

# Synthesis and Partial Characterization of Two Schiff Base Ligands with (2 and 4-Nitroaniline) and their Transition Metal (II) (Co and Cu) Complexes

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## Abstract

Two Schiff base ligands have been synthesized from 2-hydroxy-1-naphthaldehyde by its chemical interaction with ethanol solution of 2-nitroaniline and 4-nitroaniline respectively. The complexes of cobalt (II) and copper (II) derived from these Schiff bases were synthesized using a solvent-free method and studied. The ligands and complexes were characterized on the basis of solubility, melting point, conductivity, metal analysis and infrared. The Schiff base ligands and the metal (II) complexes prepared are coloured stable compounds. The results obtained showed that the compounds are all insoluble or slightly soluble in water, but are all very soluble in dimethylsulphoxide (DMSO). The melting points of the metal (II) complexes were within the range of 179°C to 183°C. The infrared spectral data of the Schiff base ligands when compared to those of their respective metal (II) complexes revealed that coordination of the metal ion to the ligand was via the azomethine nitrogen and νO-H of the Schiff base. The relatively low molar conductance values of the metal (II) complexes (5.50 - 12.10 Scm<sup>2</sup>mol<sup>-1</sup>) indicated their non-ionic nature. The metal analysis results show the metal:ligand (M:L) ratio for all the complexes to be (1:2).

**Keywords:** Schiff base, metal complexes of Co (II) and Cu (II), Antimicrobial activity, Infrared.

## INTRODUCTION

Schiff bases are condensation products of primary amines and carbonyl compounds and discovered by a German Chemist Hugo Schiff in 1864 (Ashraf *et al.*, 2011). The common structural feature of these compounds is the azomethine group (-CH=N-) with the general formula RCH=N-R', where R and R' are alkyl, aryl, cycloalkyl or heterocyclic groups which may be variously substituted. Schiff bases are common ligands in coordination chemistry. The imine nitrogen is basic and exhibit acceptor properties. Schiff bases coordinate to metal ions via azomethine nitrogen (Tawfiq, 2010, Ndahi and Pindiga, 2012). Schiff base ligands with aldehydes are formed more readily than with ketones. This is because aldehydes react faster than ketones in condensation reactions and also reactions centres of aldehydes are sterically less hindered than that of ketones (Grace, 2015). Schiff bases are prepared by condensation of carbonyl compounds with amines using different kinds of solvents with the elimination of water molecules (Atmaran and Kiran, 2011, Usharani *et al.*, 2012). Dehydrating agents normally favor the formation of Schiff bases. Though the Schiff bases are stable solids, care should be taken in the purification steps as it undergoes degradation. Chromatographic purification of Schiff bases on silica gel is not recommended as they undergo hydrolysis.

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Condensation of amines with carbonyl (ketones and aldehyde) has various applications. In coordination chemistry, Schiff bases are an important class of ligands and have widespread applications in different fields (Osowole, 2008, Abdulbaset and Ahmed, 2014). Some of the applications of Schiff base ligands include: Schiff bases serve as the basic unit in certain dyes while some are used as liquid crystals. Schiff base reactions are useful in making carbon-nitrogen bond double in organic synthesis. Schiff bases serve as an intermediate in a number of enzymatic reactions which include interaction of an enzyme with an amino or a carbonyl group of the substrate (Verma *et al.*, 2004, Anand *et al.*, 2012).

Reports show that Schiff bases and their metal complexes have been widely studied due to their important anti-parasitic, fungicidal – bactericidal and anti-cancer properties (Nirmal *et al.*, 2010, Mishra *et al.*, 2012). Due to these various applications of Schiff bases, it has continued to attract more attention from researchers. This study focused on Schiff base prepared from 2-hydroxy-1-naphthaldehyde and 2 and 4-nitroaniline and their Co (II) and Cu (II) complexes.

The main aim of this study is to synthesize two Schiff base ligands from 2-hydroxy-1-naphthaldehyde and study their transition metal (II) complexes of Co (II) and Cu (II).

