Synthesis, Characterization and Antimicrobial Activity of Mixed Ligand Complexes of 1-{(E)-[(5-fluoro-2-methoxyphenyl)imino]methyl}naphthalen-2-ol and 4-bromo-2-{(E)-[(4-methoxy-2-methylphenyl)imino]methyl}phenol with Co(II), Ni(II), Cu(II) and Zn(II) ions.

Atmaram K. Mapari*

*Ramnarain Ruia College, Matunga (E), Mumbai: - 400019, Maharashtra, India.

Abstract: The mixed ligand complexes of Co(II), Ni(II), Cu(II) and Zn(II) with Schiff bases 1-{(E)-[(5-fluoro-2-methoxyphenyl)imino]methyl} naphthalen-2-ol (L¹H) and 4-bromo-2-{(E)-[(4-methoxy-2-methylphenyl) imino]methyl} phenol (L²H) have been synthesized and characterized. The resulting complexes were characterized by elemental analysis, thermogravimetric analysis, magnetic moment measurements, conductivity measurements, 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(L¹H)(L²H)(H₂O)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 1-{(E)-[(5-fluoro-2-methoxyphenyl)imino]methyl} naphthalen-2-ol (L¹H) shown and 4-bromo-2-{(E)-[(4-methoxy-2-methylphenyl)imino]methyl} phenol (L²H) shown in Figure 1 and 2 respectively.
Figure 1. 1-{(E)-[(5-fluoro-2-methoxyphenyl)imino]methyl}naphthalen-2-ol

Figure 2. 4-bromo-2-{(E)-[(4-methoxy-2-methylphenyl)imino]methyl}phenol

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\textsuperscript{1}H and L\textsuperscript{2}H) 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 1-{(E)-[(5-fluoro-2-methoxyphenyl)imino]methyl}naphthalen-2-ol (L\textsuperscript{1}H) (1.0 mmol.) and 4-bromo-2-{(E)-[(4-methoxy-2-methylphenyl)imino]methyl}phenol (L\textsuperscript{2}H) (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\textsubscript{2}. Similarly all the complexes were prepared. The metal estimations were carried out by standard Methods [10]. 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)\textsubscript{4} as calibrant. The IR spectra of ligands and their complexes were recorded on a Shimadzu FTIR – 8400S spectrometer in KBr pellets in the range of 4000-3500 cm\textsuperscript{-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\textsuperscript{®} 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\textsuperscript{1}H: L\textsuperscript{2}H: 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\(^{-1}\) 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\(^{1}\)H, L\(^{2}\)H and their mixed ligand metal complexes.**

<table>
<thead>
<tr>
<th>Ligand / complex, Molecular Formula</th>
<th>Mol. Wt.</th>
<th>Analysis % Found (Calculated)</th>
<th>Molar Conductance ((\lambda m) Ohm(^{-1}) cm(^2) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>L(^{1})H C(<em>{18})H(</em>{14})FNO(_{2})</td>
<td>295.31 (73.21)</td>
<td>4.78 (4.75) 4.74 (4.41) -</td>
<td>-</td>
</tr>
<tr>
<td>L(^{2})H C(<em>{18})H(</em>{28})BrNO(_{2})</td>
<td>320.18 (56.27)</td>
<td>4.41 (4.43) 4.27 (4.30) -</td>
<td>-</td>
</tr>
<tr>
<td>[Co(L(^{1}))(L(^{2}))(H(<em>{2})O)(</em>{2})] C(<em>{29})H(</em>{30})F(<em>{2})N(</em>{2})O(_{6}) Co</td>
<td>683.56 (63.25)</td>
<td>4.43 (4.46) 4.10 (4.13) 8.62 (8.65)</td>
<td>0.018</td>
</tr>
<tr>
<td>[Ni(L(^{1}))(L(^{2}))(H(<em>{2})O)(</em>{2})] C(<em>{29})H(</em>{30})F(<em>{2})N(</em>{2})O(_{6}) Ni</td>
<td>683.32 (63.28)</td>
<td>4.43 (4.45) 4.10 (4.14) 8.59 (8.62)</td>
<td>0.012</td>
</tr>
<tr>
<td>[Cu(L(^{1}))(L(^{2}))(H(<em>{2})O)(</em>{2})] C(<em>{29})H(</em>{30})F(<em>{2})N(</em>{2})O(_{6}) Cu</td>
<td>688.17 (62.83)</td>
<td>4.39 (4.42) 6.67 (6.65) 9.23 (9.28)</td>
<td>0.014</td>
</tr>
<tr>
<td>[Zn(L(^{1}))(L(^{2}))(H(<em>{2})O)(</em>{2})] C(<em>{30})H(</em>{32})F(<em>{2})N(</em>{2})O(_{6}) Zn</td>
<td>690.04 (62.66)</td>
<td>4.38 (4.35) 4.06 (4.03) 9.48 (9.52)</td>
<td>0.015</td>
</tr>
</tbody>
</table>

