



# STUDY OF SOME NOVEL COMPLEXES OF Ni(II) WITH NITROGEN, OXYGEN AND SULPHUR DONOR SCHIFF BASE

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## Abstract:

Some novel complexes of Ni(II) with Schiff base 3-hydroxy-2-(2-mercaptobenzylideneimino) pyridine (LH<sub>2</sub>) in presence of auxiliary ligands ammonia, pyridine and  $\pi$ -picoline have been synthesised and characterised on the basis of elemental analysis, molar mass determination, molar conductance and magnetic susceptibility measurements, IR, UV and <sup>1</sup>H NMR spectral studies. The complexes have been formulated as [Ni(L)(B)<sub>3</sub>], where L=dideprotonated 3-hydroxy-2-(2-mercaptobenzylideneimino) pyridine and B=ammonia, pyridine and  $\pi$ -picoline. All the complexes showed non-electrolytic nature indicated by their molar conductance values of 16-24 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. The range and number of u.v. spectral bands and magnetic moment values indicated octahedral geometry of complexes. IR spectral bands indicated the nature of metal –ligand bonding in complexes whereas <sup>1</sup>H NMR spectral studies accounted for all the protons in complexes.

**Key Words:** Schiff base, magnetic susceptibility, spectral investigation, molar conductance.

## INTRODUCTION:

Schiff bases have been the area of research interest for inorganic and bioinorganic chemists since they were reported by Hugo Schiff in 1864. They are used as catalysts in several reactions such as polymerisation, reduction of thionyl chloride, aldol reaction, Henry reaction, epoxidation of alkenes, hydrolysis of ketones, etc [1, 2]. Schiff bases have remarkable biological activities against many pathogenic bacteria, fungi and certain cancerous cells [3, 4]. Azomethine group (>C=N-) present in Schiff bases is responsible for their biological activities [5]. Schiff bases exhibit biological activities such as insecticidal [6], antileukemia[7], anti-inflammatory [8], anti-HIV [9], antimycobacterial [10], antioxidant [11], anti-cancer[12] and plant growth regulatory activity [13] among others.

Keeping in view the wide range of applications of Schiff bases and their complexes, we have synthesised and characterised some novel complexes of Ni(II) with nitrogen, oxygen and sulphur donor Schiff base ligand.

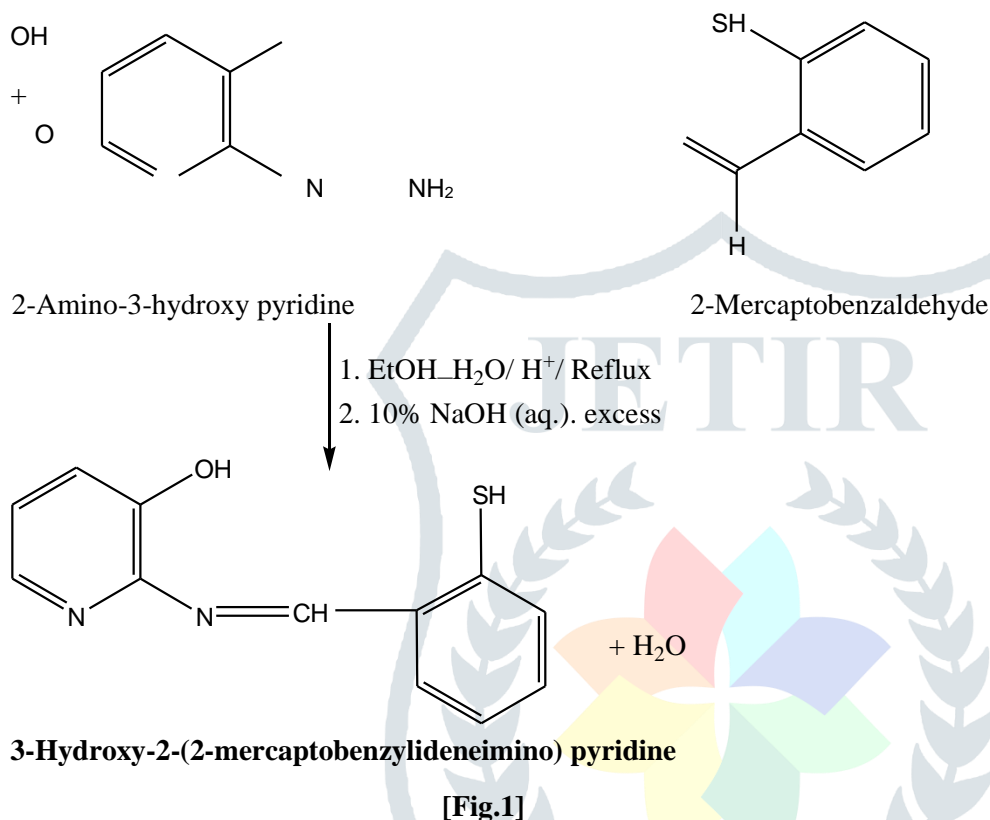
## MATERIALS AND METHODS:

- 2.1 Preparation of the ligand 3-hydroxy-2-(2-mercapto benzylideneimino) pyridine, LH<sub>2</sub>:** 0.01mole (1.10g) of 2-amino-3-hydroxy pyridine was dissolved in ethanol-water(60:40, v/v) solution. This aqueous-ethanolic solution was mixed with an ethanolic solution of 2-mercaptobenzaldehyde.

