



## Synthesis and Characterization of Mixed Ligand Transition Metal(II) Complexes of Isatinimine Schiff Bases

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Transition metal complexes of cobalt(II), nickel(II), copper(II) and zinc(II) of isatinimine Schiff base ligands (**HL<sub>1</sub>**-**HL<sub>2</sub>**) derived from isatin 5-chloro-2-hydroxy aniline (**HL<sub>1</sub>**), 2-amino-4-nitrophenol (**HL<sub>2</sub>**) and heterocyclic nitrogen base 8-hydroxyquinoline have been synthesized. All the metal complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility, SEM and spectroscopic techniques (IR, UV-visible, NMR and ESR). Transition metal complexes existed as octahedral or distorted octahedral geometries around metal centres with the donation of carbonyl oxygen, azomethine nitrogen and deprotonated enolic oxygen, whereas ligand 8-hydroxyquinoline existed as monobasic bidentate ON coordinating through oxygen of hydroxyl group and nitrogen of quinoline ring. The complexes were found to be non-electrolytic in nature.

**Keywords:** Schiff base, Octahedral, Non-electrolyte, Bidentate, Conductance.

### INTRODUCTION

The Schiff bases are widely employed as ligands in complex formation with metal ions and derived from an aldehyde and any amine which coordinate to metal ions *via* azomethine nitrogen. They are an important class of organic compounds with a wide variety of biological properties [1] and coordinate with many transition metal ions producing metal complexes that display motivating physical, chemical, biological and catalytic properties [2-10].

Many studies have been reported regarding the biological activities of Schiff bases, including their anticancer [11,12], antibacterial [13,14], antifungal and herbicidal activities [15]. They are also used as an optical and electro-sensors, as well as in various chromatographic methods, to enhance selectivity and sensitivity. The reaction occurs between the aldehyde group of 11-*cis*-retinal and the amino group of protein (Opsin) forming the rhodopsin visual pigment responsible for sending an impulse to the brain causing vision after light incidence [16].

In continuation to our interest in metal complexes of Schiff bases, the present study describes the coordination behaviour of novel Schiff base derived from the condensation of 2-amino-phenol and isatin toward some transition metals namely Co(II),

Ni(II), Cu(II) and Zn(II). All the synthesized compounds were characterized by elemental analysis and by using spectroscopic techniques like FT-IR, UV, <sup>1</sup>H NMR, <sup>13</sup>C NMR and ESR.