**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\(^{-1}\) (\(\varepsilon \sim 27\) L mol\(^{-1}\) cm\(^{-1}\)) and ~ 19047.62 cm\(^{-1}\) (\(\varepsilon \sim 60\) L mol\(^{-1}\) cm\(^{-1}\)) attributed to \(^{4}T_{1g}(F) \rightarrow ^{4}T_{2g}(F)\) (\(v_{1}\)) and \(^{4}T_{1g}(F) \rightarrow ^{4}T_{1g}(P)\) (\(v_{3}\)) 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\(^{-1}\), \(\beta = 0.731\) and \(\beta^0 = 26.9\) %. The reduction of Racah parameter from the free ion value 971 cm\(^{-1}\) and \(\beta^0\) value of 26.9 % testify the presence of considerable covalence in the complex [13]. The Co(II) complex has magnetic moment 5.12 B.M. also suggest an octahedral geometry. Ni(II) complex exhibits two electronic spectral bands at ~ 10504.20 cm\(^{-1}\) (\(\varepsilon \sim 30\) L mol\(^{-1}\) cm\(^{-1}\)) and ~ 16393.44 cm\(^{-1}\) (\(\varepsilon \sim 87\) L mol\(^{-1}\) cm\(^{-1}\)) which can be assigned to \(^{3}A_{2g}(F) \rightarrow ^{3}T_{2g}(F)\) (\(v_{1}\)) and \(^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(F)\) (\(v_{2}\)) transitions in an octahedral field [14]. The transition due to \(^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(P)\) (\(v_{3}\)) was completely obscured by the intense intra ligand transition band. The \(v_{2}: v_{1}\) 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\(^{-1}\), \(\beta = 0.703\) and \(\beta^0 = 29.7\) %. The reduction of Racah parameter from the free ion value 1030 cm\(^{-1}\) and \(\beta^0\) value of 29.7 % confirms the presence of considerable covalence in the complex [13]. The Ni(II) complex has magnetic moment 3.46 B.M. also suggest an octahedral geometry. The Cu(II) complex exhibit broad band centered at ~ 14285.71 cm\(^{-1}\) (\(\varepsilon \sim 120\) L mol\(^{-1}\) cm\(^{-1}\)) mainly due to \(^{2}E_{g} \rightarrow ^{2}T_{2g}\) transition suggesting the distorted octahedral geometry [16]. The observed magnetic moment value for Cu(II) complex is 1.82 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\(^{1}\)H and L\(^{2}\)H and their mixed ligand metal complexes are given in the Table 2. Infrared spectra of the schiff bases L\(^{1}\)H and L\(^{2}\)H show a broad band centered at around 3445 cm\(^{-1}\) and 3447 cm\(^{-1}\) due to v(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 L\(^{1}\)H and L\(^{2}\)H show a medium intensity band at around 1336 cm\(^{-1}\) and 1278 cm\(^{-1}\) due to v(C-O) (phenolic) is shifted to higher region at around 1381-1399 cm\(^{-1}\) and 1359-1363 cm\(^{-1}\) 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 1623 cm\(^{-1}\) and 1614 cm\(^{-1}\) due to \(v(C=N)\) (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 \(v(OH)\), \(\delta(OH)\) and \(\rho(OH)\) 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 \(v(M-O)\) and \(v(M-N)\) vibrations respectively [17,18].

