

## Synthesis and Characterization of some Transition metal complexes derived from Bidentate Schiff Base Ligand

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**Abstract:** A new Schiff base has been synthesized from 3-(3-nitrophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde and *O*-amino phenol. Metal complexes of the Schiff base have been synthesized from acetate salt of Cu (II), Co (II) and Ni (II) metal in the alcoholic medium. The newly prepared Schiff base ligand and metal complexes have been characterized by various physicochemical techniques such as Elemental analysis, Magnetic moment, molar conductance method, UV/ Visible, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectral technique and thermo gravimetric studies. On the basis of elemental and spectral studies, six coordinated geometry was assigned to these complexes. In the presence of these results, it is suggested that this ligand act as a bidentate ligand. UV/Visible, IR and TGA studies confirmed the presence of the coordinated water molecules in the metal complexes.

**Keywords:** Schiff base, Metal complex, Spectral studies.

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### I. Introduction

Coordination chemistry is an important branch of inorganic chemistry since the appearance of water on earth aqua complex ion of metal must have existed [1]. Schiff bases have often been used as chelating ligands in coordination chemistry [2-3], they are more effective as a chelating agent when they bear supporting and stabilizing group like -OH close to -HC=N- group. Bidentate group containing imine groups have also been used as the modulators of structure and electronic properties of transition metal centers. The ligand Schiff base finds its applications as the analytical reagent for determination of metals [4-5]. Transition metal complexes containing the Schiff base ligands have been interest for many years [6-8]. In this work, we report the results of our studies on the synthesis and spectral properties of Schiff base and its Cu (II), Ni (II) and Co (II) metal complexes.

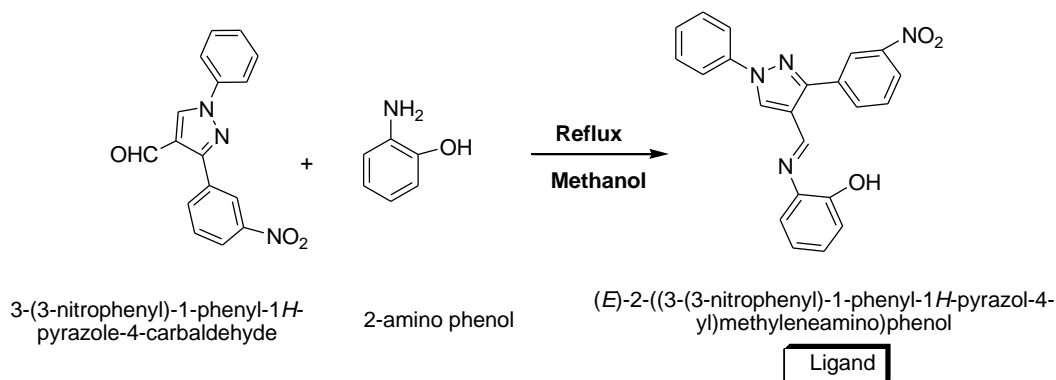
### II. Experimental

#### 2.1 Material and method

All the chemicals used were of AR grade. Cobalt (II), Nickel (II) and Copper (II) used as acetate salts were of Merck. Pyrazole aldehyde was synthesized by very well-known *Vilsmeier-Haack* [9] reaction and purified by usual separation methods. Elemental analyses were carried out on EURO EA-3000 RS-232. IR spectra were recorded on 8400 FTIR Shimadzu spectrometer. <sup>1</sup>HNMR spectra of the ligand and complexes in DMSO-d<sub>6</sub> were recorded on a Bruker Advance II 400 Spectrometer at room temperature using TMS as internal standard. UV-Visible spectra were recorded on Shimadzu Pharmaspec UV-1700 UV visible spectrometer. Mass spectra of ligands were recorded on GC-MS QP-2010 spectrometer. The ESI mass spectra of metal complexes were recorded on micromass Q-ToF Micro spectrometer. Thermal analyses have been carried out by using Shimadzu (TGA-50H) from room temperature to 1000°C under heating rate of 15<sup>0</sup>C min<sup>-1</sup>.

