

# Synthesis and Characterisation of Nickel (II) and Copper (II) Metal Complexes with 3-Hydroxy-(2hydroxynaphthalen-1-amino) Butanoic Acid Schiff base Ligand

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## Abstract

In this work, a bidentate Schiff base ligand 3-hydroxy-(2hydroxynaphthalen-1-amino) butanoic acid Schiff base ligand(HL) containing N and O as donor heteroatoms has been used to synthesize series of novel stable metal complexes of general composition of  $M(L)_2$  with  $M = Ni$  and  $Cu$ . This ligand was obtained from condensation of 2-hydroxy-1-naphthaldehyde on 2-amino-3-hydroxybutanoic acid in methanolic solutions in which its complexes were obtained by mixing the corresponding metal chloride salt and the ligand in metal 1:2 Ligand molar ratio. The resulting two complexes have been characterized by different analytical techniques like FT-IR, UV-Vis, mass spectroscopy, to identify their molecular structures. The spectroscopic data obtained suggest that the metal is bonded to the ligand through the hydroxylic-like oxygen and the imine-type nitrogen atoms. Electronic and vibrational absorption spectra of both Metal (II) complexes have been proposed for octahedral geometries.

**Keywords:** 3d-Metal Complexes, Schiff Base Ligand, NMR, IR and UV/vis Spectroscopy.

## Introduction

Recently, the coordination of Schiff bases to transition metal ions has been extensively studied in medicine and diagnostics<sup>1-5</sup>. The substituted heterocyclic moiety in combination with transition metal salts generates coordination compounds which possess enhanced physicochemical and pharmacological properties<sup>5-9</sup>. Schiff bases ligands are an important class of ligands that coordinate to transition metal ions via azomethine group. Due to high electron density on nitrogen atom of azomethine group (-CH=N-) makes them good chelating<sup>10-15</sup>. The azomethine group of transition metal complexes have been reported remarkable properties like microbial activities, anticancer, antimalarial, antipyretic, antiproliferative and antidiabetic activities. These complexes are also applicable any branch of Chemistry and technology<sup>16, 17</sup>. Schiff base ligands containing of azomethine groups especially when -OH groups are present increases their coordination ability. Schiff base ligands and their transition metal complexes are used as pigments industry, drug developments industry, dyes industry and polymer stabilizers industry. Although a huge number of Schiff base ligand and transition metal complexes have been found out, identical studies on coordinated ligands are cooperativity hard to reach.

The most metal complexes of Schiff base have been containing O-donor and N-donor ligands are well familiar. They have the most interested among the chemists due to their applications in catalysis and their relevance to bioinorganic systems<sup>18-21</sup>. During last twenty years there has been demand owing to interaction with deoxyribonucleic acid. This interaction has been broadly studied to development of new chemical compounds in the field of medicine and biotechnology. In the present study, we have synthesized Schiff base ligand by condensation and characterized by spectroscopically of nickel and copper metal complexes containing 3-hydroxy-(2-hydroxynaphthalen-1-methylene-amino) butanoic acid(HL) which are derived from 2-hydroxy-1-naphthaldehyde and 2-amino-3-hydroxybutanoic acid.

### Aim of the Study

In this study, a bidentate Schiff base ligand 3-hydroxy-(2-hydroxynaphthalen-1-amino) butanoic acid and nickel and copper complexes have been synthesized. Schiff was containing Nitrogen (N) and oxygen (O) groups. They coordinated with metal ions. These compounds analysis by different spectral and physico chemical techniques and found that Copper complexes has octahedral geometry but Nickel complex has square planer geometry. Both complexes was stable at room temperature.

