STRUCTURAL ELUCIDATION AND THERMAL STUDIES OF SOME NOVEL MIXED LIGAND SCHIFF BASE METAL (II) COMPLEXES

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Abstract
Novel mixed ligand Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff base derived through the condensation of furfurylidene-4-aminoantipyrine and 2-aminobenzothiazole with 2-aminophenol have been synthesized and characterized by various analytical and spectral techniques. The spectral results suggest octahedral geometry for Co(II), Ni(II) and Zn(II) complexes. Distorted octahedral geometry has been assigned for Cu(II) complex. The low molar conductance values of the complexes support their neutral nature. The thermal stability of the complexes was determined using TG/DTA studies. The electrochemical behavior of the complexes was studied using cyclic voltammetry. The grain size of the complex was calculated by Scherrer formula using powder XRD. Surface morphology of the complexes was determined by SEM analysis.

Key Words: Schiff Base, Mixed Ligand Complexes, TG/DTA, XRD

Introduction
Schiff base ligands have significant importance in chemistry; especially in the development of Schiff base complexes, because Schiff base ligands are potentially capable of forming stable complexes with metal ions (Souza et al., 1985). Mixed ligand complexes of transition metals containing ligands with N, S or N, S, O donors are known to exhibit interesting stereochemical, electrochemical and electronic properties (Prabhakaran et al., 2005).

In recent decades, a great deal of interest in the metal complexes of nitrogen-oxygen chelating agents derived from 4-aminoantipyrine Schiff bases have various applications in antifungal, antibacterial, analgesic, sedative, antipyretic, anti-inflammatory and greater DNA binding ability (Kumaran et al., 2013) Heterocycles containing thiazole ring is present in a number of pharmacologically and biologically active compounds. Compounds containing benzothiazole derivatives were used as antifungal, antiinflammatory, anti-HIV, anticancer, anticarbonic anhydrase, diuretic, hypoglycaemic, antithyroid, antimalarial and in therapeutic fields (Neelakantan et al., 2010) The metal complex-DNA interactions have received much importance for the development of new metal-based chemotherapeutic drugs (Afrati et al., 2009) The numerous biological experiments performed so far suggest that DNA is the primary intracellular target of anticancer drugs because the interaction between small molecules and DNA can induce DNA damages in cancer cells, blocking the division of cancer cells and resulting in the cell death (Li et al., 2009).

By considering the above, in this paper, we synthesized and characterized novel Co(II), Ni(II), Cu(II) and Zn(II) mixed ligand complexes.

Materials and Methods

Chemicals and reagents
The chemicals used were of AnalAR grade, furfuraldehyde, 4-aminoantipyrine, 2-aminophenol and 2-aminobenzothiazole were obtained from Sigma Aldrich. Metal(II) acetates were obtained from Merck and were used as received. The solvents used were purchased from Merck and used without further purification.
**Physical Measurements**

Elemental analysis of ligand and its metal complexes were carried out using Perkin-Elmer elemental analyzer. Molar conductance of the complexes was measured using a coronation digital conductivity meter. IR spectra were recorded using Jasco FTIR–410 spectrometer in KBr pellets from 4000-400 cm\(^{-1}\). \(^1\)H NMR spectra were recorded with Brucker 300 MHz spectrometer using CDCl\(_3\) solvent for ligand and DMSO-d6 for Zn(II) complex with TMS as internal standard. DART-MS spectrum was recorded on a JEOL-Accu TOF JMS mass spectrometer. Magnetic moments were measured by Guoy method and corrected for diamagnetism of the component using Pascal’s constants. Electronic spectra were recorded on Thermo Scientific Evolution-200 UV-Visible spectrophotometer in the range 190-1100 nm. ESR spectrum of the Cu(II) complex was recorded at 300 and 77 K in DMSO solution using Varian, USA E-112 ESR spectrometer using tetracyanoetthylene (TCNE) as g-marker. Thermal analysis was carried out under nitrogen atmosphere at a heating rate of 10 °C per minute using Perkin Elmer Diamond TG/DTA analyzer. SEM images were recorded in a Hitachi SEM analyzer.

**Synthesis of Mixed Ligand Complexes**

The Schiff base was prepared using the reported procedure (Leelavathy et al., 2013). The complexes were prepared by following the procedure. A methanolic solutions of Schiff base (0.004 mol), Co(II)/ Ni(II)/ Cu(II)/ Zn(II) metal acetates (0.004 mol) and 2-aminophenol (2-ap) (0.004 mol) were taken in 1:1:1 molar ratio and stirred with heating for about 4 h. The resulting mixture is then cooled to room temperature and the solid product formed was filtered, washed with methanol and dried over anhydrous calcium chloride.

