

SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF BICENTRIC SCHIFF BASE METAL COMPLEXES**Jagadale M.M. and Ubale V.P. ***Department of Chemistry, D.B.F. Dayanand College of Arts and Science, Solapur-413002, (M.S.), India.
(*Email: vpubale@yahoo.co.in)**ABSTRACT**

The new Schiff base ligand N, N' - (2 -hydroxybenzaldehyde) diamino diphenyl ether [HL] and its Ni (II) and Zn (II) metal complexes were synthesized. The ligand and metal complexes were characterized by UV-visible, FTIR and ¹H NMR spectroscopy. The ligand [HL] was synthesized by condensation of 2-hydroxybenzaldehyde and 4, 4'-diaminodiphenyl ether. The ligand and metal (II) complexes were also screened for their antimicrobial activity against microorganisms *Staphylococcus aureus* and *Pseudomonas aeruginosa*.

KEY WORDS: Antibacterial activity, 4, 4'-diaminodiphenyl ether, Schiff base, Transition metal complexes.**INTRODUCTION**

The Schiff base complexes are important as medicine and show a variety of interesting biological activities such as antibacterial and antifungal activity (Jarahour, 2004; Awad, 1988). Transition metal complexes with various donor groups have been used in organometallic chemistry. A large number of Schiff base compounds have been synthesized and structurally characterized (Swamy, 2000; Shirodkar, 2001; Rajavel, 2008). The various classes of Schiff bases that can be prepared by condensation of different types of amines and carbonyl compounds are very popular due to diverse chelating ability. Several transition metal complexes have been screened for their medicinal properties (Gangadhar, 2008; Iqbal, 2006; Chen, 2008; Narayan, 1994). These factors prompted us to carry out a study on synthesis of Schiff base and its complexes with Ni (II) and Zn(II) metal ions.

In this paper we report the synthesis of new Schiff base ligand N, N' - (2- hydroxybenzaldehyde) diamino diphenyl ether [HL] and its ligation behavior with Ni (II) and Cu(II) metals. The synthesized ligand and metal complexes were characterized by elemental analysis, UV-Visible, FTIR and ¹H NMR. They are also screened for their biological activities against the microorganism *Pseudomonas aeruginosa* and *Staphylococcus aureus*.

MATERIALS AND METHODS

All reagents used such as 2- hydroxybenzaldehyde, 4, 4'-diaminodiphenyl ether, nickel chloride and zinc chloride were pure AR grade. Solvents such as ethanol and dichloromethane were purified prior to use as per standard procedure.

2-Hydroxybenzaldehyde (4.88 g, 0.04 mol) and 4, 4'-diaminodiphenyl ether (4.0 g, 0.02 mol) were dissolved in ethanol (25 ml) separately in 2:1 molar ratio. The ethanolic solutions were mixed together. The mixture was refluxed for 3 h. Yellow coloured crystalline ligand (HL) was separated. The completion of reaction was confirmed with chromatographic method. It was subjected to filtration. Ligand was recrystallized and dried over anhydrous CaCl₂ (Scheme -1).

A ligand (1 mmol) [HL] was dissolved in (25 ml) dichloromethane and added to a metal salt [nickel chloride (2mmol) / or zinc chloride (2mmol)] ethanolic solution (25 ml). The metal-ligand molar ratio was (2:1). The mixture was refluxed for 2 h. On cooling, a crystalline complex was separated by filtration and crystals were washed and dried (Scheme -2).

The antibacterial activity of the Schiff bases and their metal complexes was tested on *Staphylococcus aureus*, *Pseudomonas aeruginosa*. The method used for antibacterial activity was Agar Well-Diffusion method (Khalood's Abou-Melha, 2008). The stock solution 1mg/ml was prepared and was used to prepare concentrations of 8, 6, 4 and 2 ug/l. The bacteria and fungi were inoculated on the surface of Nutrient agar and Sabouraud's agar, respectively. The various concentrations of the compounds were inoculated in the wells prepared on the agar plates. The plates were incubated at room temperature for 24 h. In order to clarify the effect of dimethylformamide (DMF) on the biological screening, separate studies were carried out with dimethylformamide and showed no activity against any bacteria. The results are as summarized in the Table- 3.