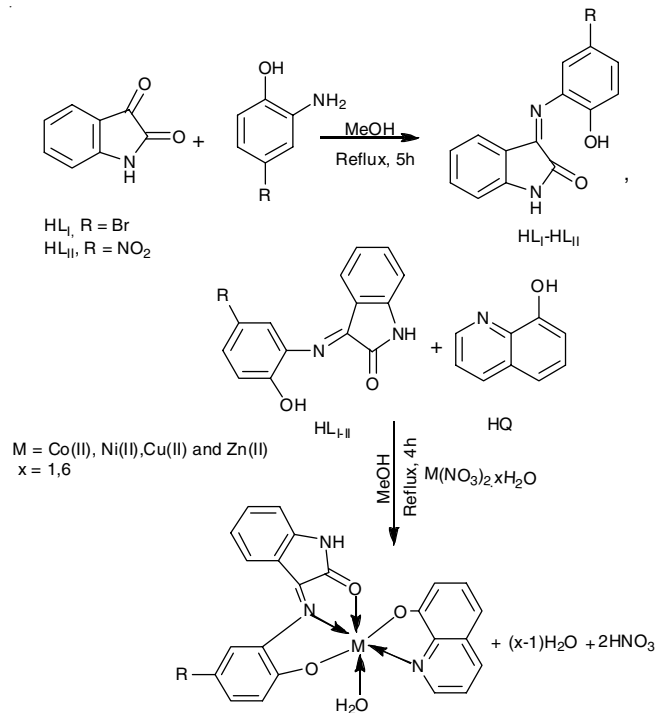
### EXPERIMENTAL

All the chemicals were obtained from Aldrich and of analytical grade. Metal contents were determined by using standard gravimetric methods *e.g.* cobalt as cobalt pyridine thiocyanate, nickel as nickel dimethylglyoximate, copper as cuprous thiocyanate and zinc as zinc ammonium phosphate. Elemental analysis of samples were carried out by using Perkin Elmer 2400 instrument. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded on Bruker Avance II 300 MHz NMR spectrometer and all chemical shifts were reported in parts per million relative to TMS as internal standard in CDCl<sub>3</sub>. IR spectra of compounds were recorded on Shimadzu IR affinity-I 8000 FT-IR spectrometer using KBr disc. UV spectra were recorded on UV-VIS-NIR Varian Cary-5000 spectrometer in DMF. Magnetic susceptibilities of compounds were measured by Gouy's method, using Hg [Co(SCN)<sub>4</sub>] as the calibrant at room temperature. SEM was carried out on SEM tracmini, microtrac Inc. USA. ESR spectra of Cu(II) complexes were carried on a Varian E 112 X-band spectrometer using tetracyanoethylene (TCNE) as the internal standard with g-

value of 2.0023. Mass spectra were recorded on a API 2000 (Applied Biosystems) mass spectrometer equipped with an electrospray source and a Shimadzu Prominence LC. Molar conductance measurement of  $1 \times 10^{-3}$  M solution in dry DMF at room temperature was carried out using a model-306-systronics conductivity bridge having cell constant equal to one.

**Synthesis of Schiff base ligands:** Schiff base ligands were synthesized by the reaction of 2-aminophenol (10 mmol) with methanolic solution (10 mL) of isatin (10 mmol) with few drops of acetic acid in 1:1 molar ratio in methanolic solution. The resulting mixture was refluxed for 5 h and excess of solvent was evaporated and solid product was filtered, washed with methanol, recrystallized from methanol and dried (**Scheme-I**).

**Synthesis of transition metal(II) complexes:** In the aqueous solution of hydrated metal salt,  $M(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (1 mmol) added methanolic solution of Schiff base ligands ( $\text{HL}_I$  and  $\text{HL}_{II}$ ) (1 mmol) and to this methanolic solution of 8-hydroxyquinoline (HQ) (1 mmol) was also added in 1:1:1 molar ratio with constant stirring. The mixture was refluxed for 4 h. Solid complex obtained after the evaporation of solvent. Solid was filtered and washed with methanol to remove unreacted metal nitrates or ligands (**Scheme-I**).



**Scheme-I:** Synthesis of Schiff base ligand and their transition metal complexes

**IR spectra:** On comparison of spectra of ligands and transition metal complexes, shifting of strong band from 1672-1658 to 1645-1628  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{N})$  azomethine group of Schiff base ligands which showed the participation of azomethine nitrogen in coordination [17]. Shift was also observed for  $\nu(\text{C}=\text{O})$  of isatin moiety was at 1714-1713  $\text{cm}^{-1}$ , which shifted on complexation at lower value from 1685-1683  $\text{cm}^{-1}$  indicated that carbonyl oxygen atom of isatin as coordinating site. The disappearance of OH band of ligand at 3275-3255  $\text{cm}^{-1}$  indicated the coordination of phenolic oxygen. Coordination of

## RESULTS AND DISCUSSION

Transition metal(II) complexes  $[(\text{ML}_1(\text{Q}) \cdot \text{H}_2\text{O})]$  and  $[(\text{ML}_2(\text{Q}) \cdot \text{H}_2\text{O})]$  (Q = 8-hydroxyquinoline) were obtained by the reaction of transition metal salts  $M(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  [M = Co(II), Ni(II), Cu(II) and Zn(II); x = 1, 6] with Schiff base ligands 3-(5-bromo-2-hydroxyphenylimino)-1,3-dihydro-indol-2-one ( $\text{HL}_I$ ), 3-(2-Hydroxy-5-nitro-phenylimino)-1,3-dihydro-indol-2-one ( $\text{HL}_2$ ). The complexes were obtained as solids and soluble in DMF and DMSO. The molar conductance values for the complexes in the range of 3.6-11.3  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  in dry DMSO which indicated the non-electrolytic nature of complexes. The analytical data (Table-1) indicated a 1:1:1 metal ligand ratio.

