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## Research Article



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## Copper (II) Complexes with Unsymmetrical Schiff base Ligands

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### Abstract

A new series of Cu(II) complexes with unsymmetrical tetradentate Schiff base ligands have been prepared from the condensation reaction of 1:1:1 molar mixture of 2-hydroxy-1-naphthaldehyde, 4-methyl-1,2-diaminobenzene and substituted salicylaldehyde in aqueous ethanolic medium. The synthesized Schiff bases and their copper (II) complexes were characterized by elemental analysis, molar conductivity measurements, magnetic moment measurements, IR and UV-Vis spectral data investigations. The copper (II) complexes are coloured and stable in air. The molar conductivity data of the complexes in DMF solution indicates they are non-electrolytic nature. All copper (II) complexes are paramagnetic in nature due to presence of one unpaired electron in 3 d-orbital. The IR spectral data indicates Schiff bases act as tetradentate and coordinate through azomethine nitrogen and phenolic oxygen atoms. The square planar geometry of the Cu(II) complexes has been proposed on the basis of magnetic moment measurements, IR and electronic absorption spectral investigations.

**Keywords:** Schiff base, Copper salt, 2-hydroxy naphthaldehyde, 4-methyl o-phenylenediamine.

### 1. Introduction

Schiff bases are the versatile class of organic compounds synthesized from the condensation of a primary amine with active carbonyl compounds [1-4]. Schiff bases may be represented as  $R-CH=N-R'$  where R and R' may be alkyl, aryl or heterocyclic. Schiff bases of aromatic

aldehydes are more stable than aliphatic aldehydes due to effective conjugation. The presence of azomethine group, which is responsible for stability, reactivity and biological activity of Schiff bases and their metal complexes [5-7]. Schiff bases and their metal complexes are used in catalyst, antimicrobials, antioxidants, dyes optical materials and analytical chemistry [8-14].

Schiff bases contains donor atoms may be nitrogen, oxygen or Sulphur which providing binding sites through nonbonding electrons with metal ions. The Schiff bases contain nitrogen and oxygen play an important role in coordination chemistry and bioinorganic compounds due to their flexibility and denticity [15-17]. A variety of physico-chemical investigations on the complexes of metals which provide electronic and stereochemical properties. Such type of properties depends on the nature of the metal as well as ligands. Unsymmetrical Schiff bases with nitrogen and oxygen donor atoms are well known to coordinate with various metal ions and this has attracted by many researchers due to their availability and catalytic and biological applications. Due to the delocalization of lone pair of electrons on nitrogen atom in the benzene ring aromatic amines are less basic than aliphatic amines. The stability constant and protonation constant of aliphatic diamines are greater than those of similar ligands derived from aromatic diamines [18]. In this paper, we report here the synthesis and characterization of copper (II) complexes with unsymmetrical Schiff base ligands.

## 2. Experimental

All the reagents and solvents used in present work were of Anal-R grade and were used without further purification. The elemental analysis data was obtained using Perkin-Elmer elemental analyser. The molar conductivity of the complexes were measured by using PW9515/10 digital conductivity meter using DMF as solvent. The IR spectra of the ligand and metal complexes were recorded on Shimadzu infrared spectrophotometer using KBr disc. The magnetic susceptibility of investigated complexes were measured by Gouy method using Hg [Co (SCN)<sub>4</sub>] as a calibrant. The electronic spectra of copper (II) complexes were recorded by using Shimadzu model UV-1900 spectrophotometer in DMSO solution.