### Experimental

#### Material and reagents

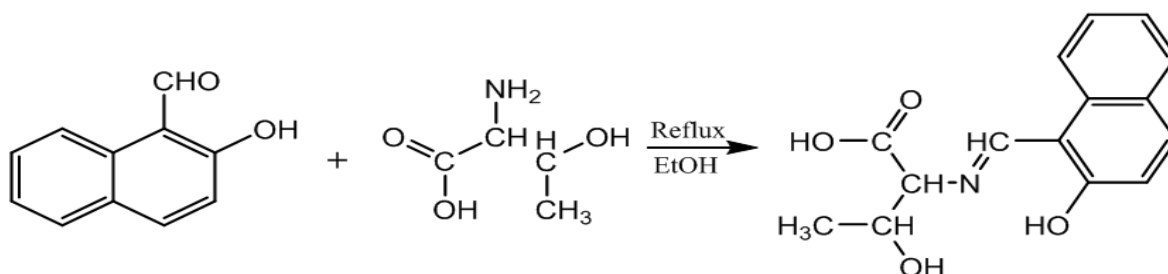
2-hydroxy-1-naphthaldehyde and 2-amino-3-hydroxybutanoic acid (Sigma) were of reagent grade and used as received. Metals chloride ( $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ ) and all solvents were purchased from Merck. All the reactions were carried out of room temperature  $25 \pm 1^\circ\text{C}$ .

### Instrumentation and Methods

The instantaneous analysis was recorded at the Regional Sophisticated Instrumentation Centre, CDRI-Lucknow. IR spectra were recorded on a "Perkin-Elmer 783" IR spectrophotometer. The TMS was used as a reference solvent to record 1 H and 13 C NMR spectra using NMR spectrometer. The UV-visible spectra of the complex were recorded on Shimadzu UV-1601 spectrophotometer. An open capillary tube method was used to determine the melting point of newly prepared compounds.

#### Synthesis of Schiff Base Ligand (HL)

2-hydroxy-1-naphthaldehyde (1.12g) and 2-amino-3-hydroxybutanoic acid (1.72 g) were heated under reflux in ethanol (20 mL) until a solid precipitate was formed (2 hrs). The mixture was allowed to cool at  $25^\circ\text{C}$  and washed with ethanol, filtered under reduced pressure. Yellowish product was obtained (Scheme 1) and monitored by TLC.



Scheme 1: synthesis of HL

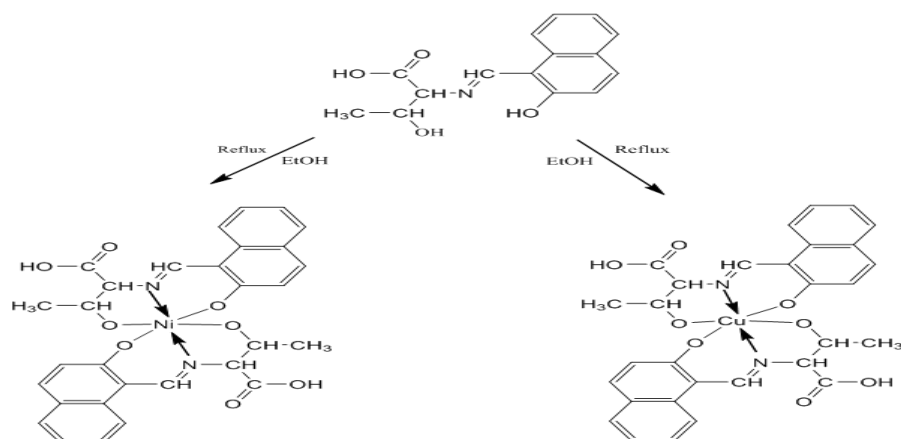
Table 1: Represent Analytical and spectral Data of Schiff Base Ligand

