



International Journal of
Medicinal Chemistry & Analysis

www.ijmca.com

e ISSN 2249 - 7587
 Print ISSN 2249 - 7595

**SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL
 ACTIVITY OF MIXED LIGAND COMPLEXES OF N-(2-HYDROXY-1-
 NAPHTHYLIDENE)-4-NITROANILINE AND N-(2-
 HYDROXYBENZYLIDENE)-2,3-DIMETHYLANILINE WITH Co(II),
 Ni(II), Cu(II) AND Zn(II) IONS**

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ABSTRACT

The mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases N-(2-hydroxy-1-naphthylidene)-4-nitroaniline (L^1H) and N-(2-hydroxybenzylidene)-2,3-dimethylaniline (L^2H) have been synthesized and characterized. The resulting complexes were characterized by elemental analysis, thermogravimetric analysis, magnetic moment measurements, conductivity measurements, 1H NMR, IR, UV-visible and ESR spectral studies. The Schiff bases acts as bidentate monobasic ligands, coordinating through deprotonated phenolic oxygen and azomethine nitrogen atoms. The complexes are non-electrolytic in DMSO. The presence of the two coordinated water molecules in these complexes was indicated by IR spectra and thermogravimetric analysis of the complexes. From the analytical and spectral data the stoichiometry of these complexes have been found to be $[M(L^1)(L^2)(H_2O)_2]$ {where $M = Co(II), Ni(II), Cu(II)$ and $Zn(II)$ }. It is found that Co(II), Ni(II), Cu(II) and Zn(II) complexes exhibited octahedral geometry. The antimicrobial activities of ligands and their mixed ligand complexes were screened by Disc Diffusion method. It was found that the metal complexes have higher antimicrobial activity than the free ligand.

Keywords: Schiff bases, Mixed ligand, Metal complexes, Antimicrobial activity.

INTRODUCTION

Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions [1, 2]. Many biologically important Schiff bases have been reported in the literature possessing, antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitumor and anti HIV activities [3-8]. The present work is the study of mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases N-(2-hydroxy-1-naphthylidene)-4-nitroaniline (L^1H) and N-(2-hydroxybenzylidene)-2,3-dimethylaniline (L^2H)

MATERIALS AND METHODS

All the chemicals used in the present work were

of analytical grade. The metal salts used were in their hydrated form.

Synthesis of ligands

The ligands (L^1H and L^2H) were prepared by the condensation of the corresponding aldehyde and amine in 1:1 molar ratio by refluxing in distilled methanol [9].

Preparation of complexes

A metal(II) chloride (1.0 mmol.) dissolved in water (2 mL) was added slowly with constant stirring to a solution of N-(2-hydroxy-1-naphthylidene)-4-nitroaniline (L^1H) (1.0 mmol.) and N-(2-hydroxybenzylidene)-2,3-dimethylaniline (L^2H) (1.0 mmol.) in ethanol (100 mL). The pH of the solution was slowly raised to obtain the

appropriate pH for the formation of the complex by the drop wise addition of 0.1 N sodium hydroxide solution. The resulting mixture was stirred for 2-3 hour. The product was digested on a hot water bath for half an hour. The complex thus formed was filtered out, washed with aqueous alcohol followed by distilled water and dried in vacuum over fused CaCl₂. Similarly all the complexes were prepared. The metal estimations were carried out by standard Methods [10]. Elemental analysis was performed at SAIF, IIT Bombay, Mumbai. The conductance was measured in DMSO solvent on an Equiptronic EQ-660 conductivity meter. The magnetic susceptibility measurements at room temperature were made on Gouy balance using HgCo(NCS)₄ as calibrant. The ¹H NMR spectrum of the ligands and Zn(II) complex was recorded on Varian Mercury plus 400 MHz spectrometer using TMS as internal standard and (D₆) DMSO as a solvent. The IR spectra of ligands and their complexes were recorded on a Shimadzu FTIR – 8400S spectrometer in KBr pellets in the range of 4000-350 cm⁻¹. UV-Visible spectra were recorded on a Jasco V-530 UV-Visible spectrometer in the range 200-1100 nm. Electron spin resonance spectra of powdered Cu(II) complex was recorded on Varian E-112x-band ESR spectrometer using TCNE as 'g' marker (g = 2.0027) at room temperature. Thermal analysis of the metal complexes was carried out using Mettler Toledo Star^c SW 7.01 thermal analyzer in an inert atmosphere of nitrogen. The antimicrobial activities of ligands and their mixed ligand complexes were screened by Disc Diffusion method.