## **MATERIALS AND METHODS**

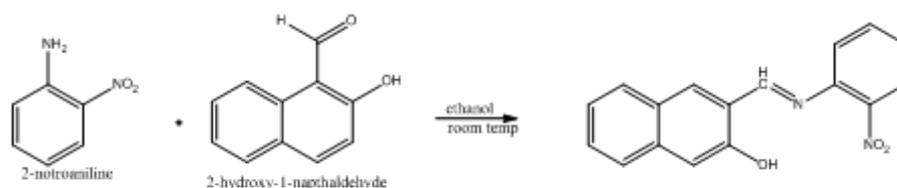
All chemicals and solvents used were of analytical grade and were used as supplied. The metal(II) salts used are Cobalt(II) acetate tetrahydrate and Copper(II) acetate dihydrate. 2-nitroaniline and 4-nitroaniline were used as amines. Ethanol was used as solvent for the synthesis of the ligands.

All the glasswares used were thoroughly washed with detergent and repeatedly rinsed with tap water after which distilled water was finally used.

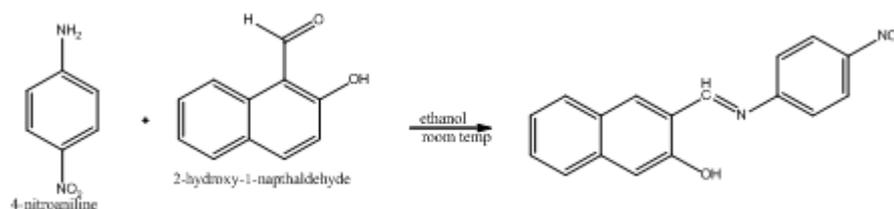
Melting points were determined using a GallanKamp Melting Point Apparatus using a thermometer range (0-360°C).

**Synthesis of the ligands(HL<sup>1</sup> and HL<sup>2</sup>):** The ligands were prepared following a literature procedure (Aliyu and Sani, 2010, Grace 2015), by condensation of the aldehyde and the corresponding amine in 1:1 mole ratio (aldehyde:amine). In a typical reaction, a solution of 2-nitroaniline(1 mmol,0.4147 g) in 20 mL ethanol was added to a solution of 2-hydroxyl-1-naphthaldehyde (1 mmol,0.5165 g) in 20 mL ethanol with constant stirring at room temperature. Two drops of concentrated sulphuric acid drops were added to the mixture above to adjust the pH and stirred for another 10 minutes at room temperature. The mixture was kept for two days in a beaker after which the orange product (HL<sup>1</sup>) formed was filtered and dried in a desiccators using anhydrous calcium chloride.

The ligand ((HL<sup>2</sup>) with 4-nitroaniline was prepared using a similar procedure as described above. A red coloured product was formed instantly in this case. The product was filtered immediately and stored in a desecrator as described above. The equations for the preparation of the ligands with 2-nitroaniline and 4-nitroaniline are shown in Schemes 1 and 2 respectively:



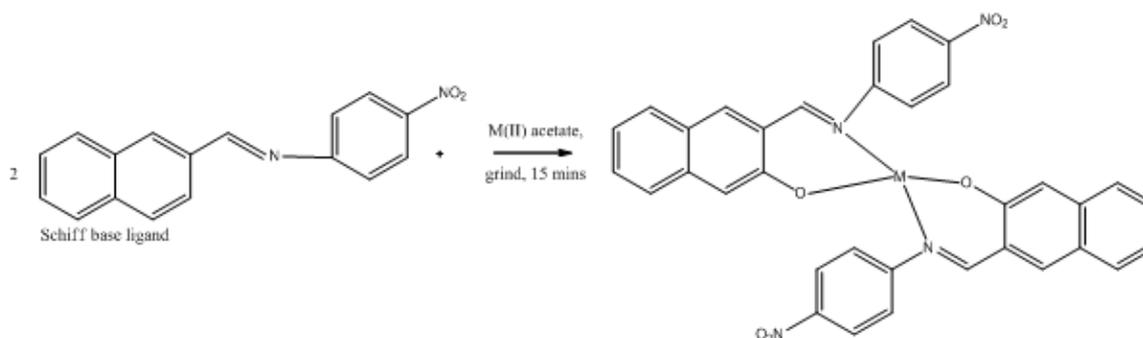
Scheme 1: Schiff base ligand with 2-nitroaniline



Scheme 2: Schiff base ligand with 4-nitroaniline

**Synthesis of the metal(II) complexes:** The cobalt(II) and copper(II) complexes were synthesized using the solvent-free method (Adedibu *et al.*, 2012, Ndahi *et al.*, 2017), in 1:2 mole ratio (metal:ligand). The two reactants were weighed carefully into a mortar and crushed (ground) for 15 minutes using a pestle in the laboratory. The product obtained was weighed and stored in a desiccator for further analysis.