Chemical Formula	$\text{C}_{15}\text{H}_{15}\text{NO}_4$
Yield	87%
Melting point	$240^\circ\text{C}$
Critical temperature	$1022.85^\circ\text{K}$
Critical pressure	31.63 Bar
Exact Mass	273.08
Molecular Mass	274.08
Mass to charge ratio (m/z)	273.08 (100%), 274 (35.3%), 275.09 (1.4%)
Elemental Analysis Found (calc.)	C, 65.96 (67.74); H, 5.32 (4.12); N, 5.99 (9.50)
IR (KBr) $\text{cm}^{-1}$	3370 (OH), 3156 (NH str.), 1658 (C=O), 1600 (N=C), 1562 (Ar-C-C), 1308 (C-N), 1213 (C-O)
$^1\text{H}$ NMR (400 MHz, $\text{DMSO-d}_6$ ) $\delta$ ppm	12.78 (s, 1H, Ar. C-OH), 9.71(1H, CH=N), 7.1-8.00 (s, 2H, aromatic ring), 7.3 (1H, OCH), 6.8 (1H, aromatic ring)
$^{13}\text{C}$ NMR (400 MHz, $\text{DMSO-d}_6$ ) $\delta$ ppm	154.7 (C=O), 151.4 (C=N), 126.6, 122.9, 115.8, 112.4, 108.3 (aromatic and furan rings)

#### Synthesis of Cobalt, Nickel and Copper metal (II) complexes

All the metal (II) complexes were synthesized by following general method as following. 50 mL ethanolic solution of HL (0.002 mmol, 0.550 g) was added dropwise into 20 mL ethanolic solution of

corresponding metal (II) chloride salts (0.001 mmol) in 1:2 M ratio. Colourful products were obtained (Scheme-2) wash with hot water and then with acetone, filtered under reduce pressure and monitored by TLC.



**Scheme 2: Synthesis of metal complexes with HL  
Analytical and Spectral Data of Metal Complexes  
Nickel (II) Complex**

Chemical formula:  $C_{30}H_{26}N_2NiO_8$ ; Yield: 75%; MP: 270 °C; Mol. wt. 603; colour: red; analytical data found (calc.): C, 59.74 (60.15); H, 4.68 (4.11); N, 4.64 (4.09); IR (KBr,  $cm^{-1}$ ): 3216 (NH), 1620 (C=O), 1580 (C=N), 3315 (OH),  $^1H$  NMR (DMSO- $d_6$ )  $\delta$  ppm: 11.60 (s, 1H, OH-Ar), 7.18-7.93 (m, 8H, Ar), 8.12 (s, 1H, CH=N).  $^{13}C$  NMR (DMSO- $d_6$ )  $\delta$  ppm: 117.53-101.07 (11C, CH-Ar.), 133.65 (1C, C=O), 144.85 (1C, CH=N). m/z: 602.10 (100 %), 604 (34%), 603 (32%), 604 (15%), 605 (6%), 603 (4%).

**Copper (II) Complex**

Chemical formula:  $C_{30}H_{26}CuN_2O_8$ ; Yield: 88%; MP: 270 °C; Mol. wt. 606; colour: blue; analytical data found (calc.): C, 59.45 (60.15); H, 4.32 (4.21); N, 4.62 (4.29); IR (KBr,  $cm^{-1}$ ): 3211 (NH), 1615 (C=O), 1586 (C=N), 3335 (OH),  $^1H$  NMR (DMSO- $d_6$ )  $\delta$  ppm: 11.60 (s, 1H, OH-Ar), 7.18-7.63 (m, 8H, Ar), 8.02 (s, 1H, CH=N).  $^{13}C$  NMR (DMSO- $d_6$ )  $\delta$  ppm: 117.03-101.02 (11C, CH-Ar.), 133.15 (1C, C=O), 144.15 (1C, CH=N). m/z: 605.10 (100 %), 607 (44%), 606 (32%), 608 (15%), 607 (5%), 609 (2%), 607 (2%)

**Results and discussion**

The ligand synthesized here is a yellow coloured, stable compound which dissolves in  $CHCl_3$ , DMF and DMSO. The analysis of the elements present in the ligand (Table 1) gives considerable evidence to the mentioned formula. The recorded mass spectrum gives the molecular ion peak at  $m/z = 274 [M+1 (35 \%)]$  for the ligand which is same as that of the formula weight of the ligand. The two azomethine protons exhibit two singlets at 9.71 ppm and 8.94 ppm in the  $^1H$ -NMR spectrum<sup>22</sup>. The protons of the aromatic ring appeared at 6.96-8.33 ppm range. The methyl protons present in Schiff base ligand moiety shows peaks at 3.11 ppm. The  $^{13}C$ -NMR spectrum, displayed the peaks of the azomethine carbons at 160.57 ppm. The carbon atoms present in the aromatic ring resonate at 117-153 ppm range. The methyl carbon atoms present in Schiff base moiety appears at 35.65 ppm. The methoxy group of methyl carbon displayed a band at 56.20 ppm. The FTIR