#### 2.2 Preparation of Schiff base

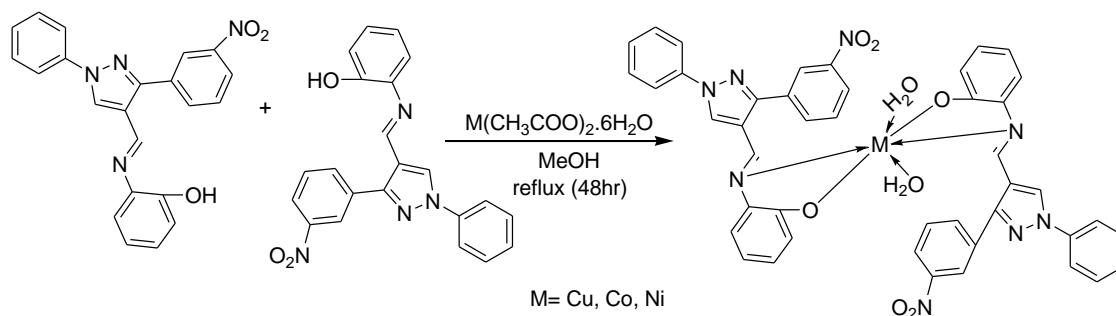
The Schiff base was prepared by condensation of 3-(3-nitrophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde (0.01 mol) with *o*-amino phenol (0.01 M) in ethanol (30 ml), and the mixture was refluxed for 8 hrs. The progress of reaction was monitored by TLC (solvent system, benzene: acetone- 8:2). After completion of the reaction, the reaction mixture was poured over crushed ice. The separated solid product was filtered and washed with cold saturated sodium bisulphate solution and recrystallized with ethanol.



Scheme-1

### 2.3 Synthesis of metal complexes

A solution of the metal salt (0.005mol) mixed drop wise with the solution of Schiff base (0.01mol) in 20 ml ethanol. The mixture was refluxed for 48 hours in 70-80°C on water bath. On cooling, colored solid product was collected by filtration and then washed several times with hot ethanol until the washing becomes colorless. The product was dried in air and stored in desiccators over anhydrous  $\text{CaCl}_2$  under vacuum. All the metal complexes were colored and stable in air and moisture.



Scheme-2

## III. Result and Discussion

The analytical and physical data of Schiff base ligand and its metal complexes are given in table-1. The data shows that the ligand L forms a 1:2 (M: L) complexes with Cu (II), Ni (II), Co (II), ions. The prepared complexes were found to have the general formulae  $[\text{M}(\text{L})_2 \cdot n\text{H}_2\text{O}]$ . Where M= Cu (II), Ni (II), Co (II), n=2 and L is Schiff base ligand. it coordinates as an anion by losing proton of the phenolic group. The charge on the complex was neutralized by the ligand L. Thus, the complexes were neutral in DMSO.

Table-1: Physical characteristics and analytical data of the complexes

Compound	Formula	Colour	M.P/D.P (°C)	Yield (%)	$\Lambda_m (\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$
L	$\text{C}_{22}\text{H}_{16}\text{N}_4\text{O}_3$	Orange	144	90%	-
$[\text{Cu}(\text{L})_2 \cdot 2\text{H}_2\text{O}]$	$\text{C}_{44}\text{H}_{34}\text{CuN}_8\text{O}_8$	Dark brown	344	72%	3.42
$[\text{Co}(\text{L})_2 \cdot 2\text{H}_2\text{O}]$	$\text{C}_{44}\text{H}_{34}\text{CoN}_8\text{O}_8$	Green	335	70%	3.55
$[\text{Ni}(\text{L})_2 \cdot 2\text{H}_2\text{O}]$	$\text{C}_{44}\text{H}_{34}\text{NiN}_8\text{O}_8$	Yellowish brown	346	68%	4.29

### 3.1 Molar conductance

Molar conductance of the complexes was measured in DMSO at a concentration of 0.001 M. The observed conductance values fall in the range of  $1\text{-}20 \text{ Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ; indicate that the complexes were non-electrolyte in nature. The C, H, and N analysis of Schiff base ligand and its metal complexes were found in good agreement with the expected values.