TABLE-1  
PHYSICAL AND ANALYTICAL DATA OF MIXED LIGAND TRANSITION METAL(II)  
COMPLEXES OF ISATINIMINE SCHIFF BASE LIGANDS AND 8-HYDROXYQUINOLINE

S. No.	Product	m.f. (m.w.)	Yield (%)	m.p. ( $^{\circ}\text{C}$ )	Colour	Elemental analysis (%): Found (calcd.)				m/z	$\Lambda_M \times 10^{-3}$
						C	H	N	M		
1	$\text{HL}_I$	$\text{C}_{14}\text{H}_9\text{N}_2\text{O}_2\text{Br}$ (317.14)	73	165	Yellow	53.59 (53.02)	3.14 (2.86)	9.08 (8.83)	—	317.8	—
2	$\text{HL}_{II}$	$\text{C}_{14}\text{H}_9\text{N}_3\text{O}_4$ (283.24)	79	210	Yellow	59.74 (59.37)	3.46 (3.20)	14.23 (14.84)	—	283.7	—
3	$\text{Co}(\text{L}_I)(\text{Q}) \cdot \text{H}_2\text{O}$	$\text{C}_{23}\text{H}_{16}\text{N}_5\text{O}_4\text{BrCo}$ (537.23)	77	> 284 <sup>d</sup>	Green	51.87 (51.42)	3.25 (3.00)	7.34 (7.82)	10.54 (10.97)	537.9	7.5
4	$\text{Ni}(\text{L}_I)(\text{Q}) \cdot \text{H}_2\text{O}$	$\text{C}_{23}\text{H}_{16}\text{N}_5\text{O}_4\text{BrNi}$ (536.99)	79	> 290 <sup>d</sup>	Brown red	51.67 (51.44)	3.45 (3.00)	7.45 (7.83)	10.43 (10.93)	537.4	8.4
5	$\text{Cu}(\text{L}_I)(\text{Q}) \cdot \text{H}_2\text{O}$	$\text{C}_{23}\text{H}_{16}\text{N}_5\text{O}_4\text{BrCu}$ (541.84)	77	> 300 <sup>d</sup>	Green	51.43 (50.98)	3.42 (2.98)	7.53 (7.76)	11.98 (11.73)	541.3	7.3
6	$\text{Zn}(\text{L}_I)(\text{Q}) \cdot \text{H}_2\text{O}$	$\text{C}_{23}\text{H}_{16}\text{N}_5\text{O}_4\text{BrZn}$ (543.68)	76	> 290 <sup>d</sup>	Colourless	51.04 (50.81)	3.34 (2.97)	7.94 (7.73)	12.43 (12.03)	543.1	4.4
7	$\text{Co}(\text{L}_{II})(\text{Q}) \cdot \text{H}_2\text{O}$	$\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_6\text{Co}$ (503.33)	70	> 280 <sup>d</sup>	Green	54.43 (54.88)	3.53 (3.20)	11.43 (11.13)	11.54 (11.71)	503.8	9.4
8	$\text{Ni}(\text{L}_{II})(\text{Q}) \cdot \text{H}_2\text{O}$	$\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_6\text{Ni}$ (503.09)	77	> 295 <sup>d</sup>	Brown red	55.08 (54.91)	3.53 (3.21)	11.54 (11.14)	11.31 (11.67)	503.9	11.3
9	$\text{Cu}(\text{L}_{II})(\text{Q}) \cdot \text{H}_2\text{O}$	$\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_6\text{Cu}$ (507.94)	78	> 290 <sup>d</sup>	Green	54.67 (54.39)	3.52 (3.17)	11.34 (11.03)	12.87 (12.51)	508.4	7.4
10	$\text{Zn}(\text{L}_I)(\text{Q}) \cdot \text{H}_2\text{O}$	$\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_6\text{Zn}$ (509.79)	74	> 290 <sup>d</sup>	Colourless	54.53 (54.19)	3.35 (3.16)	11.03 (10.99)	13.08 (12.83)	510.4	9.5

d = decomposed

8-hydroxyquinoline was confirmed by absence of band at 3428  $\text{cm}^{-1}$  due to  $\nu(\text{O-H})$  stretching vibration and band of  $\nu(\text{C=N})$  stretching vibration at 1570  $\text{cm}^{-1}$  of quinoline ring was shifted to lower value. On complexation some new vibration were appeared at 548-530 and 510-475  $\text{cm}^{-1}$  may be due to  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$  mode respectively [18]. Coordinated water molecule in the complexes was confirmed by the appearance of band between 3440-3400  $\text{cm}^{-1}$  (Table-2) due to asymmetric and symmetric  $\nu(\text{O-H})$  stretching modes, weak bands also observed at 1575-1565  $\text{cm}^{-1}$  due to H-O-H bending vibrations [19].

