

Synthesis, Characterization and Antimicrobial Activity of Mixed Schiff Base Ligand Complexes of Transition Metal(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-chloroaniline (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, ¹HNMR, 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-chloroaniline (L^1H) and N-(2-hydroxybenzylidene)-2,3-dimethylaniline (L^2H)

Experimental

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-chloroaniline (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 $CaCl_2$. 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 (D_6) 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^e 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 L^1H : L^2H : 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 (0.010 - 0.016 $ohm^{-1} mol^{-1} cm^2$) of 10^{-3} M solution in DMSO indicate that the metal complexes are non-electrolytic in nature

Table 1. Analytical and Physical data of Schiff bases L^1H , L^2H and their mixed ligand 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^1H $C_{17}H_{12}ClNO$	284.74	159	72.31 (72.47)	4.16 (4.29)	4.82 (4.97)	-	-
L^2H $C_{15}H_{15}NO$	225.29	91	79.75 (79.97)	6.63 (6.71)	6.12 (6.21)	-	-
$[Co(L^1)(L^2)(H_2O)_2]$ $C_{32}H_{29}ClN_2O_4Co$	599.97	>250	64.25 (64.06)	4.61 4.87	4.89 (4.67)	9.52 (9.82)	0.016
$[Ni(L^1)(L^2)(H_2O)_2]$ $C_{32}H_{29}ClN_2O_4Ni$	599.73	232	64.32 (64.09)	4.74 (4.87)	4.49 (4.67)	9.95 (9.79)	0.011
$[Cu(L^1)(L^2)(H_2O)_2]$ $C_{32}H_{29}ClN_2O_4Cu$	604.58	>250	63.49 (63.57)	4.62 (4.83)	4.47 (4.63)	10.39 (10.51)	0.013
$[Zn(L^1)(L^2)(H_2O)_2]$ $C_{32}H_{29}ClN_2O_4Zn$	606.45	149	63.10 (63.38)	4.73 (4.82)	4.82 (4.61)	10.58 (10.79)	0.010

Electronic spectra and Magnetic moment

The electronic spectral studies of Mixed Ligand Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases L^1H and L^2H were carried out in DMSO solution. The absorption spectrum of the Co(II) complex shows bands at $\sim 9363.30 \text{ cm}^{-1}$ ($\epsilon \sim 20 \text{ L mol}^{-1} \text{ cm}^{-1}$) and $\sim 18867.92 \text{ cm}^{-1}$ ($\epsilon \sim 50 \text{ L mol}^{-1} \text{ cm}^{-1}$) attributed to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions respectively in an octahedral field [11]. The spectral parameters of Co(II) complex are as follows [12]: $Dq = 1036.8 \text{ cm}^{-1}$, $B = 715.04 \text{ cm}^{-1}$, $\beta = 0.736$ and $\beta^0 = 26.4\%$. The reduction of Racah parameter from the free ion value 971 cm^{-1} and β^0 value of 26.4% testify the presence of considerable covalence in the complex [13]. The Co(II) complex has magnetic moment 5.10 B.M. also suggest an octahedral geometry. Ni(II) complex exhibits two electronic spectral bands at $\sim 10362.69 \text{ cm}^{-1}$ ($\epsilon \sim 30 \text{ L mol}^{-1} \text{ cm}^{-1}$) and $\sim 16260.16 \text{ cm}^{-1}$ ($\epsilon \sim 87 \text{ L mol}^{-1} \text{ cm}^{-1}$) which can be assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) transitions in an octahedral field [14]. The transition due to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) was completely obscured by the intense intra ligand transition band. The $\nu_2 : \nu_1$ ratio is 1.57 , 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]: $Dq = 1036.27 \text{ cm}^{-1}$, $B = 740 \text{ cm}^{-1}$, $\beta = 0.719$ and $\beta^0 = 28.1\%$. The reduction of Racah parameter from the free ion value 1030 cm^{-1} and β^0 value of 28.1% confirms the presence of considerable covalence in the complex [13]. The Ni(II) complex has magnetic moment 3.20 B.M. also suggest an octahedral geometry. The Cu(II) complex exhibit broad band centered at $\sim 14705.9 \text{ cm}^{-1}$ ($\epsilon \sim 95 \text{ L mol}^{-1} \text{ cm}^{-1}$) mainly due to ${}^2E_g \rightarrow {}^2T_{2g}$ 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 L^1H and L^2H and their mixed ligand complexes are given in the Table 2. Infrared spectra of the schiff bases L^1H and L^2H show a broad band centered at around 3440 and 3447 cm^{-1} due to 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 L^1H and L^2H show a medium intensity band at around 1327 and 1279 cm^{-1} due to phenolic $\nu(C-O)$ group of is shifted to higher region at around 1380 - 1385 and 1362 - 1366 respectively indicating the coordination through the phenolic oxygen atoms [14,15,17]. The IR spectra of the schiff bases L^1H and L^2H exhibit a strong band at 1620 and 1613 cm^{-1} due to $\nu(C=N)$ (azomethine) which has been shifted towards lower region at around 1614 - 1616 and 1599 - 1603 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 3100 - 3700 cm^{-1} , strong bands at 1535 - 1538 cm^{-1} and weak intensity bands at 815 - 832 cm^{-1} due to $\nu(OH)$, $\delta(OH)$ and $\rho_r(OH)$ 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 in the complexes of non-ligand bands around 497 - 545 cm^{-1} and 417 - 465 cm^{-1} are due to M-O and M-N bonds respectively [17,18].