### 3.2 IR spectra and mode of bonding

The IR spectral data of some important functional groups of the Schiff base ligand and its transition metal complexes presented in table-2. The IR spectrum of the Schiff base ligand showed strong absorption bands at  $1656\text{ cm}^{-1}$  and  $3417\text{ cm}^{-1}$ , which attributed to the characteristic band of the azomethine ( $-\text{HC}=\text{N}-$ ) and phenolic ( $-\text{OH}$ ) group respectively. These frequencies were shifted towards the lower wave number by  $15\text{-}30\text{ cm}^{-1}$  in the spectra of metal complexes suggested the coordination of nitrogen of the azomethine group to the central metal atom in these complexes [10-11]. All the complexes exhibit a broad band in the region  $3200\text{-}3453\text{ cm}^{-1}$  were assigned to the  $\nu$  ( $-\text{OH}$ ) of water, which indicate the presence of lattice or coordinated water molecule [12]. All the IR data suggested that the metal was bonded to the Schiff bases through the phenolic oxygen and the imino nitrogen [13]. The metal to nitrogen bond was detected at frequencies in the region  $400\text{-}550\text{ cm}^{-1}$  from the IR data. This was confirmed by the presence of the new bands which may be assigned  $\nu(\text{M-N})$ ,  $\nu(\text{M-O})$ . The IR spectra of Cu (II) metal complex presented in fig.1.

**Table-2: Characteristic IR stretching bonds of Schiff base ligand and its metal complexes in  $\text{cm}^{-1}$**

Compound	$\nu$ (H <sub>2</sub> O)	$\nu$ (C=N)	$\nu$ (OH)	$\nu$ (N-N)	$\nu$ (M-N)	$\nu$ (M-O)
L(ligand)	-	1656	3417	1049	-	-
Cu(L) <sub>2</sub> .nH <sub>2</sub> O	3292	1593	-	1089	542	426
Co(L) <sub>2</sub> .nH <sub>2</sub> O	3371	1595	-	1070	491	424
Ni(L) <sub>2</sub> .nH <sub>2</sub> O	3321	1590	-	1066	530	420

### 3.3 <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectrum of the Schiff base ligand was recorded in DMSO-d<sub>6</sub>. In the <sup>1</sup>H NMR spectra of Schiff base ligand, a peak appeared at 9.27ppm was assigned to the proton of phenolic group and a singlet peak appeared at 8.75ppm was assigned to protons of azomethine group.

### 3.4 <sup>13</sup>C NMR spectra

The <sup>13</sup>C NMR spectrum of the Schiff base ligand was recorded in DMSO-d<sub>6</sub>. In the <sup>13</sup>C-NMR spectra of the metal complexes, the signal appeared at 198ppm was assigned to azomethine carbon atoms (C=N). A signal at 158  $\delta$  was assigned for phenolic carbon. Phenyl rings of ligand showed following signals 114.34; 115.25, 115.52, 118.27, 118.55, 119.02, 119.40, 119.95, 121.84, 122.80, 126.75, 126.97, 129.25, 129.72, 129.99, 137.50, 139.08, 150.74, 151.15, 152.76  $\delta$  ppm.

### 3.5 Mass spectra of the compounds

The mass spectral data of Schiff base ligand and its metal chelates are given in table-3. Mass spectra of the ligand and its metal complexes showed molecular ion peaks, which were in good agreement with the expected values. The mass spectrum of ligand L gives a peak at 384 m/z, which was assigned for [HL] peak. Copper and cobalt complexes give a molecular ion peak at 866 and 864 m/z respectively, which assigned as [M] and [M+3] peak. The mass spectrum of Ni (II) complex showed a peak at 866 m/z which was assigned for [M+5] peak.