spectral signals of Schiff base<sup>23</sup> ligand exhibited bands at  $1645\text{ cm}^{-1}$  and were assigned to the stretching frequency of the azomethine groups present in the Schiff base ligand. In this ligand, sharp band present at  $1079\text{ cm}^{-1}$  was because of the stretching frequency of C-O group. A broad band present around  $3448\text{ cm}^{-1}$  is due to the OH group of the ligand.

The characterization results of the synthesized metal (II) complexes result gave the information about the metal to ligand ratio which is found to be 1:2 in both complexes. The metal(II) complexes are found to dissolve in  $CHCl_3$ , DMF and DMSO<sup>24</sup>. The mass spectra of the synthesized nickel (II) and copper (II) complexes show peaks of molecular ion at  $m/z$ : 602.10 (100 %), 604 (34%), 603 (32%), 604 (15%), 605 (6%), 603 (4%). and  $m/z$ : 605.10 (100 %), 607 (44%), 606 (32%), 608 (15%), 607 (5%), 609 (2%), 607 (2%) respectively and that is in agreement with those of the calculated formula weights of synthesized complexes. All the metal(II) complexes are known to possess non-electrolytic nature which is indicated by their low levels in the molar conductance measurement values.

FTIR spectral information for the synthesized metal(II) complexes are provided in above statements. FTIR bands at  $1645\text{ cm}^{-1}$  of the azomethine groups of the free ligand moved to low frequency range of  $1641\text{ cm}^{-1}$  in the metal complexes gave evidence for the coordination of the metal ion with azomethine nitrogen atom. Spectral broad band present in  $\sim 3400\text{ cm}^{-1}$  is assigned for the stretching vibrations of water molecules in coordination with the complex. A band seen at  $\sim 840\text{ cm}^{-1}$  in the metal (II) complexes is due to the coordinated water molecule. All the synthesized metal(II) complexes showing spectral bands in  $580\text{--}610\text{ cm}^{-1}$  range may be mainly because of the formation of M-O bonds. For the nickel (II) complex, the electronic spectrum shows three different bands in the region 1025, 620, and 390 nm assigned to  $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ ,  $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ , and  $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$  transitions<sup>25</sup>. This is an indication of octahedral geometry of the nickel (II) ion. The magnetic moment of nickel (II) complex was calculated to be 3.05 BM, which coincide with the normal observed range for nickel (II) octahedral

complexes. The UV spectrum of copper (II) complex shows a broad band in 700 nm region that can be given to  ${}^2E_g \rightarrow {}^2T_{2g}$  transition, suggesting the copper complex to possess distorted octahedral geometry. When the odd number of electrons enters the  $E_g$  orbital, of an octahedral copper complex, the Jahn-Teller effect will be most prominent. The measured magnetic moment value for copper (II) complex is 1.95 BM and that is similar in observation of octahedral copper (II) complexes<sup>26</sup>.

### Conculsion

Schiff Base Ligand and their metal complexes have various application in different fields. Due to a wide applications and used we synthesized the novel Schiff base ligand and its metal complexes and they have also charactered by NMR, IR UV/vis, spectroscopically.