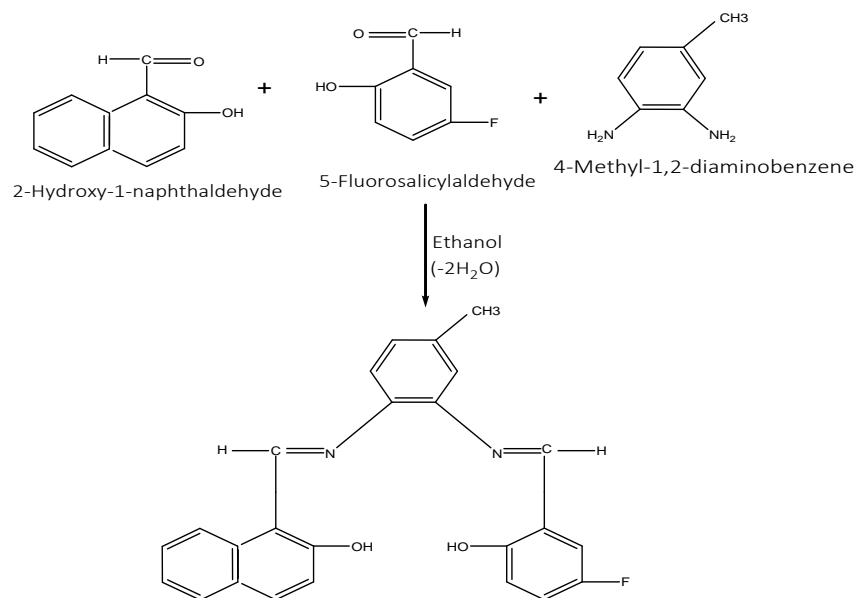
## Synthesis of Schiff base ligands:

### 1. Synthesis of Schiff base ligand N-(naphthalidene)-N'-(5-fluorosalicylidene)-4-methyl-1,2-diaminobenzene (H<sub>2</sub>L<sup>1</sup>): -

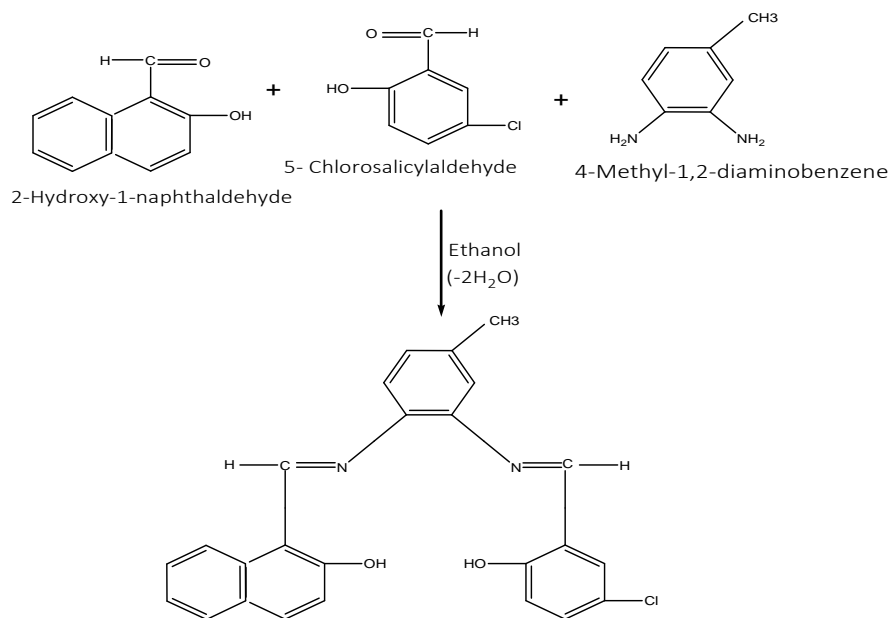
Schiff base ligand N-(naphthalidene)-N'-(5-fluorosalicylidene)-4-methyl-1,2-diaminobenzene (H<sub>2</sub>L<sup>1</sup>) was synthesized in two step process. In the first step, condensation of 15 mmol of 4-methyl-1,2-diaminobenzene with 15 mmol of 2-hydroxy-1-naphthaldehyde in an ethanolic medium monocondensed half-unit of the ligand was formed. In the second step, the product obtained in the first step was mixed with an ethanolic solution of 15 mmol of 5-fluorosalicylaldehyde. The mixture was put into ultrasonic case. Sonication was continued for 1-hour. The mixture was cooled and solid light yellowish precipitate was collected by filtration and washed with water and cold ethanol and dried under reduced pressure over anhydrous CaCl<sub>2</sub> in a desiccator. The melting point of the ligand (H<sub>2</sub>L<sup>1</sup>) was recorded to be 176<sup>o</sup>C. The molecular formula of the ligand was analysed as C<sub>25</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>F.