A general equation for the preparation of the complexes with the Schiff base ligand formed from 4-nitroaniline is given in Scheme 3:



Scheme 3: Formation of Schiff base metal(II) complexes  
Where M = Co(II) or Cu(II)

### Characterization Techniques:

**Solubility of the Ligands and the Metal(II) Complexes:** The solubility of the Schiff base ligands and complexes were determined using distilled water, methanol, ethanol, hexane and dimethylsulphoxide (DMSO). A pinch (20 mg) of each of the sample was taken and dissolved into a little amount of the corresponding solvent (about 4 cm<sup>3</sup>) in a test tube. This was shaken thoroughly and the solubility was checked at room temperature (Saal, 2010). Samples that did not dissolve in cold solvents were warmed over a water bath and solubility results were recorded.

**Melting Point:** The melting point of the ligands and complexes were recorded using a Gallenkamp Melting Point Apparatus with a thermometer range of 0-360°C.

**Metal Analysis:** Metal analysis was done using EDTA titrations in order to determine the percentage of each metal in the complexes that have coordinated with the ligands, so that the approximate ligand to metal ratio(M:L) can be determined in the complexes(Vogel, 1985)

**Molar Conductance:** The molar conductance of each of the metal(II) complexes was determined using DDS-307 conductivity meter at a concentration of  $10^{-3}$  M in methanol. This measurement is used to determine whether a given compound is an electrolyte or a non-electrolyte in solution. Molar conductance is the conductivity of an electrolyte solution divided by the molar concentration of the electrolyte and so, measures the efficiency with which a given electrolyte conducts electricity in solution.

**Infrared (IR):** The IR spectra of the ligands and complexes were recorded on FTIR -91184 (FTIR Spectrum II model) at Pharmaceutical Laboratory, Gombe State University, Gombe, in the range  $450-4000\text{ cm}^{-1}$  using KBr pellets. This was done in order to determine the coordinating atoms and the relative strength of the bonds. Each of the samples and KBr were ground to reduce the particle size to less than 5 mm in diameter. A small amount of powdered sample (about 1-2% of the KBr amount) was taken and mixed with the KBr powder. The IR of the transparent KBr pellet was then recorded using the infrared analyser. The relevant IR frequencies of the ligands and their metal (II) complexes with their proposed assignments were determined.

## Results and Discussions

### Results

The results of the physical properties and infrared of the ligands and complexes are given in the following Tables 1:

Table 1 Some physical properties of the ligands and their metal(II) complexes

Compound	Colour	M.P.( $^{\circ}\text{C}$ )	Yield(%)	Conductivity $\text{Scm}^2\text{mol}^{-1}$	%M Found(Calcd)
HL <sup>1</sup>	Orange	158 - 160	32	-	-
HL <sup>2</sup>	Red	156 - 158	72	-	-
Co(HL <sup>1</sup> ) <sub>2</sub>	Brown	179 - 183	77	7.20	8.50(9.19)
Cu(HL <sup>1</sup> ) <sub>2</sub>	Dark orange	180 - 181	62	11.4	8.70(9.84)
Co(HL <sup>2</sup> ) <sub>2</sub>	Dark orange	180 - 182	78	5.50	8.60(9.19)
Cu((HL <sup>2</sup> ) <sub>2</sub>	Dark red	178 - 180	60	12.10	9.10(9.84)

### Solubility

The solubility of the ligands and complexes in water and some common organic solvents are presented in Table 2:

Table 2: Solubility of the ligands and their metal(II) complexes

Compound	Distilled water		Methanol		Ethanol		Hexane		DMSO	
	C	H	C	H	C	H	C	H	C	H
HL <sup>1</sup>	IS	IS	S	VS	SS	S	IS	SS	VS	VS
HL <sup>2</sup>	IS	SS	S	S	SS	S	IS	IS	VS	VS
Co(HL <sup>1</sup> ) <sub>2</sub>	IS	SS	S	VS	S	VS	IS	SS	VS	VS
Cu(HL <sup>1</sup> ) <sub>2</sub>	IS	SS	S	VS	S	VS	SS	SS	VS	VS
Co(HL <sup>2</sup> ) <sub>2</sub>	IS	IS	S	VS	S	S	IS	SS	VS	VS
Cu((HL <sup>2</sup> ) <sub>2</sub>	IS	IS	SS	S	S	S	IS	SS	VS	VS

where : C=Cold solvent, H= hot solvent, IS = insoluble, SS= slightly soluble, S= soluble, VS = very soluble

## Infrared Spectra

The relevant infrared frequency of the ligands and complexes are presented in Table 3.

**Table 3: Relevant infrared bands of the ligands and their metal (II) complexes**

Compound	VO-H	VC=N	VC=C	VM-N	VM-O
HL <sup>1</sup>	3434b	1628s	1573sh	-	-
HL <sup>2</sup>	3437b	1621m	1581m	-	-
Co(HL <sup>1</sup> ) <sub>2</sub>	3384b	1598m	1514m	629sh	499w
Cu(HL <sup>1</sup> ) <sub>2</sub>	3452b	1620s	1516sh	586sh	499w
Co(HL <sup>2</sup> ) <sub>2</sub>	3333b	1598m	1547sh	488m	470w
Cu((HL <sup>2</sup> ) <sub>2</sub> )	34377b	1583s	1582m	487sh	460w

b = broad, m = medium, s = strong, sh =sharp, w =weak

## Discussion

The reaction between 2-nitroaniline or 4-nitroaniline with 2-hydroxy-1-nathaldehyde in a molar ratio of 1:1 produced the Schiff base ligands (HL<sup>1</sup> and HL<sup>2</sup>) as orange and red products with percentage yields of 32% and 72% respectively. The interaction between the Schiff base ligands and each of the metal (II) ions separately in 1:2 molar ratio (M:L) using the solvent-free method produced the metal (II) complexes of the respective metal (II) ions with a percentage yield ranging between 60-78% (Table 1). The metal (II) complexes are stable even when exposed to air i.e. they are non-hygroscopic. The colours of the complexes are typical of transition metal complexes which are attributed to d-d transitions of electrons between energy levels because of partially filled d orbitals or charge transfer transitions Cotton and Wilkinson (1972). The melting points of the Schiff bases and the metal (II) complexes are sharp and are in the range of 156-160°C and 179-183°C respectively. The high melting point indicates that the compounds are stable and not easily decomposed. (Ahmed and Akhtar, 1983). The higher melting points of the complexes also suggest the chelating 'chelating effect' of the respective ligands. Chelating ligands form more stable complexes than do an equivalent number of related of related monodentate ligands. The solubility of the Schiff bases and the complexes were determined in distilled water, methanol, ethanol, hexane and dimethylsulphoxide, (DMSO) as shown in Table 2. The ligands and the metal (II) complexes were insoluble or slightly soluble in water and hexane. They showed varying degrees of solubility in methanol and ethanol but all are very soluble in DMSO which is a coordinating solvent. Generally, transition metal complexes with organic ligands are relatively non-polar. As a result they are soluble in organic solvents but not in polar solvents like water. At molecular level, solubility is controlled by intermolecular forces. However, a simple empirical rule 'Like dissolves like' and it is based on the polarity of the systems that is polar molecules dissolve in polar solvents and non-polar molecules in non-polar solvents (Saal, 2010). The molar conductivity values (Table 1) obtained for the metal complexes in methanol are in the range of 5.50-12.10 Scm<sup>2</sup>mol<sup>-1</sup>. This low values suggest that the complexes are non-electrolytes (Osovole, 2008, Tawfiq, 2011) and also occur in solutions largely as neutral molecules since the conductance of a solution is a measure of the ability of that solution to carry a current. The use of conductivity enables the determination of ions in solution.

