RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDIES OF SCHIFF BASE COMPLEXES OF MN(II), CO(II), NI(II), CU(II) AND ZN(II) DERIVED FROM 3-AMINOPHENOL AND 2-HYDROXYNAPHTHALDEHYDE

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INTRODUCTION

Schiff base and their metal complexes have been found to possess significant biological activities (Rajendran et al., 2008). Schiff base transition metal complexes are of interest in inorganic chemistry and have been studied extensively (Tas et al., 2002). Schiff base complexes of transition metals containing ligands with N2O2 donors are known to exhibit interesting electrochemical properties, antibacterial, anticancer, catalytic (Karvembu et al., 2003, Daniel Thangadurai et al., 2002, Frey et al., and 2001Sid et al., 2001) and significant antifungal activities (Campo et al., 2002). In addition complexes containing nitrogen and oxygen donor atoms in the complexes are effective as stereospecific catalysts for oxidation (Kureshy et al., 1999), reduction (Sengupta et al., 2001), hydrolysis (Aoyama et al., 1986) and other transformations of organic and inorganic chemistry. Some amino acid derived Schiff bases show antibacterial activity (Malik et al., 1984, Cohan et al., 1998, and Sari et al., 2003). The Schiff bases bearing aryl groups or heterocyclic residues possess excellent biological activities and thus have attracted the attention of many researchers in recent years (Haddock et al., 1982, Holla et al., 2000 and Chadha et al., 1998).

Schiff base from 2-hydroxynaphthaldehyde have often been used as chelating ligand in the field of coordination chemistry (Raman et al., 2007 Rahman et al., 2001 Spinu et al., 2001). Iffet Sak Yan et al., have investigated the in-vitro antibacterial, antifungal activities of five different aminoacids, Schiff bases derived from 2-hydroxynaphthaldehyde with glycine, L-alanine, L-phenylalanine, L-histidine, L-tryptophan and the Mn(II) complexes of these bases are investigated against gram positive and gram negative bacteria. The antimicrobial activities tend to decrease with the increasing size of the amino acid residues. The present paper reports the synthesis, characterisation and biological studies on Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff base derived from 3-aminophenol and 2-hydroxynaphthaldehyde.

MATERIALS AND METHODS

All the reagents used were of AR grade (BDH / E. Merck). Solvents were purified and dried according to the standard procedures. Elemental analysis (C,H,N) were performed using elemental analyser Elementar Vario EL III. IR spectra of the Schiff base and its complexes were recorded in KBr pellets with Perkin Elmer IR RXI Spectrometer in the 4000–400 cm\(^{-1}\) range. The \(^1\)H NMR spectra were recorded on a Bruker 400 MHz FT- PMR Spectrometer (DMSO-\(d_6\)). Melting points were determined using Elico melting point apparatus. The electronic spectra were recorded in Perkin Elmer Lambda 35 spectrometer in the 190-1100 nm range. Conductivity measurements for the complexes were carried out using Elico conductivity bridge and dip type conductivity cell.

Synthesis of Schiff Base

(2HN3AP): To a hot stirred solution of 3-aminophenol (0.002 mol) in ethanol was added a solution of 2-hydroxynaphthaldehyde(0.002 mol) in ethanol. The reaction mixture was refluxed for 5h. The reaction mixture was cooled and yellow coloured compound separated was filtered and washed with small amount of ethanol and dried. The purity of the
Schiff base was checked by melting point, TLC and spectral data. (mp: 210 °C; yield: 87%)

**General method for preparation of metal complexes**

To a hot magnetically stirred 1,4-dioxan solution of Schiff base (0.004 mol), an aqueous solution of the corresponding metal (II) acetate (0.002 mol) was added. The mixture was refluxed for 5-6 h. On cooling coloured solid complex separated, filtered and washed with small amount of 1,4-dioxan and dried. The yield of the Schiff base and its metal complexes together with colour, analytical data and other physical properties are reported in Table-1.

**RESULTS AND DISCUSSION**

**Analytical data**

The analytical data obtained for the ligand and complexes (Table-1) agree very well with the proposed molecular formula and also indicates the formation of 1:2 (M:L) complexes of general formula of [M(2HN3AP)2(H2O)2] [M= Mn2+, Co2+, Ni2+, Cu2+ and Zn2+].

**Conductance and magnetic susceptibility measurements**

The molar conductance of the complexes was determined at concentration 1x10⁻³ mol L⁻¹ in DMF (Table -1). All the complexes showed very low molar conductance values 4.9-7.9 ohm cm² mol⁻¹ which indicates that the complexes are non-electrolytic in nature (W.J.Geary et al., 1971). The observed magnetic moment value of 5.84 B.M, 4.12 B.M, 3.54 B.M and 1.70 B.M for the Mn(II), Co(II), Ni(II) and Cu(II) complexes respectively (Lever et al., 1963 and Carlin1965). Evidence of the nitrogen coordination of the azomethine ν(C≡N) group to the central metal atom stems from the shift of the frequency from 1601 cm⁻¹ in the ligand to 1598-1629 cm⁻¹ in all the metal complexes. This is further supported by the appearance of the new bands at 741-750 cm⁻¹ due to the ν(M-O) bond. The coordination through the hydroxyl oxygen is revealed by disappearance of the band at 3360 cm⁻¹ and appearance of a new band in the range 3177-3427 cm⁻¹ due to the C-O mode.