### References

1. S. S. Sivakumar and M. R. P. Kurup, "Structural studies of six and four coordinate zinc(II), nickel(II) and dioxovanadium(V) complexes with thiosemicarbazones," *Journal of Molecular Structure*, vol. 655, no. 1, pp. 47-58, 2003.
2. P. Bindu, M. R. P. Kurup, and T. R. Satyakeerthy, "Epr, cyclic voltammetric and biological activities of copper(II) complexes of salicylaldehyde N(4)-substituted thiosemicarbazone and heterocyclic bases," *Polyhedron*, vol. 18, no. 3-4, pp. 321-331, 1999.
3. R. P. John, A. Sreekanth, M. R. P. Kurup, A. Usman, A. R. Ibrahim, and H. K. Fun, "Spectral studies and structure of a 2-hydroxyacetophenone 3-hexamethyleneiminy l thiosemicarbazone (-2) copper(II) complex containing 1,10-phenanthroline," *SpectrochimicaActa A*, vol. 59, no. 6, pp. 1349-1358, 2003.
4. Y. F. Yuan, J. T. Wang, M. C. Gimeno, A. Laguna, and P. G. Jones, "Synthesis and characterisation of copper complexes with N-ferrocenoyl-N'-aryl(alkyl)thioureas," *InorganicaChimicaActa*, vol. 324, no. 1-2, pp. 309-317, 2001.
5. C. K. Alphonsa and M. R. P. Kurup, "Synthesis and characterization of nickel(II) compixxes of zacetylpyridinethiosemicarb, one," *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, vol. 29, no. 5, pp. 805-815, 1999.
6. Sreekanth, U. L. Kala, C. R. Nayar, and M. R. P. Kurup, "Cobalt(III) complexes of 2-hydroxyacetophenone N(4)-phenyl semicarbazone containing heterocyclic coligands: syntheses, structure and spectral studies," *Polyhedron*, vol. 23, no. 1, pp. 41-47, 2004.
7. K. Saberyan, E. Zolfonoun, M. Shamsipur, and M. Salavati-Niasari, "Amberlite XAD-4 impregnated with a new pentadentate Schiff base: a chelating collector for separation and preconcentration of trace amounts of gallium (III) and indium (III)," *ActaChimicaSlovenica*, vol. 57, no. 1, pp. 222-229, 2010.
8. R. Paital, D. Mandal, X. Huang, G. Aromi, and D. Ray, "Structure and dimensionality of coordination complexes correlated to piperazine conformation: from discrete [Cu2II] and [Cu4II] complexes to a  $\mu$ 1,3- $N_3^-$  bridged [Cu2II]<sub>n</sub> chain," *Dalton Transactions*, vol. 23, no. 8, pp. 1352-1362, 2009.
9. J. G. Malecki, "Synthesis, crystal, molecular and electronic structures of ruthenium complexes with a benzoxazole derivative ligand," *Polyhedron*, vol. 31, pp. 159-166, 2012.
10. Demir, M. Bayrakci, K. Mutlu, and A. I. Pekacar, "Synthesis and characterization of a novel iminooximeschiff base ligand and its complexation with copper(II), nickel(II), zinc(II), cadmium(II), and cobalt(II)," *ActaChimicaSlovenica*, vol. 55, no. 1, pp. 120-124, 2008.
11. M. Kwiathowski and G. Bandoli, "Nickel(II) complexes with unsymmetrical quadridentate Schiff bases having a pendant N-acyl substituent," *Journal of the Chemical Society Dalton Transactions*, no. 3, pp. 379-384, 1992.
12. Z. X. Lei, Q. Y. Zhu, X. Zang, W. Luo, W. Q. Mu, and J. Dai, "Indium-sulfursupertetrahedral clusters integrated with a metal complex of 1,10-phenanthroline," *Inorganic Chemistry*, vol. 49, no. 10, pp. 4385-4387, 2010.
13. D. L. Grisenti, M. B. Smith, L. Fang, N. Bishop, and P. S. Wagenknecht, "A convenient synthesis of isocyclam and [16]aneN<sub>4</sub> and the photophysics of their dicyanochromium(III) complexes," *InorganicaChimicaActa*, vol. 363, no. 1, pp. 157-162, 2010.
14. C. Kriza and T. Parnau, "Complexes of tin (IV) with some bidentate Schiff bases derived from 1-H-indol-2,3-dione," *ActaChimicaSlovenica*, vol. 48, no. 3, pp. 445-452, 2001.
15. V. Aanandhi, S. George, and V. Vaidhyalingam, "Synthesis and antimicrobial activities of 1-(5-substituted-2-oxo indolin-3-ylidene)-4-(substituted pyridin-2-yl) thiosemicarbazide," *Arkivoc*, vol. 2008, no. 11, pp. 187-194, 2008.
16. Z. H. Chohan, A. Munawar, and C. T. Supuran, "Transition metal ion complexes of Schiff-bases. Synthesis, characterization and antibacterial properties," *Metal-Based Drugs*, vol. 8, no. 3, pp. 137-143, 2001. V
17. D. Kovala-Demertzi, A. Domopoulou, M. Demertzis, C. P. Raptopoulou, and A. Terzis, "Coordinating properties of 2-acetylpyridine thiosemicarbazone. Palladium (II) complexes with neutral and deprotonated ligand. X-ray structure of bromo(2-acetylpyridine thiosemicarbazonato) palladium(II)," *Polyhedron*, vol. 13, no. 12, pp. 1917-1925, 1994.
18. D. X. West, H. Gebremedhin, R. J. Butcher, and J. P. Jasinski, "Molecular structure and spectral properties of bromo(2-acetylpyridine)<sup>4</sup>Ncopper (II)," *Transition Metal Chemistry*, vol. 20, no. 1, pp. 84-87, 1995.
19. M. A. Jasim and A. Karawi, "Synthesis and characterization of a new N<sub>2</sub>S<sub>2</sub> Schiff base ligand and its complexes with nickel(II), copper(II) and cadmium(II) including the kinetics of complex

