

## Synthesis, Characterization, Electrochemistry and Biological Activities of Ni(II) and Cu(II) Complexes of Schiff Bases¶

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Some metal complexes of nickel(II) and copper(II) with Schiff bases have been prepared in an ethanolic medium and characterized by elemental analysis and molecular weight determination. The IR observations suggest that the ligands have coordinated through azomethine nitrogen atoms and reacted through hydroxy group. The magnetic susceptibility data along with electronic and ESR spectra indicates a distorted octahedral structure for the Cu(II) and Ni(II) complexes. Biological activity studies have also been presented.

**Key Words:** ESR, Schiff base, Indole, NMR, Biological activities.

### INTRODUCTION

Recent progress in several fields of coordination chemistry shows that the stereochemical considerations are gaining an increasing importance. Model compounds for bioinorganic species, catalysts for enantioselective reactions, the building blocks for supramolecular assemblies and coordination units with well defined functionalities (molecular devices) all require an understanding and control of the stereochemistry of metallic centers<sup>1</sup>. In the recent years, it has been the trend to synthesize the ligand molecules having definite framework of donor atoms and stitch them with different metal ions. Such complexes have been further explored for their catalytic and biological activities<sup>2,3</sup>. For the last few years much attention has been cast on polyfunctional ligands, which can encapsulate the metal ions. Now the chemistry of metal clusters is also gaining the momentum, the metal complexes have acquired a position of significance in the area of bioinorganic chemistry<sup>4</sup>. Many enzymes and proteins involving metal systems have also been reported<sup>5</sup>. Various spectrochemical methods have been used to elucidate the structures of the complexes and sometimes to locate the coordination centers in ligand molecules and to know the preponderance of one coordination site over the other, the molecular orbital calculations have been used<sup>6</sup>.

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¶In memory of Late Prof. B.R. Patil.

Schiff base complexes of later transition metals have been receiving the considerable research attention because of their use in biological and medicinal applications. In recent years there has been growing interest in preparing the Schiff base complexes which show high activity.

### EXPERIMENTAL

The IR spectra of the ligands and complexes were recorded on Perkin-Elmer 1000 spectrophotometer in the region 4000-300  $\text{cm}^{-1}$  in KBr discs. The NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectra were recorded in DMSO on a Bruker made AMX-400 spectrometer. EPR spectra of the complexes were recorded in DMSO on a Varian E112 X-band spectrometer. The magnetic susceptibilities of the complexes at room temperature were obtained with a Gouy balance using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as a calibrant. UV-Visible spectra of the complexes in nujol mulls were recorded in the region 340-960 nm on an Elico spectrophotometer CL-24 using calibrated glass cells. The molar conductance was measured in DMF and DMSO using Elico CM 82T conductivity Bridge with a cell of cell constant  $1.1 \text{ cm}^{-1}$ .

**Synthesis of ligands:** All the chemicals used for preparing the ligands were of reagent grade. Metal Chlorides were B.D.H. reagents. The ligands were prepared according to a method reported earlier<sup>7</sup>.

**Synthesis of complexes:** Metal chlorides (1 mmol) were refluxed with (1 mmol) of 2,3,5-trisubstituted indole-2-carboxyhydrazones (0.02 mol) in ethanolic medium for about 2 h and then was added 2 g of sodium acetate. Again the reaction mixture was refluxed for 1 h. The reaction mixture was cooled and poured into crushed ice, the precipitated complex filtered, washed with distilled water and dried in vacuum over fused  $\text{CaCl}_2$ .

### RESULTS AND DISCUSSION

The complexes were coloured and insoluble in common organic solvents but easily soluble in DMSO and DMF. The elemental analysis data suggest that the complexes have 1:2 (metal-ligand) stoichiometry. Based on the elementary chemical analysis the formula  $\text{ML}_2$  (where L = deprotonated ligand) is suggested for all compounds. The molar conductance values in DMF at the concentration  $10^{-3}$  fall in the range of 5-10  $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  indicating that all the complexes are non-electrolytes (Table-1).

$^1\text{H}$  NMR spectra of the ligand exhibit four characteristic resonance signals due to the protons of different environments. The signals at 12.7 and 8.9 ppm are attributed to *o*-hydroxy and azomethine protons, respectively. A sharp multiplet observed at 7.0-7.8 ppm is attributed to the phenyl protons whereas methylene protons are observed around 2.4-3.0 ppm.

The  $^{13}\text{C}$  spectra shows peaks at 197.4 and 158.7 ppm which are ascribed to  $-\text{C}=\text{O}$  and  $-\text{CH}=\text{N}-$  groups, respectively.