2.0 ml of bench hydrochloric acid solution was added to the mixture solution. This was refluxed in a 100 ml round bottom flask using water condenser for about 2 hours. This solution was allowed to cool in ice-cold water and excess of 10% NaOH aqueous solution was added to it. This resulted in the precipitation of a white solid which was filtered, washed with water and then crystallised in ethanol. It was then dried over anhydrous CaCl<sub>2</sub> in a desiccator. Its m.p. was recorded to be 138°C.

The yield was approximately 80%.

The scheme of preparation of the ligand is shown in Fig. 1.



## 2.2 Preparation of complexes of Ni(II) with 3-hydroxy-2-(2-mercaptobenzylideneimino) pyridine (LH<sub>2</sub>) in presence of ammonia/pyridine/□-picoline:

0.01 mole of the ligand LH<sub>2</sub> was dissolved in minimum volume of ethanol. To this solution, an aqueous solution containing 0.01 mole (2.38g) of nickel (II) chloride was added and the mixture was refluxed on a water –bath using water condenser for about 4 hours with 0.03 mole of ammonia/pyridine/□-picoline. The solution was then allowed to cool overnight when coloured solid separation out. It was filtered washed with water and then with acetone. It was then crystallised in DMF and dried over anhydrous CaCl<sub>2</sub> in a desiccator. The m.p. of the solid was recorded. The yield was approximately 75-78%.

## 2.3 Analytical Methods:

The molar conductance of complexes was determined in DMF solution by conductivity meter bridge manufactured by Wiss-Techen Stahen type- LBR at room temperature. The electronic spectra of complexes were recorded with Hitachi-320 spectrophotometer. I.R. spectra of the ligand and complexes were recorded as nujol mull on Perkin Elemer 577 sepectrometer. <sup>1</sup>H NMR spectra of the ligand and complexes was recorded in DMSO-d<sub>6</sub> on Varian Gemini XL 200 spectrophotometer taking TMS as reference. Magnetic susceptibilities of complexes were determined by Gouy's

magnetic balance. Nickel was estimated as nickel dimethyl glyoximate in slightly alkaline solution. Molar masses of complexes were determined by cryoscopic method.

## RESULTS AND DISCUSSION:

**3.1 Microanalytical data:** From microanalytical data (Table-1), the stoichiometries of complexes were established.

Table-1

Micronalytical data of complexes

Sl. No.	Complex Compound	Colour	M.P.	Mol. Mass found (calculated) g mol <sup>-1</sup>	% found (% calculated)				
					C	H	N	S	Ni
1.	[Ni(L)(NH <sub>3</sub> ) <sub>3</sub> ]	Green	170°C	336 (337.7)	42.68 (42.64)	5.15 (5.04)	20.76 (20.73)	9.38 (9.47)	17.26 (17.38)
2.	[Ni(L)(C <sub>5</sub> H <sub>5</sub> N) <sub>3</sub> ]	Light Green	178°C	528 (523.7)	61.75 (61.86)	4.44 (4.39)	13.21 (13.37)	6.08 (6.11)	11.26 (11.21)
3.	[Ni(L)(C <sub>6</sub> H <sub>7</sub> N) <sub>3</sub> ]	Green	185°C	568 (565.7)	63.58 (63.64)	5.08 (5.12)	12.41 (12.37)	5.69 (5.66)	10.36 (10.37)

L=dideprotonated 3-hydroxy-2-(2-mercaptobenzylideneimino) pyridine

C<sub>5</sub>H<sub>5</sub>N= Pyridine, C<sub>6</sub>H<sub>7</sub>N (□-picoline)

Microanalytical data and observed molar masses of complexes are in good agreement with proposed molecular formula of complexes. The observed molar masses proved monomeric nature of complexes.

**3.2 Molar conductance:** The molar conductance values of complexes were in the range 16-24 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> which indicated their non-electrolytic nature [14].

**3.3 Magnetic moment:** All the complexes were paramagnetic with magnetic moment values in the range 2.92 to 3.10 B.M. indicating octahedral environment of ligands around Ni(II) in complexes.

**3.4 Electronic spectra:** All the complexes displayed three electronic spectral binds with assignments- 3 3 □1

$A F_{2g}( ) \square T F at_{2g}( )$ , 9500 10415□  $cm_{3 3}$  □1  $A F_{2g}( ) \square T F at_{2g}( )$ , 14200  
14940□  $cm_{3 3}$  □1

$A F_{2g}( ) \square T P at_{1g}( )$ , 23500□24000 $cm$

The number and positions of electronic spectral bands indicate the octahedral nature of Ni(II) complexes.

