

Biological Screening of Square Planar Cu(II) and Ni(II) Complexes of Dibasic Nnoo Tetradentate Schiff Base Ligand

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Abstract: A new series of mononuclear Cu(II) and Ni(II) complexes of Schiff base derived from 3,5-dichloro-2-hydroxyacetophenone and 4,5-dichloro-o-phenylenediamine have been synthesized. The coordination possibility of the Schiff-base towards the metal ions have been proposed in the light of elemental analysis, spectral (IR, UV-VIS, ¹H NMR and ESR) and magnetic studies. The analytical data shows that, the stoichiometry of the complexes is 1:1. Spectroscopic data suggested square planar geometry for Cu(II) and Ni(II) complexes, respectively. Antimicrobial activity of the ligand and its corresponding Cu(II) and Ni(II) complexes were investigated against various microorganisms by paper disc method. The zone of inhibition of the ligand and its complexes were noticed and in general, Cu(II) complex was found to be more active than Ni(II) complex and free Schiff base ligand.

Keywords-NNOO Tetradentate Schiff base, 3,5- dichloro-2- hydroxy acetophenone and 4,5- dichloro-o-phenylenediamine, Antimicrobial studies

I. INTRODUCTION

Acetophenone and diamine derivatives are a group of highly reactive compounds that form potentially active Schiff bases which then form chelate complexes with metal ions. They are versatile ligands for many transition metals and provide donor atoms suitable for coordination with metal ions. On complexation, their biological activity increases which including anticancer and this led to metal-based pharmaceuticals [1]. In the light of above observations, we have prepared Cu(II) and Ni(II) complexes of the NNOO donor ligand from 3,5-dichloro-2-hydroxyacetophenone and 4,5-dichloro-O-phenylenediamine.

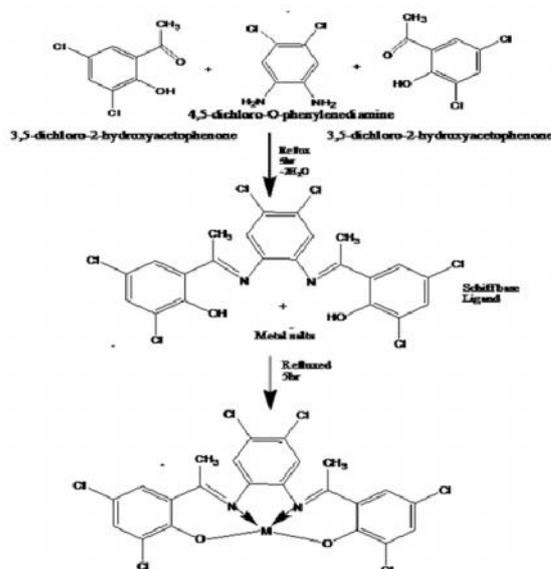
II. EXPERIMENTAL

A. SYNTHESIS OF LIGAND

Ligand is synthesized by refluxing ethanolic solution of 3,5- dichloro-2- hydroxy acetophenone(2mmol) and 4,5- dichloro- o- phenylene diamine(1mmol) for five hours [2].

B. Synthesis of Mononuclear complex

The complex is synthesized by adding 1mmol ethanolic solution of M(Cu,Ni) to 1mmol ethanolic solution of ligand followed by refluxing the contents for 5 hrs as shown in Fig. 1 [3].



Where M= Cu(II) and Ni(II) ions

Fig.1 Synthesis of Schiff base ligand and its complexes

III. RESULTS AND DISCUSSION

The values obtained from elemental analysis are in good agreement with the values calculated. The molar conductance value of all the complexes in DMF reveals their non-electrolytic nature and the values are shown in Table1.

TABLE 1. ANALYTICAL AND PHYSICAL DATA OF THE COMPOUNDS

Compounds	Mol. formula	Found (calcd) %				$\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
		C	H	N	M	
L	$\text{C}_{22}\text{H}_{14}\text{Cl}_6\text{N}_2\text{O}_2$	47.89 (47.95)	2.51 (2.56)	5.01 (5.08)	-	-
[CuL]	$[\text{CuC}_{22}\text{H}_{12}\text{Cl}_6\text{N}_2\text{O}_2]$	43.09 (43.14)	1.92 (1.97)	3.49 (4.57)	10.31 (10.37)	11
[NiL]	$[\text{NiC}_{22}\text{H}_{12}\text{Cl}_6\text{N}_2\text{O}_2]$	43.42 (43.48)	1.95 (1.99)	4.55 (4.61)	9.63 (9.66)	9