**IR Spectra**

The important IR spectral bands of the ligand and its metal complexes are given in Table -2. In the IR spectra of the ligand a broad band observed at 3360 cm⁻¹ and a sharp band at 1601 cm⁻¹ are assigned to the ν(OH) and ν(C≡N) modes respectively (Lever et al., 1963 and Carlin1965). Evidence of the nitrogen coordination of the azomethine ν(C≡N) group to the central metal atom stems from the shift of the frequency from 1601 cm⁻¹ in the ligand to 1598-1629 cm⁻¹ in all the metal complexes. This is further supported by the appearance of the new band at 741-750 cm⁻¹ due to the ν(M-O) bond. The coordination through the hydroxyl oxygen is revealed by disappearance of the band at 3360 cm⁻¹ and appearance of a new band in the range 3177-3427 cm⁻¹ due to the C-O mode. This is further confirmed by the appearance of the new band at 467-505 cm⁻¹ due to ν(M-O) in the metal complexes (Carlin et al., 1965, Maurya et al., 1991, Ferrero et al., 1971, Temel et al., 2001& 2004).

**Figure 1**

![Figure 1](image_url)

**Table 1** Physical Characteristics and analytical data of Schiff base and the complexes

<table>
<thead>
<tr>
<th>S. No</th>
<th>Schiff base &amp; Complexes</th>
<th>Molecular Formula</th>
<th>Colour</th>
<th>Elemental analysis % Found (Calcd)</th>
<th>Metal % Found (Calcd)</th>
<th>M.Pt °C</th>
<th>Yield %</th>
<th>Molar Conductance ohm⁻¹ cm² mol⁻¹</th>
<th>Magnetic moment R.M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2HN3AP</td>
<td>C₇H₅N₂O₃</td>
<td>Yellow</td>
<td>C 77.32 (77.57) H 5.30 (4.94) N 5.29 (5.32)</td>
<td>-</td>
<td>210</td>
<td>87</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>[Mn(2HN3AP)₂(H₂O)₂]</td>
<td>MnC₇H₅N₂O₃</td>
<td>Cream</td>
<td>65.83 (66.54) 4.13 (4.55) 4.84 (4.55)</td>
<td>10.11 (10.80)</td>
<td>250</td>
<td>82</td>
<td>6.4</td>
<td>5.84</td>
</tr>
<tr>
<td>3</td>
<td>[Co(2HN3AP)₂(H₂O)₂]</td>
<td>CoC₇H₅N₂O₃</td>
<td>Pale Yellow</td>
<td>65.18 (65.92) 4.04 (4.52) 4.00 (4.52)</td>
<td>21.87 (21.50)</td>
<td>320</td>
<td>75</td>
<td>5.3</td>
<td>4.12</td>
</tr>
<tr>
<td>4</td>
<td>[Ni(2HN3AP)₂(H₂O)₂]</td>
<td>NiC₇H₅N₂O₃</td>
<td>Dark Yellow</td>
<td>65.33 (65.95) 4.92 (4.53) 4.88 (4.53)</td>
<td>13.07 (13.70)</td>
<td>220</td>
<td>80</td>
<td>7.9</td>
<td>3.54</td>
</tr>
<tr>
<td>5</td>
<td>[Cu(2HN3AP)₂(H₂O)₂]</td>
<td>CuC₇H₅N₂O₃</td>
<td>Black</td>
<td>65.94 (65.43) 4.97 (4.49) 3.86 (4.49) 11.70 (12.10)</td>
<td>300 (300)</td>
<td>&gt; 68</td>
<td>4.9</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>[Zn(2HN3AP)₂(H₂O)₂]</td>
<td>ZnC₇H₅N₂O₃</td>
<td>Pale Yellow</td>
<td>65.45 (65.24) 4.95 (4.48) 4.86 (4.48) 10.69 (11.09)</td>
<td>200 (200)</td>
<td>51</td>
<td>5.6</td>
<td>dia</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2** Infra red and Electronic Absorption Spectral data of Schiff base and the complexes