**3.5. Infrared spectra:** The medium intensity band at 1680  $cm^{-1}$  in the I.R. spectrum of the ligand

(LH<sub>2</sub>) assignable to  $\square_{C=N}$  (azomethine) mode of vibration got red-shifted by 10-20  $cm^{-1}$  in spectra of complexes indicating coordination of nitrogen of  $>C=N-$  to Ni(II) in complexes. The broad band in the

IR spectrum of the ligand (LH<sub>2</sub>) at 3510  $cm^{-1}$  due to  $\square_{OH}$  (hydrogen bonded) disappeared in all  $-OH$  group and

coordination of deprotonated  $-OH$  to metal ion through the oxygen atom. It is further supported by the appearance of

new bands in the region 420-450  $cm^{-1}$  assignable to  $\square_{Ni-O}$  mode of vibrations [15]. The band at 2480  $cm^{-1}$  in the spectrum

of the ligand (LH<sub>2</sub>) due to  $\square_{S-H}$  mode of vibrations disappeared in all the complexes. This indicated the deprotonation of

$-SH$  group and coordination of deprotonated  $-SH$  through sulphur atom to the metal ion. The coordination through

sulphur atom is further supported by the appearance of new bands in the region 285–295  $cm^{-1}$  in spectra of complexes

which may be assigned to  $\square_{Ni-S}$  mode of vibrations [16]. Two new bands appear at 3380 and 3260  $cm^{-1}$  in ammine

complexes. These bands may be assigned to antisymmetric and symmetric modes of vibrations respectively due to

$\square_{NH_2}$  of coordinated ammonia. New bands at

1014  $cm^{-1}$  and 936  $cm^{-1}$  appeared in complexes of pyridine and  $\square$ -picoline respectively which may be reasonably

assigned to breathing mode of vibration of pyridine ring. New bands in far infrared region at 355-380  $cm^{-1}$  appeared in

complexes assignable to  $\square_{Ni-N}$  mode of vibrations. This indicated the coordination of the ligand (s) through nitrogen atom

to the metal ions. IR spectra of complexes established the nature of metal-ligand bonding in complexes.

**3.6. <sup>1</sup>H NMR spectra:** All the complexes displayed a multiplet centred at  $\square=7.2-7.4$ ppm corresponding to four protons

which may be assigned to four protons of the disubstituted benzene ring. All the complexes displayed a multiplet signal

centred at  $\square=8.3-8.5$  ppm corresponding to three protons which are assignable to three protons of the disubstituted

pyridine moiety. A singlet signal is displayed at  $\square=9.8-9.9$  ppm corresponding to one proton which may be assigned to

the proton of the azomethine ( $-CH=N-$ ) group of the ligand (LH<sub>2</sub>). Ammine complexes exhibited a singlet signal

corresponding to nine protons at  $\square=4.2-4.3$  ppm assignable to the nine protons of the three coordinated ammonia

molecules. Pyridine and  $\square$ -picoline complexes exhibited an additional multiplet signal centred at  $\square=8.8-8.9$  ppm

corresponding to 15 and 12 protons respectively. This signal may be assigned to the fifteen protons of the three

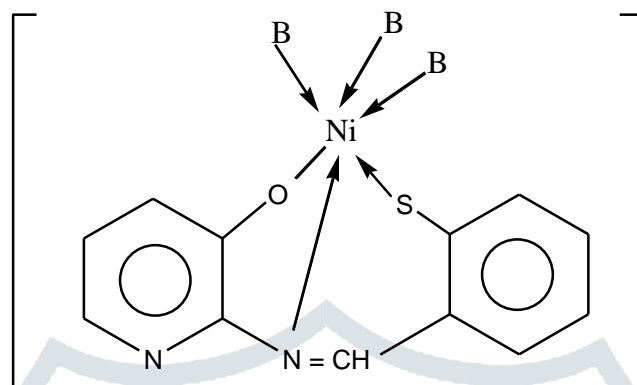
coordinated pyridine molecules and twelve protons of the three  $\square$ -picoline molecules. The  $\square$ -picoline complex displayed

a singlet signal at  $\square=1.2-1.4$  ppm corresponding to nine protons which may be assigned to the nine protons of three

methyl groups of coordinated  $\square$ -picoline molecules. <sup>1</sup>H NMR spectra accounted for all the protons present in complexes.

#### 4. CONCLUSION:

On the basis of elemental analysis, molar mass determination, molar conductance and magnetic moment measurements, IR, UV and  $^1\text{H}$  NMR spectral studies, the following octahedral geometry for the complexes has been proposed-



$\text{B}=\text{NH}_3$ , pyridine ( $\text{C}_6\text{H}_5\text{N}$ ),  $\square\square$ picoline( $\text{C}_6\text{H}_7\text{N}$ )

[Fig. 2]

All the complexes are paramagnetic and non-electrolytic in nature. The ligand 3-hydroxy-2-(2mercaptobenzylideneimino) pyridine ( $\text{LH}_2$ ) behaves as dianionic tridentate ligand in all the complexes.

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