A. IR studies

The infrared spectrum of synthesized ligand and their complexes is very much consistent with the structural data presented in the Table 2. The spectral changes observed in Schiff base ligand and its mononuclear complexes are

- ❖ The bands of azomethine group in Schiff base ligand (Fig. 2) shifts to lower frequency in metal complexes due to coordination through azomethine nitrogen group.
- ❖ The bands of -OH group of aromatic ring disappears in complexes due to M-O bond formation [4].
- ❖ The frequency of C-O in complexes shifts to lower wave number due to M-O bond.
- ❖ The presence of non-ligand band observed between $450\text{-}550 \text{ cm}^{-1}$ indicates the formation Schiff base complexes.

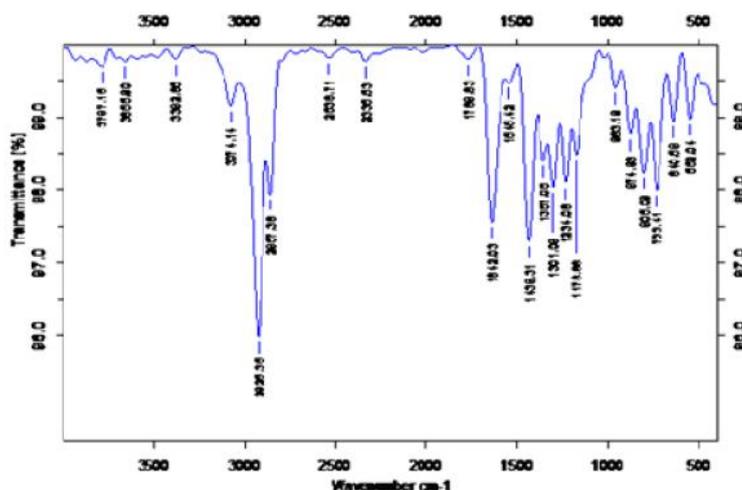


Fig.2 FTIR spectra of Schiff base ligand

TABLE 2. IR AND UV SPECTRAL DATA OF THE LIGAND AND ITS COMPLEXES

Compounds	(C=N) cm^{-1}	(C-O) cm^{-1}	(M-O) cm^{-1}	(M-N) cm^{-1}	λ_{max} nm
L	1642	1301	-	-	-
[CuL]	1616	1232	551	492	578,457
[NiL]	1610	1254	563	477	524

Electronic spectra and Magnetic Moment studies

- ❖ The UV-Visible spectrum of free ligand consist of an intense band centered at 340 nm attributed to $n \rightarrow \pi^*$ transition of azomethine group. Another intense band in higher energy region was related to $\pi \rightarrow \pi^*$ transition of benzene ring. These transitions are also found in the spectra of the complexes, but they shifted towards lower frequencies confirming the coordination of the ligand to the metal ions.
- ❖ The copper complex in DMF showed an intensive band at about 578 and 457 nm bands could be assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ respectively, this indicates square planar geometry for Cu(II) complex. The magnetic moment for complex is 1.80 B.M. which is consistent with one unpaired electron (d^9).
- ❖ The nickel complex exhibits only one band in addition to the intense charge transfer band, in the 524 nm region owing to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition characteristic of square planar geometry which is confirmed by the diamagnetic properties of the complex (Table 2).

NMR Spectra

- ❖ The ${}^1\text{H}$ NMR spectrum of the free Schiff-base shows singlet peaks at 8.24 ppm assigned to $-\text{CH}=\text{N}-$ (imine) protons.
 - ❖ In addition, the chemical shift for the O-H group was observed at 12.73 ppm
 - ❖ The multiplet at 6.67-7.65 ppm is assigned to protons of aromatic ring.
- Hence confirms the structure of the synthesized Schiff base ligand.

ESR spectra

The ESR spectra of copper complexes provide information of importance in studying the metal ion environment. The synthesized Cu(II) complex exhibit an isotropic signal, without any hyperfine splitting, with $g_{\text{iso}} = 2.041$ is shown in the Fig 3. The g values obtained in the present study when compared to the g value of a free electron, 2.0023, indicates an increase of the covalent nature of the bonding between the metal ion and the ligand molecule. Isotropic lines are usually the results due to occupancy of the unpaired electron in a degenerate orbital in square planar geometry.