- formation," *Transition Metal Chemistry*, vol. 34, no. 8, pp. 891-897, 2009.
21. K. Clegg, D. J. Bray, K. Gloe et al., "Synthetic, structural, electrochemical and solvent extraction studies of neutral trinuclear Co(ii), Ni(ii), Cu(ii) and Zn(ii) metallocycles and tetrahedral tetranuclear Fe(iii) species incorporating 1,4-aryl-linked bis- $\beta$ -diketonato ligands," *Dalton Transactions*, no. 10, pp. 1331-1340, 2008.
  22. Z. F. Dawood, T. J. Mohammed, and M. R. Sharif Iraqi, "New nickel (II) complexes with benzilbis (semicarbazone) and dithiocarbamate ligands," *Journal of Veterinary Science*, no. 23, supplements 2, pp. 135-141, 2009.
  23. E. Champeil, M. M. Paz, S. Ladwa, C. C. Clement, A. Zatorski, and M. Tomasz, "Synthesis of an oligodeoxyribonucleotide adduct of mitomycin C by the postoligomerization method via a triaminomitosene," *Journal of the American Chemical Society*, vol. 130, no. 29, pp. 9556-9565, 2008.
  24. V. Philip, V. Suni, M. R. PrathapachandraKurup, and M. Nethaji, "Structural and spectral studies of nickel(II) complexes of di-2-pyridyl ketone N4,N4-(butane-1,4-diyl) thiosemicarbazone," *Polyhedron*, vol. 23, no. 7, pp. 1225-1233, 2004.
  25. P. Bindu, M. R. P. Kurup, and T. R. Satyakeerthy, "Epr, cyclic voltammetric and biological activities of copper(II) complexes of salicylaldehyde N(4)-substituted thiosemicarbazone and heterocyclic bases," *Polyhedron*, vol. 18, no. 3-4, pp. 321-331, 1999.
  26. S. Arayne, N. Sultana, U. Haroon, and M. A. Mesaik, "Synthesis, characterization, antibacterial and anti-inflammatory activities of enoxacin metal complexes," *Bioinorganic Chemistry and Applications*, vol. 2009, Article ID 914105, 6 pages, 2009.
  27. H. Torayama, T. Nishide, H. Asada, M. Fujiwara, and T. Matsushita, "Preparation and characterization of novel cyclic tetranuclear manganese (III) complexes: MnIII<sub>4</sub>(X-salmphen)<sub>6</sub> (X-salmphenH<sub>2</sub> = N,N-di-substituted-salicylidene-1,3-diaminobenzene (X = H, 5-Br))," *Polyhedron*, vol. 16, no. 21, pp. 3787-3794, 1997.