<table>
<thead>
<tr>
<th>S. No</th>
<th>Schiff base &amp; Complexes</th>
<th>IR in (cm⁻¹)</th>
<th>UV-Vis in (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2HN3AP</td>
<td>ν(OH) 3360 1601</td>
<td>39621,32169,27451</td>
</tr>
<tr>
<td>2</td>
<td>[Mn(2HN3AP)₂(H₂O)₂]</td>
<td>ν(C≡N) 3372 1629, 474</td>
<td>31670,27440,25830</td>
</tr>
<tr>
<td>3</td>
<td>[Co(2HN3AP)₂(H₂O)₂]</td>
<td>ν(M-O) 3420 1627, 503</td>
<td>38155,36920,31963,26131</td>
</tr>
<tr>
<td>4</td>
<td>[Ni(2HN3AP)₂(H₂O)₂]</td>
<td>ν(M-N) 3177 1627, 505</td>
<td>31644,26737,26314, 21541</td>
</tr>
<tr>
<td>5</td>
<td>[Cu(2HN3AP)₂(H₂O)₂]</td>
<td>ν(M-O) 3394 1598, 467</td>
<td>29934,26139</td>
</tr>
<tr>
<td>6</td>
<td>[Zn(2HN3AP)₂(H₂O)₂]</td>
<td>ν(M-N) 3427 1616, 473</td>
<td>38312,37871,3144</td>
</tr>
</tbody>
</table>

81
The test was carried out in DMSO solution at a concentration of 100 ppm. The Schiff base and its metal complexes were recorded in DMSO and given in Table –2. The synthesized Schiff base and its metal (II) complexes were chosen for antibacterial (two gram positive bacteria Staphylococcus aureus and Bascillus substilis, two gram negative bacteria E.Coli and Pseudomonas aeruginosa) and antifungal studies (Candida albicans and Aspergillus niger). The test was carried out in DMSO solution at a concentration of 100 ppm (Al-Ajrawy et al., 2011). All the complexes show better antibacterial and antifungal activity when compared to the Schiff base as indicated in table -3. However the Ni(II) complex is highly active when compared to Schiff base and other metal complexes.

CONCLUSION

Based on the conductance measurements, magnetic susceptibility measurements, elemental analysis, infrared spectra, 1H NMR and electronic spectra, the probable structure of the complexes proposed in the present work is given in Figure 1.

Acknowledgements

We are indebted to the University Grants Commission, Hyderabad, India, for the financial support and also thank the Management, Seethalakshi Ramaswami College, Tiruchirappalli, Tamil Nadu, India for providing laboratory facilities.

Table 3 Antimicrobial Activity of Schiff base and complexes

<table>
<thead>
<tr>
<th>S.No</th>
<th>Antimicrobial activity of the and complexes</th>
<th>Staphylococcus aureus</th>
<th>Bascillus substilis</th>
<th>E.Coli</th>
<th>Pseudomonas aeruginosa</th>
<th>Candida albicans</th>
<th>Aspergillus niger</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2HN3AP</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>2</td>
<td>[Mn(2HN3AP)(HO2)]</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>3</td>
<td>[Co(2HN3AP)(HO2)]</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>4</td>
<td>[Ni(2HN3AP)(HO2)]</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>5</td>
<td>[Cu(2HN3AP)(HO2)]</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>6</td>
<td>[Zn(2HN3AP)(HO2)]</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
</tbody>
</table>

Standards = Ciprofloxacin 5 μg/disc for bacteria; Nystatin = 100 units/disc for fungi.

Highly active = +++ (inhibition zone > 15mm); Moderately active = ++ (inhibition zone >10mm); Slightly active = + (inhibition zone > 5mm); Inactive = - (<5 mm)

The Schiff base is yellow in colour and shows three absorption bands at 39621 cm⁻¹, 32169 cm⁻¹ and 27451 cm⁻¹. The Mn(II) complex has bands at 25830 cm⁻¹ and 27440 cm⁻¹ which may be due to A₁g → E₂g and A₁g → T₂g(D) transitions respectively. The band at 31670 cm⁻¹ is due to M → L charge transfer transitions. The Co(II) complex is pale yellow in colour and shows absorption band at 26,131 cm⁻¹ which may be due to the transition from T₁g → T₈g(P) (Temel et al., 200). The Ni(II) complex is dark yellow in colour exhibits four absorption bands at 31644 cm⁻¹, 26737 cm⁻¹, 26314 cm⁻¹ and 21541 cm⁻¹. One band at 31644 cm⁻¹ may be attributed to L → M charge-transfer transition. The bands in the region around 25000 cm⁻¹ can be assigned to A₁g(F) → T₈g(P) d-d transition. The Cu(II) complex exhibits two absorption bands at 29934 cm⁻¹ and 26139 cm⁻¹ may be due to the promotion of an electron or the transfer of a hole from E₂g → T₄g transition (Temel et al., 2004). The Zn (II) complex exhibits three absorption bands at 38312 cm⁻¹, 37871 cm⁻¹ and 31442 cm⁻¹ due the ligand-metal (Lever et al., 1984) charge transfer transitions.

Antimicrobial activity

The synthesized Schiff base and its metal (II) complexes were chosen for antibacterial (two gram positive bacteria Staphylococcus aureus and Bascillus substilis, two gram negative bacteria E.Coli and Pseudomonas aeruginosa) and antifungal studies (Candida albicans and Aspergillus niger). The test was carried out in DMSO solution at a concentration of 100 ppm (Al-Ajrawy et al., 2011). All the complexes show

References


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