RESULTS AND DISCUSSION

The elemental analysis shown in the Table 1 indicates that, all the metal complexes have 1:1:1 stoichiometry with respect to L¹H: L²H: M {where M = Co(II), Ni(II), Cu(II) and Zn(II)} and are dark colored amorphous substances, soluble in DMF and DMSO. The molar conductance values (0.012 - 0.015 ohm⁻¹ mol⁻¹ cm²) of 10⁻³ M solution in DMSO indicate that the metal complexes are non-electrolytic in nature.

Electronic spectra and Magnetic moment

The electronic spectral studies of Mixed Ligand Complexes of Co(II), Ni(II), Cu(II) and Zn(II) were carried out in DMSO solution. The absorption spectrum of the Co(II) complex shows bands at ~ 9523.81 cm⁻¹ (ε ~ 27 L mol⁻¹ cm⁻¹) and ~ 19047.62 cm⁻¹ (ε ~ 60 L mol⁻¹ cm⁻¹) attributed to ⁴T_{1g}(F) → ⁴T_{2g}(F) (ν₁) and ⁴T_{1g}(F) → ⁴T_{1g}(P) (ν₃) transitions respectively in an octahedral field [11]. The spectral parameters of Co(II) complex are as follows [12] : Dq = 1064.85 cm⁻¹, B = 709.9 cm⁻¹, β = 0.731 and β⁰ = 26.9 %. The reduction of Racah parameter from the free ion value 971 cm⁻¹ and β⁰ value of 26.9 % testify the presence of considerable covalence in the complex [13]. The Co(II) complex has magnetic moment 5.14 B.M. also suggest an octahedral geometry. Ni(II)

complex exhibits two electronic spectral bands at ~ 10504.20 cm⁻¹ (ε ~ 30 L mol⁻¹ cm⁻¹) and ~ 16393.44 cm⁻¹ (ε ~ 87 L mol⁻¹ cm⁻¹) which can be assigned to ³A_{2g}(F) → ³T_{2g}(F) (ν₁) and ³A_{2g}(F) → ³T_{1g}(F) (ν₂) transitions in an octahedral field [14]. The transition due to ³A_{2g}(F) → ³T_{1g}(P) (ν₃) was completely obscured by the intense intra ligand transition band. The ν₂: ν₁ ratio is 1.56, which is in the usual range reported for an octahedral Ni(II) complexes [15]. The spectral parameters of the Ni(II) complex are as follows [12] : Dq = 1050.23 cm⁻¹, B = 724.30 cm⁻¹, β = 0.703 and β⁰ = 29.7 %. The reduction of Racah parameter from the free ion value 1030 cm⁻¹ and β⁰ value of 29.7 % confirms the presence of considerable covalence in the complex [13]. The Ni(II) complex has magnetic moment 3.47 B.M. also suggest an octahedral geometry. The Cu(II) complex exhibit broad band centered at ~ 14285.71 cm⁻¹ (ε ~ 120 L mol⁻¹ cm⁻¹) mainly due to ²E_g → ²T_{2g} transition suggesting the distorted octahedral geometry [16]. The observed magnetic moment value for Cu(II) complex is 1.81 B.M. suggestive of distorted octahedral nature for the complex [16]. Zn(II) complex does not exhibit any characteristic d-d transitions and also found to be diamagnetic in nature.

Infrared spectra

The important infrared frequencies exhibited by the ligands L¹H and L²H and their mixed ligand metal complexes are given in the Table 2. Infrared spectra of the schiff bases L¹H and L²H show a broad band centered at around 3437 cm⁻¹ and 3447 cm⁻¹ due to ν(OH) of the phenolic hydroxyl group respectively in free ligands, which disappeared in spectra of their complexes indicating probably the coordination through phenolic oxygen moiety. The schiff bases L¹H and L²H show a medium intensity band at around 1335 cm⁻¹ and 1279 cm⁻¹ due to ν(C-O) (phenolic) is shifted to higher region at around 1381-1399 cm⁻¹ and 1359-1369 cm⁻¹ respectively indicating the coordination through the phenolic oxygen atoms [14,15,17]. The IR spectra of the schiff bases L¹H and L²H exhibit a strong band at 1622 cm⁻¹ and 1613 cm⁻¹ due to ν(C=N) (azomethine) which has been shifted towards lower region at around 1613-1616 cm⁻¹ and 1601-1602 cm⁻¹ respectively in the spectra of complexes indicating the participation of the azomethine groups in the complex formation [17,18]. The spectra of the complexes show a broad diffused bands in the region at around 3150-3700 cm⁻¹, strong bands at 1534-1537 cm⁻¹ and weak intensity bands at 829-836 cm⁻¹ due to ν(OH), δ(OH) and ρ_r(OH) respectively of the coordinated water molecules [14,15]. The coordination through nitrogen of azomethine and oxygen of (C-O) group of ligands are further evidenced by the appearance of non-ligand bands in the complexes at around 503-557 cm⁻¹ and 416-463 cm⁻¹ are due to ν(M-O) and ν(M-N) vibrations respectively [17,18].