**$^1\text{H}$  and  $^{13}\text{C}$  NMR analysis:** The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of Schiff base ligands (**HL<sub>I</sub>** and **HL<sub>II</sub>**), 8-hydroxyquinoline and their zinc(II) complexes are present in Table-3. On comparison of  $^1\text{H}$  NMR spectra of ligands and its zinc(II) complexes, showing the deprotonation of the phenolic OH signal at  $\delta$  11.05-11.37 ppm of Schiff base ligands **HL<sub>I</sub>** and **HL<sub>II</sub>** and at  $\delta$  12.92 ppm of 8-hydroxyquinoline. In ligands (**HL<sub>I</sub>** and **HL<sub>II</sub>**), NMR spectra also showed a peak at  $\delta$  9.26-9.23 ppm due to -NH- proton remains unaltered showing non-participation of NH in bonding with metal

ions. Aromatic protons were in the range of  $\delta$  6.77-8.71 ppm for **HL<sub>I</sub>** and **HL<sub>II</sub>** and  $\delta$  7.01-8.84 ppm for 8-hydroxyquinoline ligand which shows the deshielded at very low value.

The presence of water molecule in complexes was confirmed by the appearance of signal around  $\delta$  3.50 ppm [20]. In  $^{13}\text{C}$  NMR spectra of complexes, signals of azomethine carbon atom of Schiff base ligands **HL<sub>I</sub>** and **HL<sub>II</sub>** was shifted from  $\delta$  164.72-164.95 to  $\delta$  166.04 ppm, carbonyl carbon of ligands from  $\delta$  158.48-160.03 to  $\delta$  160.34-162.46 ppm and carbon attached to hydroxyl of phenolic ring was shifted from  $\delta$  143.45-145.60 to  $\delta$  144.31-147.23 ppm suggested coordination of ligand with zinc metal atom. The signal of carbon attached to hydroxyl group of ligand 8-hydroxyquinoline was shifted from  $\delta$  153.74 to  $\delta$  154.36-154.98 ppm, and shift in (C=N) carbon atom was observed from  $\delta$  150.30 to  $\delta$  152.18-152.40 and not much variation is observed in other aromatic carbon atom signals (Table-3).

**Electronic spectra and magnetic susceptibility measurements:** The geometry of transition metal complexes were obtained from the electronic spectral data and magnetic susceptibility

TABLE-2  
INFRARED SPECTRAL CHARACTERISTICS ( $\nu$ ,  $\text{cm}^{-1}$ ) OF ISATINIMINE SCHIFF BASE  
LIGANDS AND MIXED LIGAND TRANSITION METAL(II) COMPLEXES

Ligands/Complexes	(N-H)	(C=O) indole ring	(C=N)	(M-O)	(M-N)	(H-O-H)
HL <sub>I</sub>	3195	1713	1672	-	-	-
HL <sub>II</sub>	3192	1714	1658	-	-	-
Co(L <sub>I</sub> )(Q)H <sub>2</sub> O	3192	1685	1645	475	530	1565
Ni(L <sub>I</sub> )(Q)H <sub>2</sub> O	3192	1684	1636	494	532	1564
Cu(L <sub>I</sub> )(Q)H <sub>2</sub> O	3190	1683	1642	507	538	1559
Zn(L <sub>I</sub> )(Q)H <sub>2</sub> O	3191	1685	1636	509	545	1565
Co(L <sub>II</sub> )(Q)H <sub>2</sub> O	3192	1684	1630	498	548	1568
Ni(L <sub>II</sub> )(Q)H <sub>2</sub> O	3190	1683	1640	510	550	1560
Cu(L <sub>II</sub> )(Q)H <sub>2</sub> O	3191	1684	1635	504	546	1564
Zn(L <sub>II</sub> )(Q)H <sub>2</sub> O	3192	1685	1628	499	548	1570