**RESULTS AND DISCUSSION**

The mixed ligand complexes synthesized are stable at room temperature. They are soluble in DMF and DMSO. The analytical, physical properties and molar conductance data of the complexes are given in Table 1. Elemental analysis indicates that the found and calculated values were within acceptable limits (± 0.5). The molar conductance data of the mixed ligand complexes fall in the range of 3.3-12.5 Ω\(^{-1}\)cm\(^2\) mol\(^{-1}\), which confirms the present complexes, are non-electrolytic in nature (Geary, 1971).

**IR Spectra**

A comparative study of IR spectra of the mixed ligand complexes with ligand reveals that several peaks are shifted, vanished or have newly appeared. The infrared spectrum of the Schiff base showed two strong bands, one at 1590 cm\(^{-1}\) and another at1652 cm\(^{-1}\). These bands are assigned to the (\(-\)CH=N) and (\(>\)C=N) stretching frequency vibrations respectively (Ali et al., 2013). A shift in these frequencies (Table: 2) is observed in all complexes due to the coordination of metal through nitrogen atoms of the -CH=N and >C=N groups. In all the complexes a broad band is present in the region 3435-3406 cm\(^{-1}\), indicates the presence of coordinated water molecules (Mashaly et al., 2004). The band at 3354 cm\(^{-1}\) for ν(OH) in the free 2-aminophenol ligand disappeared on complexation, indicating coordination of –OH group through deprotonation (Krishnankutty et al., 2007). The absence of the bands due to NH\(_2\) group in the spectra of complexes indicating the involvement of amino group in coordination through deprotonation.

The complexes also display bands in the 439-417, 590-497 cm\(^{-1}\) region due to the formation of M-N and M-O bonds respectively (El-Shahawi et al., 2013). From the IR spectra, it is concluded that the Schiff base behaves as a bidentate ligand coordinated to the metal ions via (-CH=N) and (>C=N) groups. The other coordination sites of metal(II) ions were occupied by two water molecules and two positions were occupied by the –OH and NH\(_2\) groups of 2-aminophenol through deprotonation.
### Table 1: Physical properties and analytical data of mixed ligand complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>Molecular weight</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>S</th>
<th>M</th>
<th>Molar conductivity (Ω^−1 cm^2 mol^−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{29}H_{28}CoN_{6}O_{4}S</td>
<td>67</td>
<td>615.57</td>
<td>56.73</td>
<td>4.38</td>
<td>13.62</td>
<td>10.35</td>
<td>5.17</td>
<td>9.68</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(56.58)</td>
<td>(4.58)</td>
<td>(13.65)</td>
<td>(10.40)</td>
<td>(5.21)</td>
<td>(9.57)</td>
<td></td>
</tr>
<tr>
<td>C_{29}H_{28}NiN_{6}O_{4}S</td>
<td>52</td>
<td>615.33</td>
<td>56.70</td>
<td>4.35</td>
<td>13.78</td>
<td>10.60</td>
<td>5.13</td>
<td>9.42</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(56.61)</td>
<td>(4.59)</td>
<td>(13.66)</td>
<td>(10.40)</td>
<td>(5.21)</td>
<td>(9.54)</td>
<td></td>
</tr>
<tr>
<td>C_{29}H_{28}CuN_{6}O_{4}S</td>
<td>72</td>
<td>620.18</td>
<td>56.43</td>
<td>4.43</td>
<td>13.61</td>
<td>10.72</td>
<td>5.29</td>
<td>10.21</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(56.16)</td>
<td>(4.55)</td>
<td>(13.55)</td>
<td>(10.32)</td>
<td>(5.17)</td>
<td>(10.55)</td>
<td></td>
</tr>
<tr>
<td>C_{29}H_{28}Ni_{6}O_{4}Szn</td>
<td>58</td>
<td>622.03</td>
<td>56.21</td>
<td>4.59</td>
<td>13.42</td>
<td>10.50</td>
<td>5.35</td>
<td>10.31</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(56.00)</td>
<td>(4.54)</td>
<td>(13.51)</td>
<td>(10.29)</td>
<td>(5.15)</td>
<td>(10.51)</td>
<td></td>
</tr>
</tbody>
</table>
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Table 2: IR spectral data of ligand and its complexes (cm⁻¹)