**Table-3: Mass spectral data of Schiff base ligand and its metal complexes**

S.No.	Compound	Cal. Mass	Obtained mass	Peak assigned
1	C <sub>22</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub>	384	384	[M]
2	C <sub>44</sub> H <sub>34</sub> CuN <sub>8</sub> O <sub>8</sub>	866.34	866.34	[M]
3	C <sub>44</sub> H <sub>34</sub> CoN <sub>8</sub> O <sub>8</sub>	861.72	864	[M+3]
4	C <sub>44</sub> H <sub>34</sub> NiN <sub>8</sub> O <sub>8</sub>	860	865	[M+5]

### 3.6 Magnetic moment and electronic absorption spectra

The electronic absorption spectral data and magnetic moment values of Schiff base ligand and its transition metal complexes are given in table-4. The electronic spectrum of Schiff base ligand exhibit strong absorption bands at 282nm and 294nm, which were attributed to  $\pi-\pi^*$  and  $n-\pi^*$  transitions respectively [14]. The observed magnetic momentum value of Cu (II) complex was 1.75 BM, falls within the range observed for distorted octahedral geometry [15]. UV/Visible spectra of Cu (II) complex presented in fig.2. The magnetic moment value of Ni (II) complex was found to be 3.23 BM, falls within the range of 2.8-3.5 BM for metal complexes, suggesting octahedral geometry [16]. The magnetic moment of Co (II) complex has been found to be 4.94 B.M, and it lies within the range expected for octahedral geometry [17].

**Table-4: Electronic absorption spectral data and magnetic moment values of Schiff base ligand and its transition metal chelates**

Compound	Absorption in nm	Transitions	Mag. Moment $\mu$ (B.M.)	Geometry
$C_{22}H_{16}N_4O_3$	282, 294.	$\pi-\pi^*$ , $n-\pi^*$	-	
$C_{44}H_{34}CuN_8O_8$	740	${}^2E_g \rightarrow {}^2T_{2g}$	1.75	Octahedral
$C_{44}H_{34}CoN_8O_8$	431 439 727	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	4.59	Octahedral
$C_{44}H_{34}NiN_8O_8$	415 433 765	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	3.32	Octahedral