Table 2. Characteristic IR bands of the Schiff Bases L^1H , L^2H and their mixed ligand complexes.

Schiff base / Complex	IR bands (cm^{-1})							
	ν_{OH} (phenolic)	ν_{OH} (H_2O)	$\nu_{C=N}$	δ_{OH} (H_2O)	ν_{C-O} (phenolic)	ρ_{rOH} (H_2O)	ν_{M-O}	ν_{M-N}
L^1H	3440	-	1620	-	1327	-	-	-
L^2H	3447	-	1613	-	1279	-	-	-
$[Co(L^1)(L^2)(H_2O)_2]$	-	3150-3650	1614, 1599	1535	1381, 1365	832	545, 506	465, 421
$[Ni(L^1)(L^2)(H_2O)_2]$	-	3100-3700	1615, 1599	1536	1380, 1362	827	540, 497	464, 419
$[Cu(L^1)(L^2)(H_2O)_2]$	-	3150-3650	1615, 1603	1538	1385, 1366	815	534, 501	461, 417
$[Zn(L^1)(L^2)(H_2O)_2]$	-	3150-3600	1616, 1602	1535	1384, 1363	826	539, 498	462, 419

¹H NMR spectra

The ¹H NMR spectrum of the ligand (L¹H) showed singlet at 15.59 δ (s, 1H, OH) due to proton of phenolic –OH group. The azomethine proton have resonated as singlet at 9.63 δ (s, 1H, CH=N). The ten aromatic protons have resonated in the region 6.999-8.470 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(II) complex showed two singlet at 9.286 δ (s, 1H, CH=N) and 8.473 δ (s, 1H, CH=N) due to two protons of the two azomethine groups. The seventeen aromatic protons have resonated in the region 6.650-8.188 δ (m, 17H, Ar-H) as multiplet. The six protons of two methyl groups resonated as two singlets at 1.867 δ (s, 3H, Ar-CH₃) and 2.098 δ (s, 3H, Ar-CH₃). The proton of phenolic –OH group which was observed at 15.59 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 ~ 135-270 °C, 135-250 °C, 120-250 °C and 135-280 °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 peak 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 for the [Cu(L¹)(L²)(H₂O)₂] complex are g_{||} = 2.137, g_⊥ = 2.082 and G = 1.589. The observed g_{||} value is less than 2.3 in agreement with the covalent character of the metal – ligand bond [13]. The trend g_{||} > g_⊥ > 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 [13,19]. The anisotropic G values have been calculated by using the equation $G = (g_{||} - 2.002) / (g_{⊥} - 2.002)$. 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 = 1.571 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

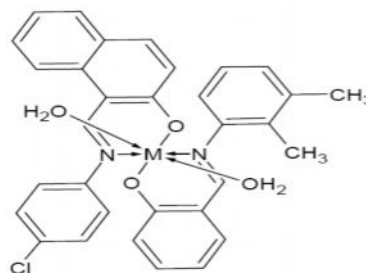
Synthesized Schiff bases and their corresponding mixed ligand metal complexes were screened against *E.coli*, *S.aureus*, *B.subtilis*, and *S.typhi* to assess their potential as antimicrobial agent by Disc Diffusion method. The zones of inhibition based upon zone size around the discs were measured. 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 3. Antimicrobial activity data of the ligands L¹H, L²H and their mixed ligand complexes.

Schiff base / Complex	Zone of inhibition (mm)			
	S.aureus	B.subtilis	E.coli	S.typhi
L ¹ H	2.5	2.8	0.0	2.7
L ² H	0.0	2.5	2.8	2.6
[Co(L ¹)(L ²)(H ₂ O) ₂]	3.8	4.2	4.1	5.1
[Ni(L ¹)(L ²)(H ₂ O) ₂]	9.0	5.5	6.5	5.3
[Cu(L ¹)(L ²)(H ₂ O) ₂]	9.7	3.8	6.8	7.1
[Zn(L ¹)(L ²)(H ₂ O) ₂]	9.2	7.3	8.5	7.0

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.



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

Figure 1. Proposed structure for the complexes.

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