TABLE-1  
MICROANALYTICAL AND MAGNETIC SUSCEPTIBILITY  
DATA OF THE COMPLEXES

m.f.	Elemental analysis (%): Found (Calcd.)					$\mu_{\text{eff}}$ (BM)
	M	C	H	N	Cl	
Ni(C <sub>23</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	9.45 (9.47)	61.47 (61.50)	6.84 (6.85)	7.61 (7.63)	8.47 (8.50)	2.90
Cu(C <sub>23</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	9.19 (9.22)	61.12 (61.16)	6.74 (6.77)	7.49 (7.51)	8.29 (8.31)	1.85
Ni(C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> Cl) <sub>2</sub> Cl <sub>2</sub>	8.60 (8.62)	58.20 (58.24)	6.39 (6.42)	7.07 (7.09)	7.78 (7.81)	3.10
Cu(C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> Cl) <sub>2</sub> Cl <sub>2</sub>	8.37 (8.39)	57.87 (57.92)	6.34 (6.36)	6.94 (6.97)	7.61 (7.64)	1.97

The important IR frequencies of the complexes along with their assignments are listed in Table-2. The band due to the intramolecular hydrogen bonded OH<sup>8,9</sup> appearing in the region 2700-2650 cm<sup>-1</sup> in the ligands disappears in the metal complexes and high intensity band of the ligands around 1280 cm<sup>-1</sup> due to the phenolic C-O vibration appears in the vicinity of 1320 cm<sup>-1</sup>. These observations emphasize that the -OH group of the ligands have reacted with metal(II) *via* deprotonation.

TABLE-2  
KEY IR BANDS (cm<sup>-1</sup>) OF THE COMPLEXES

Complex	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
Ni(C <sub>23</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	3292	1658	1611	1317	477	396
Cu(C <sub>23</sub> H <sub>18</sub> N <sub>3</sub> O <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	3286	1661	1603	1321	461	382
Ni(C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> Cl) <sub>2</sub> Cl <sub>2</sub>	3306	1664	1592	1317	480	400
Cu(C <sub>22</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> Cl) <sub>2</sub> Cl <sub>2</sub>	3301	1666	1590	1318	467	387

The information regarding coordination of (C=N) groups<sup>10</sup> of the ligands to M(II) moiety is obtained by the low frequency shift from  $\nu(\text{C}=\text{N})$  1630-1610 to 1620-1580 cm<sup>-1</sup>.

The *keto-enol* tautomerism is common in hydrazones so they exist in one of the two forms in the complexes<sup>11</sup>. A medium intensity broad band observed around 3260 cm<sup>-1</sup> and another strong band *ca.* 1650 cm<sup>-1</sup> are assigned to  $\nu(\text{NH})$  and  $\nu(\text{C}=\text{O})$ , respectively. These bands remain unperturbed in the complexes suggest that NH and C=O groups are not involve in bond formation.

The electrochemical behaviours of the Cu(II) complexes were investigated by cyclic voltammetry with silver electrode. Fig. 1 shows the cyclic voltammogram of  $[\text{Cu}(\text{II})(\text{C}_{23}\text{H}_{18}\text{N}_3\text{O}_3)_2\text{Cl}_2]$  in DMSO solution at room temperature. The voltammogram shows the redox process corresponding to the copper(II)/copper(III) couple at  $E_{\text{pa}} = 1.19$  V and the associated cathodic peak at  $E_{\text{pc}} = 0.47$  V. This couple is observed to be quasi-reversible as the peak separation between the anodic and cathodic potential is very high<sup>12</sup>. The number of electrons transferred in the electrode reaction for a reversible couple can be determined from the separation between the peak potentials. At slower scan rate, the high peak potential, indicates that the number of electrons transferred should be  $n = 1$ . So this process is best classified as a quasi-reversible couple<sup>13</sup>.

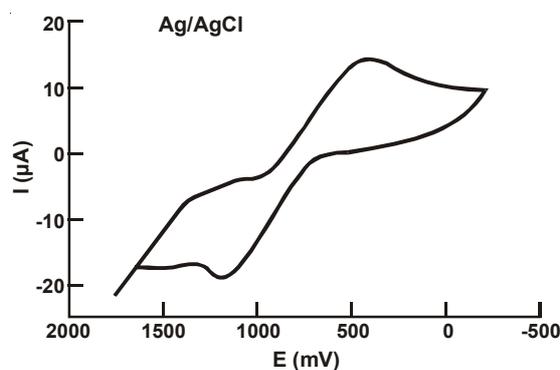


Fig. 1. Cyclic voltammogram of  $[\text{Cu}(\text{II})(\text{C}_{23}\text{H}_{18}\text{N}_3\text{O}_3)_2\text{Cl}_2]$  in DMSO solution

Two absorption bands are observed in the UV-spectrum of the ligand which are assigned to the transition  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  at 41777 and 35109  $\text{cm}^{-1}$ , respectively. These transitions are also observed in the spectra of the complexes, but they are shifted to lower frequencies ( $\Delta\nu = 1100\text{-}3000$   $\text{cm}^{-1}$ ), confirming the coordination of the ligand to the metal ions.