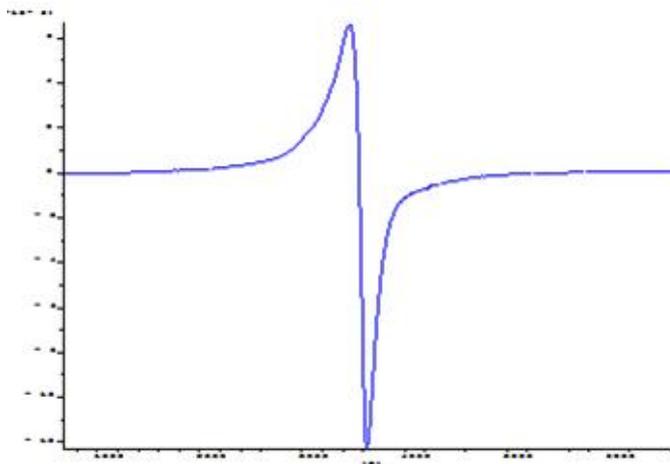


Fig.3 ESR Spectra of Cu(II) Schiff base complexes

Antibacterial Activity

The *in vitro* antibacterial activity of the complexes was tested against the bacterial species like *Bacillus subtilis*, and *Pseudomonas*. The complexes containing (C=N) group have enhanced antimicrobial activity than (C=C) group. This activity can be explained based on Overtone's concept and Tweedy's chelation theory [5]. According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only the lipid-soluble materials. Chelation reduces the polarity of the metal ion because of the partial sharing of its +ve charge with the donor groups and possible electron delocalization over the chelation ring, such chelation enhances the lipophilicity of the central metal atom and favours the permeation through the lipid layer of cell membrane and thus disturbs the respiration process of the cell and this restricts further growth of the organisms. Thus chelation increases the antibacterial activity of the metal complexes. In these prepared complexes, copper complex shows more antibacterial activity than nickel complex as presented in Fig. 4.

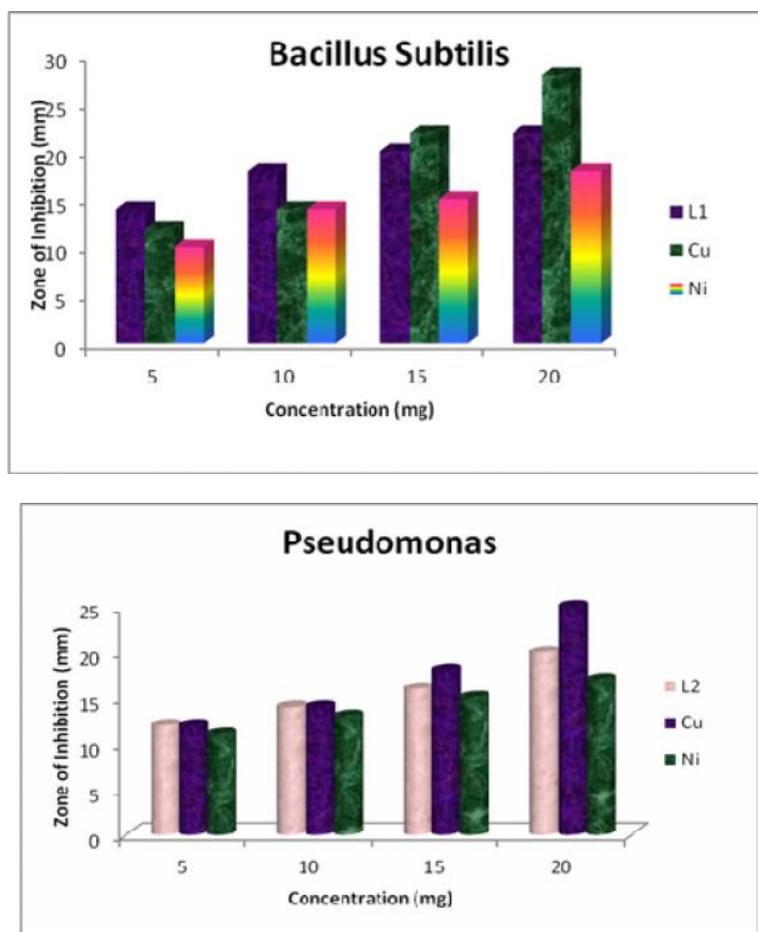


Fig.4 Antibacterial Activity of Schiff base ligand and its complexes

CONCLUSION

Based on the spectral studies, the structural properties of synthesized ligand and its complexes were tentatively proposed. The complexes seem to have greater antibacterial activity than the free ligands.

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