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(HC=N)</th>
<th>ν(OH)water</th>
<th>ν(C=O)</th>
<th>ν(M-N)</th>
<th>ν(M-O)</th>
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<tbody>
<tr>
<td>Ligand</td>
<td>1590</td>
<td>-</td>
<td>1646</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Co(II) complex</td>
<td>1593</td>
<td>3420</td>
<td>1644</td>
<td>438</td>
<td>590</td>
</tr>
<tr>
<td>Ni(II) complex</td>
<td>1572</td>
<td>3406</td>
<td>1644</td>
<td>439</td>
<td>590</td>
</tr>
<tr>
<td>Cu(II) complex</td>
<td>1587</td>
<td>3435</td>
<td>1641</td>
<td>417</td>
<td>497</td>
</tr>
<tr>
<td>Zn(II) complex</td>
<td>1581</td>
<td>3432</td>
<td>1639</td>
<td>430</td>
<td>588</td>
</tr>
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</table>

Electronic Spectra and Magnetic Susceptibility

The electronic absorption spectra of the ligand and its mixed ligand complexes were recorded at room temperature in DMF solution. The absorption assignments and magnetic susceptibility values of the complexes along with the geometry are given in Table 3. The electronic spectra of the ligand shows broad band 318 and 370 nm which can be assigned to π-π* transitions of the azomethine (-CH=N) chromophore. On complexation this was shifted to lower wavelength, suggesting the coordination of azomethine nitrogen. In addition, other intense absorption band at higher energy 220-265 nm is due to π-π* transition of the benzene ring of the Schiff base ligand. The electronic spectrum of Co(II) complex show two absorption bands one at ~1075 nm and another one at ~345 nm assignable to 4T₁g (F)→4T₂g (F) and 4T₁g (F)→4T₄g (P) transitions respectively, which is characteristic for the octahedral Co(II) complex. The magnetic moment value of the Co(II) complex is 5.14 BM. The electronic spectrum of the Ni(II) complex show one absorption band at 387 nm assignable to 3A₂g (F)→3T₁g (P) transition. This is characteristic of six coordinated octahedral Ni(II) complexes. The magnetic moment value is 3.20 BM for the Ni(II) complex confirms six coordinate octahedral geometry. The distorted octahedral Cu(II) complex, display one absorption band at 464 nm, corresponding to 2B₃g→2E₉g transition. The µ_eff for the complex is 1.91 BM, which is characteristic for distorted octahedral geometry around Cu(II). The Zn(II) complex exhibited two intra ligand transitions at 287 and 335 nm and is diamagnetic. According to the empirical formula, an octahedral geometry is proposed for the Zn(II) complex (Nag et al., 2005; Banerjea, 1993; Kettle, 1969).

Table 3: Electronic spectral data and magnetic moment values of Metal complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_max (nm)</th>
<th>Band assignments</th>
<th>Magnetic moment (BM)</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II) complex</td>
<td>1075</td>
<td>⁴T₁g (F)→⁴T₂g (F)</td>
<td>5.14</td>
<td>Octahedral</td>
</tr>
<tr>
<td></td>
<td>345</td>
<td>⁴T₁g (F)→⁴T₄g (P)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(II) complex</td>
<td>387</td>
<td>³A₂g (F)→³T₁g (P)</td>
<td>3.20</td>
<td>Octahedral</td>
</tr>
<tr>
<td>Cu(II) complex</td>
<td>464</td>
<td>²B₁g→²E₁g</td>
<td>1.91</td>
<td>Distorted Octahedral</td>
</tr>
<tr>
<td></td>
<td>287</td>
<td>π-π*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(II) complex</td>
<td>335</td>
<td>n-π*</td>
<td></td>
<td>Diamagnetic</td>
</tr>
<tr>
<td></td>
<td>335</td>
<td></td>
<td></td>
<td>Octahedral</td>
</tr>
</tbody>
</table>

¹H NMR Spectra

The ¹H NMR spectra of ligand and Zn(II) complex were recorded in DMSO d₆. The signal for azomethine proton (-CH=N-) in the ligand appears as a singlet at 9.6 ppm (Amer et al., 2013). In the ¹H NMR spectrum of the Zn(II) complex, the azomethine proton signal is shifted downfield compared to the free ligand due to the deshielding of the azomethine group on coordination with Zn(II) ion. The multiplet obtained in the 7.2-7.5 ppm range is due to the aromatic protons of the ligand as expected. The signal for pyrazolone ring carbon attached methyl proton (-CH₃) appear as a singlet at 2.5 ppm, while pyrazolone
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ring nitrogen attached methyl protons (>N-CH₃) appear as a singlet at δ 3.3 ppm (Aupama et al., 2012). The peaks at 6.5 and 6.8 ppm are due to furfuryl protons.