TABLE-3  
 $^1\text{H}$  AND  $^{13}\text{C}$  NMR SPECTRAL CHARACTERISTICS ( $\delta$ ) OF ISATINIMINE SCHIFF BASE  
LIGANDS AND MIXED LIGAND TRANSITION METAL (II) COMPLEXES

Ligands	$^1\text{H}$ NMR ( $\text{CDCl}_3$ ) $\delta$ (ppm)	$^{13}\text{C}$ NMR ( $\text{CDCl}_3$ ) $\delta$ (ppm)
HL <sub>I</sub>	11.05 (s, 1H, OH), 9.23 (s, 1H, NH), 7.62 (d, 1H, C <sub>4</sub> -H, $J$ = 8.74 Hz), 7.38 (t, 1H, C <sub>5</sub> -H), 7.45 (t, 1H, C <sub>6</sub> -H), 7.68(d, 1H, C <sub>7</sub> -H, $J$ = 8.74 Hz), 8.15(s, 1H, C <sub>3</sub> '-H), 7.87 (d, 1H, C <sub>5</sub> '-H, $J$ = 8.40 Hz), 7.54 (d, 1H, C <sub>6</sub> '-H, $J$ = 8.40Hz)	164.73 (C=N), 159.03 (C=O), 132.40 (C <sub>4</sub> ), 127.48 (C <sub>5</sub> ), 134.18 (C <sub>6</sub> ), 123.64 (C <sub>7</sub> ), 142.84 (C <sub>8</sub> ), 128.15 (C <sub>9</sub> ), 152.82 (C <sub>1</sub> '), 145.60 (C <sub>2</sub> '), 129.74 (C <sub>3</sub> '), 120.04 (C <sub>4</sub> '), 134.72 (C <sub>5</sub> '), 122.45(C <sub>6</sub> ')
HL <sub>II</sub>	11.37 (s, 1H, OH), 9.26 (s, 1H, NH), 7.67 (d, 1H, C <sub>4</sub> -H, $J$ = 9.14 Hz), 7.38 (t, 1H, C <sub>5</sub> -H), 7.47(t, 1H, C <sub>6</sub> -H), 7.69 (d, $J$ = 9.14 Hz, 1H, C <sub>7</sub> -H), 8.71 (s, 1H, C <sub>3</sub> '-H), 7.98 (d, 1H, C <sub>5</sub> '-H, $J$ = 9.02 Hz), 7.60 (d, 1H, C <sub>6</sub> '-H, $J$ = 9.02Hz)	164.95 (C=N), 160.03 (C=O), 132.40 (C <sub>4</sub> ), 127.45 (C <sub>5</sub> ), 135.03 (C <sub>6</sub> ), 123.84 (C <sub>7</sub> ), 142.61 (C <sub>8</sub> ), 128.14 (C <sub>9</sub> ), 153.43 (C <sub>1</sub> '), 144.38 (C <sub>2</sub> '), 122.34 (C <sub>3</sub> '), 145.45 (C <sub>4</sub> '), 127.62 (C <sub>5</sub> '), 120.98 (C <sub>6</sub> ')
HQ	12.92 (s, 1H, OH), 8.84 (d, 1H, C <sub>5</sub> '-H, $J$ = 9.02 Hz), 7.28 (t, 1H, C <sub>3</sub> '-H), 7.99 (d, 1H, C <sub>4</sub> '-H, $J$ = 8.04 Hz), 7.36 (d, 1H, C <sub>5</sub> '-H, $J$ = 8.28 Hz), 7.28 (t, 1H, C <sub>6</sub> '-H), 7.01 (d, 1H, C <sub>7</sub> '-H, $J$ = 9.18 Hz)	150.30 (C <sub>2</sub> "), 125.64 (C <sub>3</sub> "), 137.40 (C <sub>4</sub> "), 120.42 (C <sub>5</sub> "), 128.92 (C <sub>6</sub> "), 116.40 (C <sub>7</sub> "), 153.74 (C <sub>8</sub> "), 138.81 (C <sub>9</sub> "), 130.52 (C <sub>10</sub> "