### 2. Synthesis of Schiff base ligand N-(naphthalidene)-N'-(5-chlorosalicylidene)-4-methyl-1,2-diaminobenzene (H<sub>2</sub>L<sup>2</sup>): -

Schiff base ligand N-(naphthalidene)-N'-(5-chlorosalicylidene)-4-methyl-1,2-diaminobenzene (H<sub>2</sub>L<sup>2</sup>) was synthesized in two step process. In the first step, condensation of 15 mmol of 4-methyl-1,2-diaminobenzene with 15 mmol of 2-hydroxy-1-naphthaldehyde in an ethanolic medium monocondensed half-unit of the ligand was formed. In the second step, the product obtained in the first step was mixed with an ethanolic solution of 15 mmol of 5-chlorosalicylaldehyde. The mixture was put into ultrasonic case. Sonication was continued for 1-hour. The mixture was cooled and solid yellowish precipitate was collected by filtration. The precipitate was washed with water and cold ethanol and dried under reduced pressure over anhydrous CaCl<sub>2</sub> in a desiccator. The melting point of the ligand (H<sub>2</sub>L<sup>2</sup>) was found to be 184.3<sup>o</sup>C. The molecular formula of the ligand was analysed as C<sub>25</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>Cl.



Scheme 1. Synthesis of Schiff base ligand (H<sub>2</sub>L<sup>1</sup>)



Scheme 2. Synthesis of Schiff base ligand (H<sub>2</sub>L<sup>2</sup>)

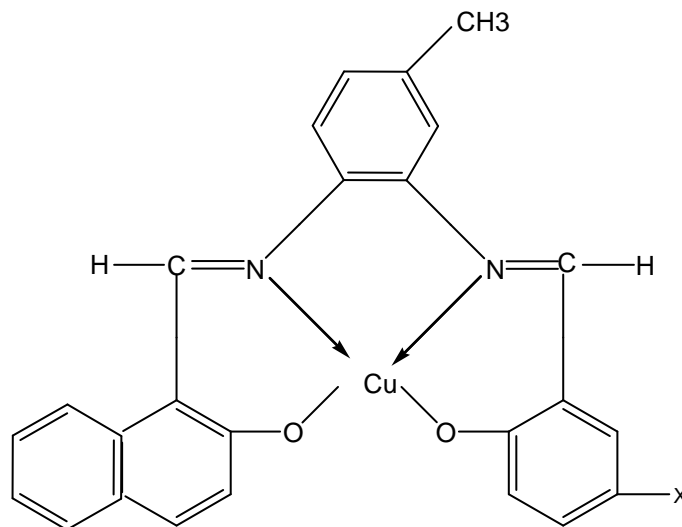


Fig 1. Proposed structure of Cu(II) complexes  
X = F, Cl

### Synthesis of Cu (II) complexes: -

The undertaken Cu(II) complexes were obtained by refluxing ethanolic solution of unsymmetrical Schiff base ligands and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in a molar ratio 1:1 (ligand : metal) and refluxed for 3 hours in the presence of 1 mmol of sodium carbonate

( $\text{Na}_2\text{CO}_3$ ). The solution was cooled to room temperature when a solid separated. The coloured solid was filtered, washed with cold ethanol and then dried under reduced pressure over anhydrous  $\text{CaCl}_2$  in a desiccator. The purity and progress were monitored by thin layer chromatography using silica gel.

Table 1.