¹H NMR spectra

The ¹H NMR spectrum of the ligand (L¹H) showed singlet at 15.217 δ (s, 1H, OH) due to proton of phenolic –OH group. The azomethine proton have resonated as singlet at 9.682 δ (s, 1H, CH=N). The ten aromatic protons have resonated in the region 6.594-8.545 δ (m, 10H, Ar-H) as multiplet. The ¹H NMR spectrum of the ligand (L²H) showed singlet at 13.291 δ (s, 1H, OH) due to proton of phenolic -OH group. The azomethine proton have resonated as singlet at 8.77 δ (s, 1H, CH=N). The seven aromatic protons have resonated in the region 6.956 – 7.622 δ (m, 7H, Ar-H) as multiplet. The six protons of two methyl groups resonated as two singlets at 2.198 δ (s, 3H, Ar-CH₃) and 2.251 δ (s, 3H, Ar-CH₃).

The ¹H NMR spectrum of the [Zn(L¹)(L²)(H₂O)₂] complex showed singlet at 9.281 δ (s, 1H, CH=N) and 8.511 δ (s, 1H, CH=N) due to two protons of the two azomethine groups. The seventeen aromatic protons have resonated in the region 6.303-8.306 δ (m, 17H, Ar-H) as multiplet. The six protons of two methyl groups resonated as two singlets at 1.975 δ (s, 3H, Ar-CH₃) and 2.115 δ (s, 3H, Ar-CH₃). The proton of phenolic –OH group which was observed at 15.217 δ (s, 1H, OH) and 13.291 δ (s, 1H, OH) for Schiff bases L¹H and L²H respectively has disappeared in Zn(II) complex, indicating coordination through phenolic oxygen moiety to the metal ion via deprotonation [15,17].

Thermogravimetric analysis

The dynamic TGA with the percentage mass loss at different steps have been recorded. The elimination of lattice and coordinated water molecules take place in the first step. The Co(II), Ni(II), Cu(II) and Zn(II) complexes lose their weight in the temperature range ~ 125-290 °C, 130-285 °C, 125-285 °C and 130-290 °C respectively corresponding to two coordinated water molecules with an endothermic peak in DTA curve. After the total loss of water, the organic moiety decomposes on further increment of temperature. The complete decomposition of ligands occurs at ~ 450-650 °C and the observed residue corresponds to the respective oxide. The occurrence of

endothermic peaks in DTA curves and elimination of the two water molecules at comparatively higher temperature unambiguously confirm our earlier observation based upon the IR spectrum that the water molecules are coordinated in the metal complexes [11,14].

ESR spectra

The ESR spectrum of the powdered sample of the Cu(II) complex was recorded at room temperature. The observed value of ESR spectral parameters for the [Cu(L¹)(L²)(H₂O)₂] complex are $g_{\parallel} = 2.137$, $g_{\perp} = 2.083$ and $G = 1.667$. The observed g_{\parallel} value is less than 2.3 in agreement with the covalent character of the metal – ligand bond [13]. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0023) observed for this complex shows that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of Cu(II) ion and the spectral

features are characteristic of axial symmetry; tetragonal elongated structure may be assumed for this Cu(II) complex [13]. The anisotropic G values have been calculated by using the equation $G = (g_{\parallel} - 2.002) / (g_{\perp} - 2.002)$. If the G value is less than 4.0, the ligand forming the copper(II) complex is regarded as strong field ligand while a value of G greater than 4.0 indicates weak field ligand. As $G = 1.667$ for the present complex indicates that the ligands L¹H and L²H are strong field ligands and the metal-ligand bonding in this complex is covalent [13].

Antimicrobial activity

Synthesized Schiff bases and their corresponding mixed ligand metal complexes were screened against microorganisms such as *E.coli*, *S.aureus*, *B.subtilis*, and *S.typhi* to assess their potential as antimicrobial agent by Disc Diffusion method. The zones of inhibition based upon zone size around the discs were measured. The measured zone of inhibition against the growth of various microorganisms is listed in Table 3. It is found that the metal complexes have higher antimicrobial activity than the free ligand. Hence complexation increases the antimicrobial activity [15,17].