Zn(LI)(Q)H <sub>2</sub> O	9.24 (s, 1H, NH), 7.62 (d, 1H, C <sub>4</sub> -H, $J$ = 8.74 Hz), 7.39 (t, 1H, C <sub>5</sub> -H), 7.45 (t, 1H, C <sub>6</sub> -H), 7.69 (d, 1H, C <sub>7</sub> -H, $J$ = 9.02 Hz), 8.21 (s, 1H, C <sub>3</sub> '-H), 7.86 (d, 1H, C <sub>5</sub> '-H, $J$ = 6.04 Hz), 7.58 (d, 1H, C <sub>6</sub> '-H, $J$ = 6.18 Hz), 8.91 (d, 1H, C <sub>2</sub> '-H, $J$ = 8.16 Hz), 7.28 (t, 1H, C <sub>3</sub> '-H), 8.01 (d, 1H, C <sub>4</sub> '-H, $J$ = 9.18 Hz), 7.36 (d, 1H, C <sub>5</sub> '-H, $J$ = 6.08 Hz), 7.28 (t, 1H, C <sub>6</sub> '-H), 7.08 (d, 1H, C <sub>7</sub> '-H, $J$ = 8.04 Hz), 3.52 (s, 2H, H <sub>2</sub> O)	166.01 (C=N), 162.46 (C=O), 132.84 (C <sub>4</sub> ), 127.48 (C <sub>5</sub> ), 134.98 (C <sub>6</sub> ), 123.94 (C <sub>7</sub> ), 141.02 (C <sub>8</sub> ), 128.85 (C <sub>9</sub> ), 152.94 (C <sub>1</sub> '), 147.23 (C <sub>2</sub> '), 129.92 (C <sub>3</sub> '), 120.45 (C <sub>4</sub> '), 134.90 (C <sub>5</sub> '), 122.45(C <sub>6</sub> '), 152.40 (C <sub>2</sub> "), 126.40 (C <sub>3</sub> "), 138.01 (C <sub>4</sub> "), 120.89 (C <sub>5</sub> "), 129.15 (C <sub>6</sub> "), 118.02 (C <sub>7</sub> "), 154.60 (C <sub>8</sub> "), 137.97 (C <sub>9</sub> "), 131.01 (C <sub>10</sub> "
Zn(LII)(Q)H <sub>2</sub> O	9.26 (s, 1H, NH), 7.67 (d, 1H, C <sub>4</sub> -H, $J$ = 9.08 Hz), 7.39 (t, 1H, C <sub>5</sub> -H), 7.47 (t, 1H, C <sub>6</sub> -H), 7.71 (d, $J$ = 6.04 Hz, 1H, C <sub>7</sub> -H), 8.84 (s, 1H, C <sub>3</sub> '-H), 7.98 (d, 1H, C <sub>5</sub> '-H, $J$ = 8.84 Hz), 7.60 (d, 1H, C <sub>6</sub> '-H, $J$ = 7.28 Hz), 8.90 (d, 1H, C <sub>2</sub> '-H, $J$ = 8.41 Hz), 7.28 (t, 1H, C <sub>3</sub> '-H), 7.99 (d, 1H, C <sub>4</sub> '-H, $J$ = 9.24 Hz), 7.38 (d, 1H, C <sub>5</sub> '-H, $J$ = 4.38 Hz), 7.29 (t, 1H, C <sub>6</sub> '-H), 7.04 (d, 1H, C <sub>7</sub> '-H, $J$ = 8.04 Hz), 3.54 (s, 2H, H <sub>2</sub> O)	166.04 (C=N), 162.04 (C=O), 132.98 (C <sub>4</sub> ), 127.87 (C <sub>5</sub> ), 135.97 (C <sub>6</sub> ), 124.01 (C <sub>7</sub> ), 142.61 (C <sub>8</sub> ), 128.43 (C <sub>9</sub> ), 153.84 (C <sub>1</sub> '), 146.89 (C <sub>2</sub> '), 123.04 (C <sub>3</sub> '), 146.01 (C <sub>4</sub> '), 128.01 (C <sub>5</sub> '), 121.07 (C <sub>6</sub> '), 152.38 (C <sub>2</sub> "), 125.79 (C <sub>3</sub> "), 138.18 (C <sub>4</sub> "), 121.65 (C <sub>5</sub> "), 129.01 (C <sub>6</sub> "), 118.02 (C <sub>7</sub> "), 154.98 (C <sub>8</sub> "), 138.81 (C <sub>9</sub> "), 130.97 (C <sub>10</sub> "