The estimated metal ion percentages in the complexes agree closely with theoretical values ( $\pm 0.5$ ). Results are presented in Table 1.

Infrared spectroscopy is widely used as a characterization technique for coordination compounds. The basic theory involved is that the stretching modes of a ligand changes upon complexation due to weakening or strengthening of the bonds involved in the bond formation resulting in subsequent changes in the positions of the bands appearing in the

infrared spectrum (Nakamoto, 1970). The IR spectra, were assigned by comparing the spectra of the ligands with those of the metal complexes and also with literature reports on similar systems (Aliyu and Sani, 2010 Atmaran and Kiran, 2011, Muzamil *et al.*, 2015, Iniama *et al.*,2015 ).

In the infrared spectra of the ligands prepared (Table 3), the broad bands at  $3434\text{ cm}^{-1}$  and  $3439\text{ cm}^{-1}$  are assigned to  $\nu\text{O-H}$  of the ligands. In the IR spectrum of the ligand HL<sup>1</sup>, the most characteristic band at  $3434\text{ cm}^{-1}$  was assigned to  $\nu\text{O-H}$  and  $1628\text{ cm}^{-1}$  was assigned to  $\nu(\text{C}=\text{N})$  azomethine(Figure 4.3) In the ligand HL<sup>2</sup>,  $\nu\text{O-H}$  was found at  $3437\text{ cm}^{-1}$  and the  $\nu\text{C}=\text{N}$  at  $1621\text{ cm}^{-1}$ . The azomethine bands  $\nu\text{C}=\text{N}$  were shifted to lower frequencies in the complexes  $1583\text{-}1620\text{ cm}^{-1}$  which indicates coordination of the metal ions to the azomethine nitrogen of the ligands, these values agree with a similar work reported by some earlier workers (Niven and Memet, 2009, Atmaram and Kiran, 2011).

In the complexes, weak bands at  $629, 488, 586$  and  $487\text{ cm}^{-1}$  were assigned to  $\nu\text{M-N}$  and those in the range  $460\text{-}499\text{ cm}^{-1}$  are attributed to  $\nu\text{M-O}$ . (Nakamoto, 1970, Sultan, 2012, Tawfiq, 2011).

From the IR results, it may hint that the Schiff base ligands coordinated to the metal ions through the azomethine nitrogen and oxygen atoms of the hydroxyl groups of the ligands.

## CONCLUSION

The synthesized Schiff base ligands and their metal (II) complexes are all stable at room temperature. Their melting points indicated that the compounds are not pure this may be due to impurities present in the complexes. The insolubility of all the compounds in water may be due to their non-polar nature. The low molar conductance values of the metal (II) complexes showed their non-electrolytic nature. The infrared spectral data of the ligands when compared to those of their respective metal (II) complexes showed that coordination of the metal ion to the ligand is via the azomethine nitrogen and  $\nu\text{OH}$  of the Schiff base ligands. The metal analysis results agree closely with the expected values from proposed structures. From the analysis carried out and literature available, the formation of the Schiff base ligands and the metal(II) complexes prepared in this study are shown in Schemes 1, 2 and Scheme 3 respectively, and the proposed structures of the ligands and the metal (II) complexes are shown in Figures 1 and 2 respectively.

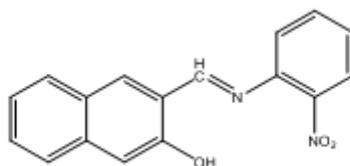


Figure 1: Proposed structure of Schiff base ligand with 2-nitroaniline

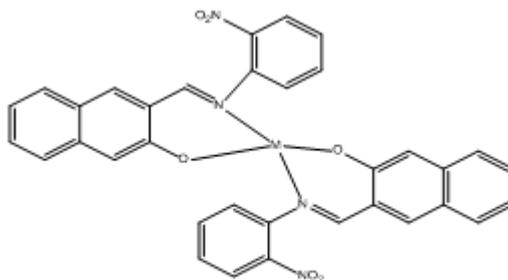


Figure 2: Proposed structure of Schiff base metal(II) complex where M= Co(II) or Cu(II)

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