Table 1. Analytical and Physical data of Schiff bases L¹H, L²H and their mixed ligand metal complexes

Ligand / complex, Molecular Formula	Mol. Wt.	M.P / Decomp. Temp. °C	Analysis % Found (Calculated)				Molar Conductance (λm) Ohm ⁻¹ cm ² mol ⁻¹
			C	H	N	M	
L ¹ H C ₁₇ H ₁₂ N ₂ O ₃	292.29	138	69.65 (69.86)	4.34 (4.14)	9.71 (9.58)	-	-
L ² H C ₁₅ H ₁₅ NO	225.29	91	79.75 (79.97)	6.63 (6.71)	6.12 (6.21)	-	-
[Co(L ¹)(L ²)(H ₂ O) ₂] C ₃₂ H ₂₉ N ₃ O ₆ Co	610.25	>250	62.67 (62.95)	4.71 (4.79)	6.67 (6.88)	9.78 (9.65)	0.018
[Ni(L ¹)(L ²)(H ₂ O) ₂] C ₃₂ H ₂₉ N ₃ O ₆ Ni	610.28	>250	62.81 (62.98)	4.91 (4.79)	6.78 (6.890)	9.75 (9.62)	0.012

[Cu(L ¹)(L ²)(H ₂ O) ₂] C ₃₂ H ₂₉ N ₃ O ₆ Cu	615.14	>250	62.57 (62.48)	4.87 (4.75)	6.67 (6.83)	10.42 (10.33)	0.014
[Zn(L ¹)(L ²)(H ₂ O) ₂] C ₃₂ H ₂₉ N ₃ O ₆ Zn	617.00	>250	62.11 (62.29)	4.92 (4.74)	6.67 (6.81)	10.51 (10.60)	0.015

Table 2. Characteristic IR bands of the Schiff Bases L¹H, L²H and their mixed ligand metal complexes

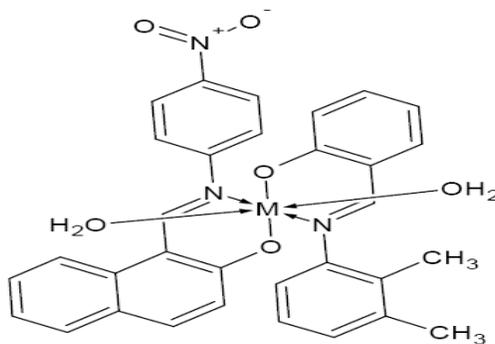
Schiff base / Complex	IR bands (cm ⁻¹)							
	ν_{OH} (phenolic)	ν_{OH} (H ₂ O)	$\nu_{C=N}$	δ_{OH} (H ₂ O)	ν_{C-O} (phenolic)	ρ_{OH} (H ₂ O)	ν_{M-O}	ν_{M-N}
L ¹ H	3437	-	1622	-	1335	-	-	-
L ² H	3447	-	1613	-	1279	-	-	-
[Co(L ¹)(L ²)(H ₂ O) ₂]	-	3150- 3650	1614, 1601	1535	1381, 1359	834	550, 511	457, 416
[Ni(L ¹)(L ²)(H ₂ O) ₂]	-	3150- 3700	1615, 1602	1534	1399, 1369	831	554, 503	459, 418
[Cu(L ¹)(L ²)(H ₂ O) ₂]	-	3200- 3650	1613, 1601	1536	1383, 1360	829	555, 508	461, 421
[Zn(L ¹)(L ²)(H ₂ O) ₂]	-	3150- 3700	1616, 1602	1537	1381, 1362	836	557, 510	463, 422

Table 3. Antimicrobial activity data of the ligands L¹H, L²H and their mixed ligand metal complexes

Schiff base / Complex	Zone of inhibition (mm)			
	<i>S.aureus</i>	<i>B.subtilis</i>	<i>E.coli</i>	<i>S.typhi</i>
L ¹ H	-	-	-	-
L ² H	-	-	-	-
[Co(L ¹)(L ²)(H ₂ O) ₂]	+	+	+	-
[Ni(L ¹)(L ²)(H ₂ O) ₂]	+	+	+	-
[Cu(L ¹)(L ²)(H ₂ O) ₂]	-	+	+	-
[Zn(L ¹)(L ²)(H ₂ O) ₂]	+	++	-	+

Highly active = +++ (inhibition zone > 12 mm); moderately active = ++ (inhibition zone > 9-12 mm); slightly active = + (inhibition zone > 6-9 mm); Inactive = - (inhibition zone < 6 mm)

Figure 1. Proposed structure for the complexes



M = Co(II), Ni(II), Cu(II) and Zn(II).

CONCLUSION

The elemental analysis, magnetic susceptibility, electronic, ¹H NMR, IR and ESR spectral observations suggest the octahedral geometry for the Co(II), Ni(II), Cu(II) and Zn(II) complexes and exhibit coordination

number six. The general structure of the complexes is shown in figure 1. The Schiff's bases do show some antimicrobial activity to certain extent but their complexes exhibit comparatively greater amount of activity against the microorganisms.

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