RESULTS AND DISCUSSION

Analytical and physical data of the compounds studied is reported in Table- 1. The ligand and the metal (II) complexes are soluble in common polar solvents like chloroform, dichloromethane and dimethylacetamide. Synthesized ligand and the metal complexes were characterized by spectroscopic methods. Biological activity of the ligand and the metal complexes were also studied.

The electronic spectra are very useful in the evaluation of results obtained by other methods of structural investigation. Information regarding the geometry of the complexes around the Ni(II) and Zn(II) ions was obtained from electronic spectral studies. The electronic spectra of ligand and their metal complexes were recorded at room temperature using dichloromethane as a solvent.

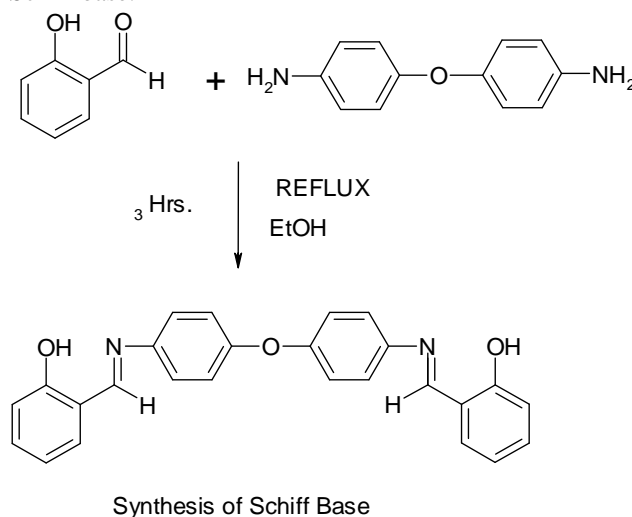
The electronic spectra of ligand show bands in the region of 234 nm and 278 nm but in the complexes they are slightly shifted to longer wavelength frequencies. The band between 375 nm can be assigned to $n \rightarrow \pi^*$ of transition of azomethine group. In the spectra of complexes the bands of azomethine chromophore $n \rightarrow \pi^*$ transition are shifted to lower frequencies indicates that imine nitrogen is involved in the co-ordination of metal ion. A very weak low intensity absorption band associated with d-d transition for Zn(II) complexes at 465 nm, 532 nm (typical octahedral transition) and for Ni(II) complexes at 470 nm (Charge transfer), 525 nm $\rightarrow [^3A_{2g}(F) \rightarrow ^3T_{1g}(P)]$, 985 nm $[^3A_{2g} \rightarrow ^3T_{1g}(F)]$ respectively supports the octahedral geometry of metal complexes (Yamgar, 2009).

IR spectral data of Schiff base [HL] and their metal complexes are presented in Table 2. IR spectra of complexes are compared with those of ligand in order to determine the coordination sites that may be involved in chelation. A strong absorption band at 1620 cm^{-1} in a ligand [HL] is a characteristic band of (C=N) azomethine group. The shifting of this band towards lower frequency region by $10\text{--}15\text{ cm}^{-1}$ in complexes indicates involvement of azomethine nitrogen in coordination with metal ion (Thankamony, 2007; Gehad, 2007; Wang, 1995). The assignment of the proposed coordination sites is further supported by appearance of band at $521\text{--}544\text{ cm}^{-1}$ suggesting the ν (M-N) bond. The presence of ν (M-O) stretching vibration at $740\text{--}750\text{ cm}^{-1}$ supports the involvement of oxygen atom in complexation with metal ions. The ligand and metal complexes were characterized mainly using the azomethine and -O-H str. absorption bands in IR spectra. In the complexes, the broad band in the range of $3357\text{--}3365\text{ cm}^{-1}$ is attributed to the presence of -O-H str. It shows that the ligand coordinates to the metal ions via azomethine nitrogen and deprotonated oxygen atom from 2-hydroxybenzaldehyde.

