; Ni, 15.65. IR (KBr, Cm<sup>-1</sup>): ν (C=N), 1617; ν (C=O), 1533; ν (H<sub>2</sub>O), 821; ν (Ni-O), 568; ν (Ni-N), 421. Anal. Calc. for C<sub>17</sub>H<sub>12</sub>NO<sub>3</sub> CuCl (%): C, 54.14; H, 3.78; N, 3.71; Cu, 16.85. Found (%): C, 53.98; H, 3.87; N, 3.76; Cu, 16.78. IR (KBr, Cm<sup>-1</sup>): ν (C=N), 1615; ν (C=O), 1536; ν (H<sub>2</sub>O), 823; ν (Cu-O), 503, 565; ν (Cu-N), 458. Anal. Calc. for C<sub>17</sub>H<sub>12</sub>NO<sub>3</sub> ZnCl (%): C, 53.85; H, 3.86; N, 3.89; Zn, 17.26. Found (%): C, 53.76; H, 3.97; N,

3.80 ; Zn, 17.23. IR (KBr,  $\text{Cm}^{-1}$ ) :  $\nu(\text{C}=\text{N})$ , 1618;  $\nu(\text{C}=\text{O})$ , 1540;  $\nu(\text{H}_2\text{O})$ , 829;  $\nu(\text{Zn}-\text{O})$ , 492, 548;  $\nu(\text{Zn}-\text{N})$ , 415.  $^1\text{H}$  NMR (DMSO):  $\text{C}_6\text{H}_5$  multiplet at 6.87- 8.47  $\delta$  range, imine ( $\text{CH}=\text{N}$ ) at 9.65  $\delta$

## RESULTS AND DISCUSSION

### 3.1. Synthesis of the Complexes

We have synthesized Schiff base ligand, 1-[N-(5-chloro-2-hydroxyphenyl)imino]methyl]-2-naphthol and allowed them to react with acetate salts of Ni(II), Cu(II) and Zn(II) in equimolar ratios. Based on spectroscopic and thermal data,  $\text{H}_2\text{L}$  acts as a terdentate (ONO) bivalent anion via two phenolic oxygen and imine nitrogen (Scheme 2). The Schiff base is insoluble in water and soluble in all common organic solvents. However, all complexes are insoluble in water and in common organic solvents. Both Schiff base and complexes have intense colors and absorption bands in visible spectra and may be having potential applications as azomethine pigments and dyes.



**Scheme 2. Suggested structure for complexes (M = Ni, Cu and Zn)**

### 3.2. Spectroscopic studies

In the  $^1\text{H}$  NMR spectra of the Zn (II) complex, the complete absence of the signals due to the phenolic protons suggests deprotonation of ligands and coordination of corresponding anionic groups to zinc. In this spectrum all other proton signals are shifted to low field due to a charge transfer from the ligand to  $\text{Zn}^{2+}$  acceptor and confirms the coordination of the ligand to metal. The azomethine  $\text{C}=\text{N}$  band which appears at  $1630\text{ cm}^{-1}$  in the IR spectra of free ligands considerably shifts to the lower wavenumber in the all complexes. This observation indicates that the imine nitrogen atom is involved in coordination to the metal ion. The appearance of new bands in the IR spectrum of two complexes in the range of  $\sim 400\text{-}600\text{ cm}^{-1}$  which may be assigned to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$ , supports the bonding of oxygen and nitrogen to the metal atom. The UV-Vis spectra of complexes show  $\pi-\pi^*$  and  $n-\pi^*$  transitions of aromatic rings and azomethine moiety of Schiff base, d-d and CT transitions. These spectra in dilute solution of DMSO are done.

### 3.3. Thermal analysis

In view of industrial application of azomethine pigments and dyes, it has been considered worthwhile to study thermal behavior of these compounds. Thermal behaviour of complexes has been studied by thermogravimetry technique. The thermogravimetric and derivative thermogravimetric (TG and DTG) analysis curves are represented in (fig 1). Analysis of obtained curves is in Table 1. As shown, the calculated values for weight loss are in good agreement with observed TG values that confirm the structural integrity of the complexes.

**Table 1 Thermal decomposition data for complexes**

Complex	Temp. range ( $^{\circ}\text{C}$ )	DTG peak temp. ( $^{\circ}\text{C}$ )	Weight loss(%) obs.(calcd.)	Evolved product
1	400-580	450	39.4 (38.8)	$\text{C}_6\text{H}_5\text{OCl}+\text{H}_2\text{O}$
	580-835		54.3 (54.5)	$\text{C}_{11}\text{H}_7\text{N}+2/3\text{NiO}$
2	350-500	405	77.6 (78.9)	$\text{C}_{17}\text{H}_{10}\text{NClO}+\text{H}_2\text{O}$
	500-1000		22.0 (21.0)	$\text{CuO}$
3	475-550	548	48.2 (49.3)	$\text{C}_{11}\text{H}_7\text{ON}+\text{H}_2\text{O}$
	550-1300		52.8 (50.6)	$\text{C}_6\text{H}_5\text{OCl}+\text{Zn}$

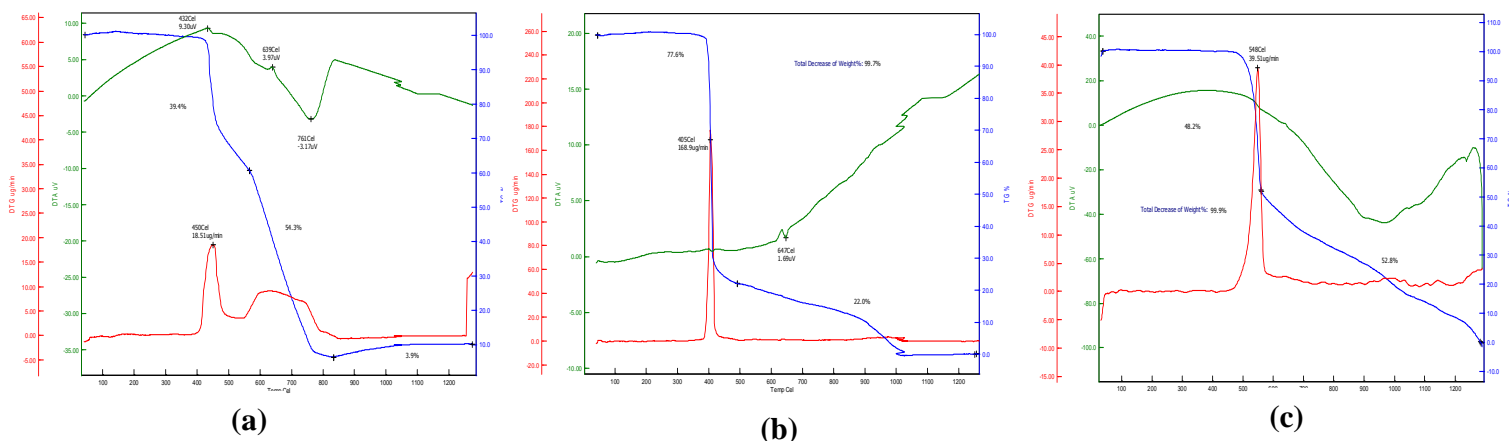


Fig 1: TG, DTG and DTA curve of complexes (a) 1, (b) 2 and (c) 3

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