measurements. Cobalt(II) complexes exhibited absorption bands in the region 24,320-8790 and 24610-8805  $\text{cm}^{-1}$  due to  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$  ( $\nu_1$ ),  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  ( $\nu_2$ ) and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) transitions. The  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  ( $\nu_2$ ) band involving two electron transition was not observed as sharp peak in the spectra because of weak intensity. The ligand field parameters Racah interelectronic repulsion parameter B, nephelauxetic ratio  $\beta$  value calculated for Co(II) complexes were found to be 573-663 and 0.59-0.68  $\text{cm}^{-1}$ , respectively, these parameters along with the transition indicated  $d^7$  high spin system and characteristics of octahedral geometry around metal ion in the complexes [21]. Co(II) complexes have magnetic moment in the range of 4.28-4.42 BM which was higher than spin only value (3.87) because of small contribution of orbital motion due to unpaired electron present in  $d^7$  system of Co(II).

The electronic spectra of nickel(II) mixed ligand complexes exhibited three absorption bands at 24,310-9,742 and 24350-9710  $\text{cm}^{-1}$  attributed to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$  ( $\nu_1$ ),  ${}^3\text{A}_{2g}(\text{F}) \rightarrow \text{T}_{1g}(\text{F})$  ( $\nu_2$ ),  ${}^3\text{A}_{2g}(\text{F}) \rightarrow 3\text{T}_{1g}(\text{P})$  ( $\nu_3$ ) transition, respectively [22]. The ligand field parameters B,  $\beta$  calculated for Ni(II) complex was found to be 680-702  $\text{cm}^{-1}$  and 0.67-0.68, respectively. For complexes B value was less than the free ion value because of the decreased interelectronic repulsion from electron delocalization. The magnetic moment value fall in the range of 2.89-2.98 BM which has been expected for the  $d^8$  octahedral geometry.

Copper(II) mixed ligand complexes exhibited broad band in the range of 24387-15,570  $\text{cm}^{-1}$  and weak shoulder at 24,205-24,415  $\text{cm}^{-1}$  due to  $d-d$  transition  ${}^2e_g \rightarrow {}^2t_{2g}$  and symmetry forbidden ligand  $\rightarrow$  metal charge transfer [23]. Magnetic moment of

Cu(II) complexes have normal value in the range of 1.85-1.98 BM as expected for  $d^9$  system with octahedral geometry. The observed values of magnetic moment for all the metal complexes are greater than expected because of little contribution of orbital motion due to unpaired electron. Zinc(II) mixed ligand complexes showed absorption band at 23,450-23,510  $\text{cm}^{-1}$  due to ligand to metal charge transfer with zero magnetic moment and found to be diamagnetic as expected for  $d^{10}$  system.

**ESR of copper(II) complexes:** The ESR spectral studies of Cu(II) complexes provides information of metal ion environment. ESR spectra of Cu(II) complexes were recorded in DMF solvent at room temperature and data summarized in Table-5. The copper(II) complex  $\text{Cu}(\text{L}_i)(\text{Q})\cdot\text{H}_2\text{O}$  in solid state exhibited anisotropic signals with g tensor parameters  $g_{\parallel} = 2.28$  and  $g_{\perp} = 2.07$  and  $g_{\parallel} > g_{\perp} > 2.0023$  that was characteristics of axial symmetry of Cu(II) complexes and unpaired electron located in  $d_{x^2-y^2}$  orbital of Cu(II) ions (Table-5). The  $g_{\parallel}$ ,  $g_{\perp}$  close to 2 suggested tetragonal distortion around Cu(II) and corresponded to elongation along fourfold symmetry z-axis [24].

In addition to these, an exchange coupling interaction between Cu(II) ions was explained by Hathaway expression. The value of G (4.10) showed that there was no interaction between copper centers. The spin orbital coupling constant  $\lambda$  (536  $\text{cm}^{-1}$ ) was found to be less than Cu(II)  $\lambda$  (832  $\text{cm}^{-1}$ ) for free ion complex and supported the covalent character of M-L bond in complexes. The value of  $\alpha^2$  (0.62) indicated that complex had some covalent character. The parameter  $\beta^2$  (0.93) gave an indication of covalency of in-plane  $\pi$  bonding for copper(II) complexes.