Mass Spectra

The mass spectrum of ligand and its Co(II), Ni(II), Cu(II) and Zn(II) mixed ligand complexes were recorded. The molecular ion peak for ligand, L (C₂₃H₁₉N₅O₂S) was observed at 413 m/z. Whereas the molecular ion peaks of Co(II), Ni(II), Cu(II) and Zn(II) mixed ligand complexes were observed at 617, 616, 621 and 623 m/z which confirms the stoichiometry of the metal complexes to be [ML(H₂O)₂(2-ap)]. The mass spectra of ligand and its complexes exhibited other molecular ion peaks for several fragments. Elemental analysis values are in agreement with the values calculated from the molecular formulae assigned to these complexes which are further supported by DART-mass studies.

ESR Spectra

ESR spectra of the Cu(II) complex was recorded at room temperature and at liquid nitrogen temperature in DMSO. The g∥ and g⊥ values were calculated from the spectrum using tetracyanoethylene (TCNE) free radical as the “g” marker. In the present Cu(II) complex, g∥ is less than 2.3 is an indication of significant covalent character to M-L bond. The g∥ and g⊥ values are >2.04, consistent with an elongated tetragonally distorted octahedral stereochemistry. The G factor [G = (g∥-2)/(g⊥-2)] is >4.0 suggests that the exchange interactions between Cu(II) centers in the solid state are negligible (El-Bindary et al., 2000). The absence of half field signal at 1600 G due to the ∆ms = ± 2 transitions, ruling out any Cu-Cu interaction. The g values are in the order g∥ > g⊥ > 2.0023 corresponding to the presence of an unpaired electron in the dx²−y² orbital. From the observed values, it is clear that A∥=110 > A⊥=82; g∥=2.13 > g⊥=2.03 > 2 and the ESR parameters of the Cu(II) complex suggest that the complex have tetragonally distorted octahedral geometry and the unpaired electron lies predominantly in the dx²−y² orbital.

Thermal Studies

The thermal stabilities of ligand and its mixed ligand metal complexes were investigated using TG and DTA under nitrogen atmosphere with a heating rate of 10 ºC per minute from 40 ºC to 700 ºC. The Co(II) and Zn(II) complexes show four stages of decomposition. While the Ni(II) and Cu(II) complexes complex exhibited three stage of decomposition. Thermograms of Co(II), Ni(II), Cu(II) and Zn(II) complexes show weight loss around 151-223 ºC indicates the presence of two coordinated water molecules in these complexes (Dhanaraj et al., 2014). The other decomposition stages correspond to the loss of 2-aminophenol ligand and decomposition of organic moieties of the Schiff base ligand. The initial decomposition temperature of Co(II) complex is higher compared to the remaining complexes, indicating it is more thermally stable. The Zn(II) complex shows the final decomposition at 457 ºC, which is the higher final decomposition temperature compared to the rest of the complexes. Based on the elemental analysis, IR, electronic spectra, magnetic moments, ¹H NMR, mass, ESR spectral data and thermal analysis, the proposed structure of the complexes are given in Figure: 1.

Figure 1: Proposed structure of metal complexes (where M=Co(II), Ni(II), Cu(II) and Zn(II))
Powder XRD

The X-ray diffraction pattern of the mixed ligand complexes is shown in Figure: 2(a-d). From the observed $d_{\text{XRD}}$ patterns, the crystalline size of the complexes were calculated from Scherre’s formula $d_{\text{XRD}} = 0.9\lambda / \beta \cos \theta$, where $\lambda$ is the wave length, $\beta$ is the full-width half maximum of the characteristic peak and $\theta$ is the diffraction angle for the hkl plane (Tabassum et al., 2012). In the present study, Co(II), Ni(II), Cu(II) and Zn(II) complexes are amorphous in nature.

SEM

The SEM micrographs of the Co(II), Ni(II), Cu(II) and Zn(II) mixed ligand complexes are shown in Figure: 3(a-d). The SEM micrograph of Co(II) complex exhibit spherical structured particles with small grains. Ni(II) complex exhibited irregularly shaped particles with small grains. The Cu(II) and Zn(II) complexes showed cauli flower like morphology.

Conclusion

Mixed ligand Co(II), Ni(II), Cu(II) and Zn(II) complexes with Schiff base derived from furfurylidene-4-aminoantipyrine and 2-aminobenzothiazole and 2-aminophenol have been synthesized and characterized by elemental analysis, molar conductance, magnetic moment and spectral data. DART mass spectra gave the molecular weight of the complexes. The physico-chemical data suggest octahedral geometry for
Co(II), Ni(II) and Zn(II) complexes and distorted octahedral geometry for Cu(II) complex. Powder XRD studies revealed that all the complexes are amorphous. The complexes exhibit different surface morphologies.

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