<table>
<thead>
<tr>
<th>Schiff base / Complex</th>
<th>(v_{OH}) (phenolic)</th>
<th>(v_{OH}) (H(_2)O)</th>
<th>(v_{C=O}) (phenolic)</th>
<th>(\delta_{OH}) (H(_2)O)</th>
<th>(v_{C-O}) (phenolic)</th>
<th>(\rho_{OH}) (H(_2)O)</th>
<th>(v_{M-O})</th>
<th>(v_{M-N})</th>
</tr>
</thead>
<tbody>
<tr>
<td>L^1H</td>
<td>3445</td>
<td>-</td>
<td>1623</td>
<td>-</td>
<td>1336</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L^2H</td>
<td>3447</td>
<td>-</td>
<td>1614</td>
<td>-</td>
<td>1278</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[Co(L^1)(L^2)(H(_2)O)(_2)]</td>
<td>-</td>
<td>3150-3650</td>
<td>1614, 1601</td>
<td>1534</td>
<td>1381, 1359</td>
<td>835</td>
<td>550, 510</td>
<td>457, 421</td>
</tr>
<tr>
<td>[Ni(L^1)(L^2)(H(_2)O)(_2)]</td>
<td>-</td>
<td>3150-3700</td>
<td>1615, 1602</td>
<td>1535</td>
<td>1399, 1363</td>
<td>831</td>
<td>553, 503</td>
<td>459, 419</td>
</tr>
<tr>
<td>[Cu(L^1)(L^2)(H(_2)O)(_2)]</td>
<td>-</td>
<td>3200-3650</td>
<td>1613, 1601</td>
<td>1536</td>
<td>1383, 1360</td>
<td>834</td>
<td>556, 509</td>
<td>461, 416</td>
</tr>
<tr>
<td>[Zn(L^1)(L^2)(H(_2)O)(_2)]</td>
<td>-</td>
<td>3150-3700</td>
<td>1616, 1602</td>
<td>1537</td>
<td>1381, 1362</td>
<td>836</td>
<td>557, 510</td>
<td>463, 422</td>
</tr>
</tbody>
</table>

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

**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 ~ 125-285 °C, 130-288 °C, 125-280 °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(L^1)(L^2)(H\(_2\)O)\(_2\)] complex are \(g_{||} = 2.136\), \(g_{\perp} = 2.084\) and \(G = 1.634\). The observed \(g_{||}\) value is less than 2.3 in agreement with the covalent character of the metal – ligand bond [13]. The trend \(g_{||} > g_{\perp} > g_e (2.0023)\) 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 [13,19]. The anisotropic G values have been calculated by using the equation \(G = (g_{||}-2.002) / (g_{\perp}-2.002)\). 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 \(G = 1.634\) for the present complex indicates that the ligands L^1H and L^2H 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.aurious*, *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 metal complexes.

<table>
<thead>
<tr>
<th>Schiff base / Complex</th>
<th>S.aureus</th>
<th>B.subtilis</th>
<th>E.coli</th>
<th>S.typhi</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₁H</td>
<td>2.6</td>
<td>2.8</td>
<td>0.0</td>
<td>2.6</td>
</tr>
<tr>
<td>L₂H</td>
<td>0.0</td>
<td>2.6</td>
<td>2.9</td>
<td>2.7</td>
</tr>
<tr>
<td>[Co(L₁)(L₂)(H₂O)₂]</td>
<td>8.0</td>
<td>7.5</td>
<td>6.5</td>
<td>4.1</td>
</tr>
<tr>
<td>[Ni(L₁)(L₂)(H₂O)₂]</td>
<td>6.3</td>
<td>7.7</td>
<td>6.5</td>
<td>3.8</td>
</tr>
<tr>
<td>[Cu(L₁)(L₂)(H₂O)₂]</td>
<td>3.6</td>
<td>6.5</td>
<td>7.1</td>
<td>4.8</td>
</tr>
<tr>
<td>[Zn(L₁)(L₂)(H₂O)₂]</td>
<td>8.0</td>
<td>9.3</td>
<td>4.5</td>
<td>6.3</td>
</tr>
</tbody>
</table>

**Conclusion**

The elemental analysis, magnetic susceptibility, electronic, 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 3. The Schiff’s bases do show some antimicrobial activity to certain extent but their complexes exhibit comparatively greater amount of activity against the microorganisms.

![Figure 3](image)

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

**References**

5. Singh W.M. and Dash B.C., Synthesis of some new Schiff bases containing thiazole and oxazole nuclei and their fungicidal activity, Pesticides, 1988, 22, 33.

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