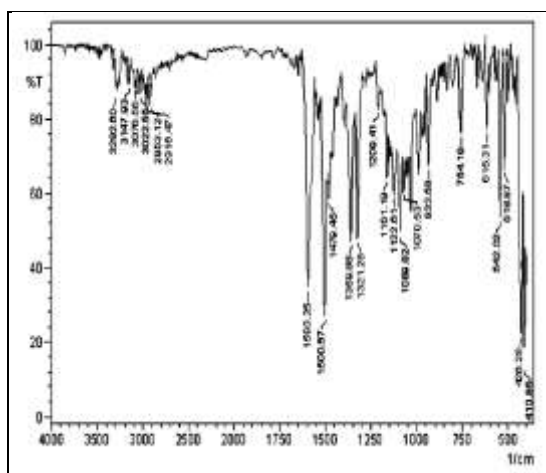


Fig-1:-IR spectra of Cu (II) Complex

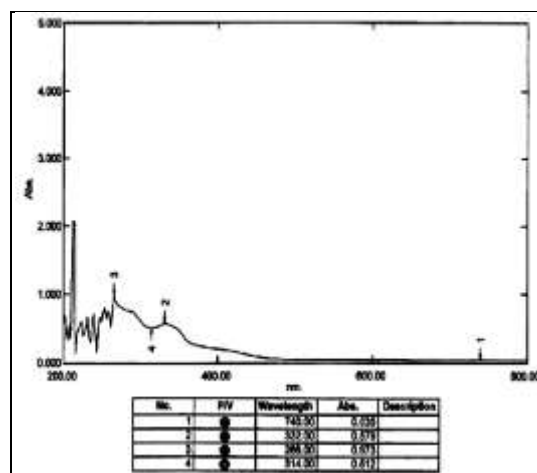


Fig-2:-UV/Visible spectra of Cu (II) Complex

### 3.7 Thermal analysis

Thermal stability of complexes was studied in the range of 50-1000<sup>o</sup>C by controlling heating rates 15<sup>o</sup>C/minute. The TG curve for Cu complex showed weight loss initially at 90<sup>o</sup> C (4.0%) which indicate the presence of lattice water molecules in complex. Weight loss at 257.1<sup>o</sup>C (7.5%) indicate the coordinated water molecule in the metal complexes. The percentage wt. loss indicates 1.5 molecule of water. The complex then after starts decomposing above 257<sup>o</sup>C, and it completely decomposed at 550<sup>o</sup>C, which correspond to 85% weight loss. Above 550<sup>o</sup>C complex gets converted into CuO/Cu metal residue. Thermo gravimetric study of Co (II) complex showed three steps thermogram curve. Weight loss up to 236<sup>o</sup> C (7.6%) indicates the presence of lattice and coordinates water molecules. Above 236<sup>o</sup>C, the loss was continuous in two steps and at 650<sup>o</sup>C ligand was completely decomposed (87%). Above 650<sup>o</sup>C complex converted into CoO/Co metal residue. Thermo gram curve of Ni (II) complex also showed three steps decomposition pattern. Weight changes up to 297<sup>o</sup>C indicate the loss of two lattice and two coordinated water molecules. The loss of mass at this stage is 8.4%, which was very well agreement with calculated value [8.45%]. Above 297<sup>o</sup>C, the loss is continuous in two stages and at 778<sup>o</sup>C, the complex gets converted into NiO/Ni metal residue. The thermo gravimetric analysis (TGA) provides authentic information regarding the presence of water molecules in the coordination sphere of all complexes [18]. The TGA curves of all metal complexes are presented in Fig-3, 4 and 5.

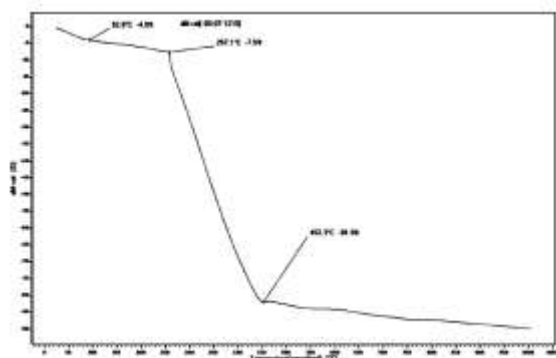


Fig-3:-TGA curve of Cu (II) metal complex

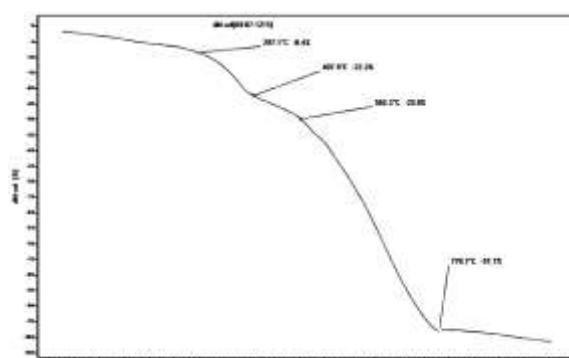


Fig-4:-TGA curve of Co (II) metal complex

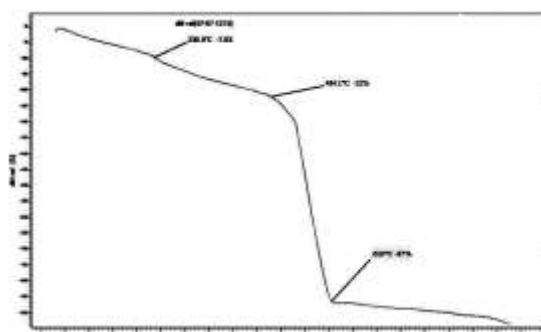


Fig-5:- TGA Curve of Ni (II) metal complexe

#### IV. Conclusion

2-(3-(3-nitrophenyl)-1-phenyl-1H-pyrazole-4-yl) methylene amino) phenol and its transition metal complexes have been synthesized in 2:1 molar ratio of ligand to metal ion. They have been characterized by the analytical, spectral, thermal and magnetic studies. The results of these investigations support the suggested structure of the metal complexes. Molar conductance values, analytical data suggests that the complexes are neutral in DMSO [19]. The UV/Visible spectrum and value of magnetic susceptibility suggest the octahedral geometry of complexes. Thermal analysis of metal complexes indicates the presence of coordinated water molecules in the complexes. TGA supported the octahedral environment around the metal ion. Complete analysis suggests a plausible octahedral structure of metal complex.

#### Acknowledgement

Authors are thankful to Head, Dept.of Chemistry Saurashtra University for providing necessary facilities, UGC New Delhi for the award of meritorious fellowship and SAIF Chandigarh, for ESI mass, <sup>1</sup>HNMR and <sup>13</sup>CNMR analysis.

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