### Microanalytical data of the Schiff bases and their metal complexes

Coordination compounds	M.P	Colour	% Found (Calculated)			
			C	H	N	M
$\text{H}_2\text{L}^1$	176 <sup>o</sup> C	Light Yellow	75.31 (75.38)	4.72 (4.77)	6.69 (6.75)	-
$[\text{Cu}(\text{H}_2\text{L}^1)]$	254.7 <sup>o</sup> C	Light Yellow	65.23 (65.29)	3.64 (3.70)	6.01 (6.09)	13.78 (13.81)
$\text{H}_2\text{L}^2$	184.3 <sup>o</sup> C	Yellow	72.26 (72.34)	4.51 (4.55)	6.69 (6.74)	-
$[\text{Cu}(\text{H}_2\text{L}^2)]$	258.3 <sup>o</sup> C	Yellow	62.94 (63.02)	3.51 (3.57)	5.82 (5.88)	13.29 (13.34)

**Table 2.**  
**Molar conductance and magnetic moment data of coordination compounds**

Coordination compounds	Solvent	Molar conductance ( $\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$ )	Observed magnetic moment (B.M)
[Cu(H <sub>2</sub> L <sup>1</sup> )]	DMF	12	1.76
[Cu(H <sub>2</sub> L <sup>2</sup> )]	DMF	18	2.20

**Table 3.**  
**Infrared spectral data of Schiff base ligands and their complexes.**

Compound	$\nu(\text{O}-\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
H <sub>2</sub> L <sup>1</sup>	2725	1618	1327	–	–
[Cu (H <sub>2</sub> L <sup>1</sup> )]	–	1609	1361	530	472
H <sub>2</sub> L <sup>2</sup>	2705	1616	1325	–	–
[Cu (H <sub>2</sub> L <sup>2</sup> )]	–	1608	1352	537	486

### 3. Results and Discussion

The analytical data of the Schiff bases and their copper (II) complexes are listed in Table 1. The molar conductivity and magnetic moment data of Cu(II) complexes are listed in Table 2. The lower molar conductance values of investigated copper complexes in DMF at room temperature revealed their non-electrolytic nature. All copper complexes are coloured and stable in air.

#### IR Spectra

The IR spectral data of Schiff base ligands and their copper (II) complexes are listed in Table 3. A strong absorption band around 1618-1616  $\text{cm}^{-1}$  in free Schiff base ligands due to azomethine (C=N) vibration, which shifted to lower frequency in the investigated complexes suggests the bond formation of azomethine nitrogen with metal ion [19-21]. The disappearance of the amino group in the spectra of Schiff bases indicates the condensation of diamino groups of diamines with aldehyde groups. The Schiff base ligands show a broad band at 2725-2705  $\text{cm}^{-1}$  is

due to the phenolic stretching vibration (O-H). These are absent in the spectra of investigated copper complexes. The (C-O) stretching vibration appeared at 1327-1325  $\text{cm}^{-1}$  in Schiff bases shifted toward higher frequencies (27-34  $\text{cm}^{-1}$ ) in investigated complexes confirms the phenolic oxygen coordinated with metal ion. Thus, the IR spectral data indicates that Schiff base ligands in the metal complexes behaves as tetradentate and coordinated through two azomethine nitrogen atoms and two phenolic oxygen atoms.

#### Electronic spectra

The electronic absorption spectra of Cu (II) complexes showed a broad unsymmetrical band around 21000 – 24200  $\text{cm}^{-1}$  assigned to the  ${}^2\text{B}_{1g}$   ${}^2\text{A}_{1g}$  transitions and other intense absorption bands are due to charge transfer and intra – ligand transitions. The magnetic moment of Cu (II) complexes has been found to be in the range of 1.76 - 2.20 B.M, square planar geometry has been suggested for these investigated Cu (II) complexes.


## 4. Conclusion

The unsymmetrical Schiff bases were synthesized from the condensation of 1:1:1 molar mixture of 2-hydroxy-1-naphthaldehyde, 4-methyl-1,2-diaminobenzene and substituted salicylaldehyde in ethanolic medium. The synthesized Schiff bases and their copper (II) complexes were characterized by elemental analysis, molar conductivity measurements, magnetic moment measurements, IR and UV-Vis spectral data investigations. The IR spectral data indicates that Schiff base ligands in the metal complexes behaves as tetradentate and coordinated through two azomethine nitrogen atoms and two phenolic oxygen atoms. On the basis of magnetic moment measurements, IR and electronic absorption spectral investigations square planar geometry of the Cu(II) complexes has been proposed.

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