TABLE-4  
ELECTRONIC ABSORPTION SPECTRAL DATA AND MAGNETIC MOMENT ( $\mu$ ) OF TRANSITION METAL(II) COMPLEXES OF ISATINIMINE SCHIFF BASE LIGANDS AND 8-HYDROXYQUINOLINE

Complexes	Absorption ( $\text{cm}^{-1}$ )	Band assignment	Geometry	B value	$\beta$ value	$\nu_2/\nu_1$	$\mu_{\text{eff}}$ (BM)
Co(L <sub>I</sub> )(Q)·H <sub>2</sub> O	24320	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	Octahedral	573	0.59	1.98	4.40
	17450	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$					
	8790	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$					
Ni(L <sub>I</sub> )(Q)·H <sub>2</sub> O	24310	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$	Octahedral	695	0.67	1.57	2.98
	15355	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$					
	9742	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$					
Cu(L <sub>I</sub> )(Q)·H <sub>2</sub> O	24387	$\pi\text{N} \rightarrow \text{Cu}^*$	Distorted	-	-	-	1.85
	15570	${}^2\text{E}_g(\text{D}) \rightarrow {}^2\text{T}_{2g}(\text{D})$	Octahedral				
Zn(L <sub>I</sub> )(Q)·H <sub>2</sub> O	23495	LMCT	Octahedral	-	-	-	-
Co(L <sub>II</sub> )(Q)·H <sub>2</sub> O	24610	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	Octahedral	598	0.61	1.96	4.38
	17340	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$					
	8805	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$					
Ni(L <sub>II</sub> )(Q)·H <sub>2</sub> O	24350	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$	Octahedral	702	0.68	1.57	2.89
	15315	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$					
	9710	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$					
Cu(L <sub>II</sub> )(Q)·H <sub>2</sub> O	24205	$\pi\text{N} \rightarrow \text{Cu}^*$	Distorted	-	-	-	1.94
	15337	${}^2\text{E}_g(\text{D}) \rightarrow {}^2\text{T}_{2g}(\text{D})$	Octahedral				
Zn(L <sub>II</sub> )(Q)·H <sub>2</sub> O	23510	LMCT	Octahedral	-	-	-	-

TABLE-5  
ESR SPECTRAL DATA OF MIXED LIGAND COPPER(II) COMPLEXES OF ISATINIMINE SCHIFF BASE LIGANDS AND 8-HYDROXY QUINOLINE

Complexes	$g_{\parallel}$	$g_{\perp}$	$g_{\text{av}}$	G	$\lambda$ (-)	$\alpha^2$	$\beta^2$	$K_{\parallel}$	$K_{\perp}$
Cu(L <sub>I</sub> )(Q)·H <sub>2</sub> O	2.26	2.06	2.12	4.46	467	0.60	0.93	0.96	1.07
Cu(L <sub>II</sub> )(Q)·H <sub>2</sub> O	2.30	2.07	2.14	4.39	536	0.65	0.96	0.96	1.06

Higher value of  $\beta^2$  in comparison of  $\alpha^2$  indicated that in-plane  $\pi$  bonding is less covalent than in-plane  $\sigma$  bonding [25]. The orbital reduction factors  $K_{\parallel}$  (0.96) and  $K_{\perp}$  (0.99) were also calculated from the following equations:

$$K_{\parallel} = (g_{\parallel} - 2.0023) d-d \text{ transition}/8\lambda$$

$$K_{\perp} = (g_{\perp} - 2.0023) d-d \text{ transition}/2\lambda$$

For these copper complexes, the observed value of  $K_{\perp}$  was greater than  $K_{\parallel}$  which implied a greater presence of significant in-plane  $\pi$  bonding.

## Conclusion

From the various spectroscopic techniques (IR, NMR, ESR, electronic and mass) and magnetic susceptibility measurements, it was observed that the Schiff base ligands (**HL**<sub>1</sub> and **HL**<sub>2</sub>) existed as tridentate ONO bonded to metal ion through carbonyl oxygen, azomethine nitrogen, deprotonated enolic oxygen and heterocyclic nitrogen base 8-hydroxyquinoline ligand existed as bidentate ON bonded through oxygen of hydroxyl group and nitrogen of quinoline ring. The geometry of metal complexes are octahedral or distorted octahedral.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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