The Ni(II) complexes are greenish yellow in colour. It is obvious from the literature<sup>14</sup> that octahedral complexes display three bands attributable to the  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\nu_1)$ ,  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\nu_2)$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\nu_3)$  transitions in the following regions; 7000-13000, 11000-20000 and 19000-27000  $\text{cm}^{-1}$ . The low energy band of the complexes is broad and split in two components (around 8550 and 7200  $\text{cm}^{-1}$ ) indicating the tetragonal distortion. The magnetic moment (2.9-3.1 BM) lie in the region expected for octahedral complexes.

The Cu(II) complexes are green in colour. These exhibit only one broad symmetric band around 11700-16600  $\text{cm}^{-1}$ . The calculated values of Dq (1400  $\text{cm}^{-1}$ ), LFSE (24.7-25 Kcal/mol) and effective magnetic moments (1.85-1.97 BM) suggest a distorted octahedral geometry<sup>14</sup>.

The anisotropic EPR spectrum is characteristic of a the tetragonal copper(II) complex. The g-tensor has been calculated by Kneubuhl<sup>15</sup>, El-Sonbati and El-Bindary<sup>16</sup> methods.

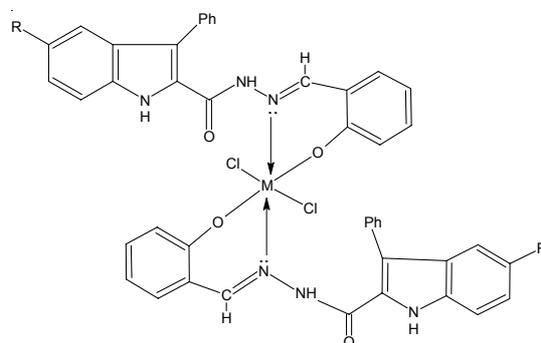
The g-tensor copper(II) complexes can be used to derive the ground state<sup>17</sup>. In an elongated octahedral geometry, the unpaired 3d electron for Cu<sup>2+</sup> ion lies in  $d_{x^2-y^2}$  orbital ( ${}^2B_1$  as ground state). The g-values are then given by  $g_{\parallel} = 2[1-(4\lambda/\Delta_1)]$  and  $g_{\perp} = 2[1-(\lambda/\Delta_2)]$ . On the other hand, in a compressed octahedral, the unpaired 3d electron lies in  $d_z^2$  orbital ( ${}^2A_1$  ground state) and so gives the g-value expressions:  $g_{\parallel} = 2$  and  $g_{\perp} = [1-(3\lambda/\Delta_3)]$ . Here,  $\Delta_1$ ,  $\Delta_2$  and  $\Delta_3$  are  $d_{x^2-y^2} \rightarrow d_{xy}$ ,  $d_{x^2-y^2} \rightarrow d_{xz}$  and  $d_{x^2-y^2} \rightarrow d_z^2$  excitation energies, respectively. From the g-values it is evident, that the unpaired electron lies predominantly in the  $d_{x^2-y^2}$  orbital with the possibility of some  $d_z^2$  character, being mixed with it because of low symmetry. A parameter G has been calculated by  $g = (g_{\parallel} - 2)/(g_{\perp} - 2)$ . A value of g larger than four indicates that considerable exchange interaction is absent.  $g_{\parallel} > g_{\perp} > 2$  indicates that the unpaired electron is located mainly in the  $d_{x^2-y^2}$  orbital. We also measured the covalent character of the metal-ligand bond by using  $g_{\parallel}$ -value by the following equations<sup>17</sup>.

$$a_{Cu}^2 = -(A_{\parallel} / 0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

$$b^2 = (g_{\parallel} - 2.0023)E / -8 |a^2$$

where  $a^2$  = covalent in-plane s-bonding,  $b^2$  = covalent in-plane p-bonding.

The  $a^2$  value for copper(II) complex indicates a considerable covalent character in the bonding between the Cu(II) ion and the ligand. The small  $g_{\parallel}$  value can be attributed to the large covalent interaction. Furthermore,  $g_{\parallel}$  value for the copper complex is 2.235, which is between the reported  $g_{\parallel}$  value (2.4) for copper-oxygen bonds and (2.3) copper-nitrogen bonds<sup>18</sup>. Thus, it confirms the presence of mixed copper-nitrogen and copper-oxygen bonds in these bidentates. On the basis of these values the suggested structure of the complexes (Fig. 2).



M = Ni(II) or Cu(II); R = OCH<sub>3</sub> or Cl

Fig. 2

**Biological activity:** Since indole ring is well known for its diverse biological properties, synthesis and the study of antimicrobial activity of various indole derivatives have been reported<sup>19,20</sup>. Antibacterial properties of ligands and complexes have been tested, against the two bacteria species, *E. coli* and *S. aureus*.

The Cu(II) complexes are less fungitoxic towards *A. solani* and *F. equiseti* than the free ligands. All the Cu(II) complexes show some antibacterial activity against the organism *S. aureus* but none is active against *E. coli*.

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