Structure of N, N'- (2- hydroxybenzaldehyde) diamino diphenyl ether [HL] is confirmed by ^1H NMR spectra (Ahmed, 2007).

A ligand (HL) and their Ni(II) and Zn(II) complexes shows good antibacterial and antifungal activity.

Scheme -1: Synthesis of Schiff base.



Scheme -2: Synthesis of metal complexes.

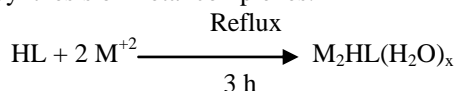


Table -1: Analytical and Physical data of the compounds.

Sr. No.	Sample code	Molecular formula (Mol.Wt.)	Colour	M.P./decomposition Temp.(^o C)	Yield %
1	HL	C ₂₆ H ₂₀ N ₂ O ₃ (408)	Faint Yellow	215	95
2	HL-Ni	C ₂₆ H ₂₀ N ₂ O ₃ ·2Ni·4H ₂ O (870)	Yellowish Green	>295	85
3	HL-Zn	C ₂₆ H ₂₀ N ₂ O ₃ ·2Zn·4H ₂ O (822)	Yellowish Orange	>295	87

Table -2: FTIR spectral data.

Sample Code	$\nu_{(C=N)}$ cm ⁻¹	$\nu_{(C-O)}$ cm ⁻¹	$\nu_{(M-O)}$ cm ⁻¹	$\nu_{(M-N)}$ cm ⁻¹	$\nu_{(O-H)}$ cm ⁻¹
HL	1620	1188	-	-	3380
HL -Ni	1605	1148	460	521	3357
HL -Zn	1602	1145	465	544	3360

Table -3: Biological activity of HL and its Metal Complexes.

Sample Code	Conc. $\mu\text{g} / \text{mL}$	<i>Staphylococcus Aureus</i>	<i>Pseudomonas Aeruginosa</i>
HL	2	-	-
	4	+	-
	6	+	+
	8	+	+
HL-Zn	2	+	-
	4	+	-
	6	+	+
	8	+	+
HL-Ni	2	++	+
	4	++	++
	6	++	++
	8	+++	++

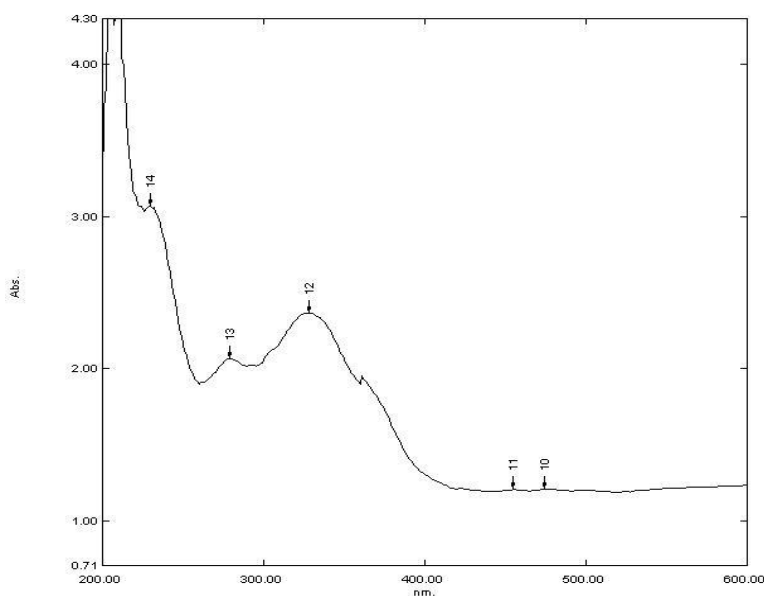


Figure -1 : UV-Visible spectra of Schiff base ligand [HL]

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