Synthesis, Physico-chemical and Antimicrobial Studies of Bidentate Schiff Base Complexes of Co(II), Ni(II) and Cu(II)*

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ABSTRACT

Neutral bidentate Schiff base ligand 3, 4-diethyl isoquinoline semicarbazone [DIES] and its complexes of Co(II), Ni(II) and Cu(II) complexes have been prepared. The ligand as well as metal complexes were characterized by analytical and physicochemical methods such as elemental analyses, molar mass, IR, U.V., magnetic susceptibility, molar conductance measurements. On the basis of these studies, it is proposed that DIES acts as neutral bidentate ligand and coordination proposed through azomethine nitrogen and carbonyl oxygen of semicarbazone moiety. On the basis of electronic spectra and magnetic susceptibility measurements, it is proposed that complexes have monomeric octahedral geometry. The ligand as well as metal complexes were also screened for their antimicrobial study.

Key words: Schiff base/ Co(II), Ni(II) and Cu(II)/ Semicarbazone/ Antimicrobial/ Antifungal studies.

EXPERIMENTAL

Preparation of ligand [DIES]
The ligand 3, 4-diethyl isoquinoline semicarbazone [DIES] was prepared by condensing quimolar quantities of 0.01 M of each 3, 4-diethyl isoquinolone (2.59 g) in 20 ml ethanol with aqueous ethanolic solution of semicarbazide hydrochloride (1.2 g). The reaction mixture was refluxed on water bath for 3 h. The solid which separated at the end of the refluxing period, was filtered, dissolved in boiling water and purified (charcol). Neutralisation with sodium carbonate solution gave colourless solid. m.p –221±1°C; yield (60%).
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Preparation of the complexes

The Co(II), Ni(II) and Cu(II) complexes were synthesized by refluxation-precipitation method. The ethanolic solution of the ligand [0.002 M] was mixed with ethanolic solution of corresponding salts (metal halide/ metal nitrate/ 0.001 M) with occasional stirring. The resulting mixture refluxed for 3-4 h on water bath. On cooling, coloured complexes were precipitated out. It was filtered washed with cold ethanol and dried in electric oven. Yield 60-65%.

The percentage of C, H, N metal ions, IR, U.V. spectra were recorded at CDRI, Lucknow. Magnetic susceptibility were measured by Gouy method using Hg[Co(NCS)4] as a calibrant. Molar conductance were recorded on Systronics conductivity meter model 303 in DMF.

RESULTS AND DISCUSSION

The IR spectrum of the ligand DIES shows a broad band of medium intensity at 3460 cm⁻¹ assigned¹⁸,¹⁹ to \( \nu_{\text{N-H}} \). The band without change in intensity indicating non-participation of N atom of either amino or imino group in the coordination with metal ion. The spectrum of the ligand shows a sharp and strong band at 1720 cm⁻¹ assigned²⁰,²¹ to \( \nu_{\text{C=O}} \) group. In the complexes this band suffered a downward shift by 20-30 cm⁻¹ in the complexes indicating the coordination of the carbonyl oxygen to the metal ion.

The spectrum of the ligand shows a strong and broad band at 1480 cm⁻¹ assigned²¹,²² to \( \nu_{\text{C=N}} \). On complexation this band also suffered a downward shift in the spectra of the complexes indicating coordination of the metal ion through azomethine nitrogen atom of semicarbazone moiety.

The coordination through azomethine nitrogen and carbonyl oxygen atom of semicarbazone moiety as well as oxygen atom of NO₃⁻ are further supported by the appearance of bands in the far IR region at 570-540 and 470-420 assigned²³-²⁵ to \( \nu_{\text{M-O}} \) and \( \nu_{\text{M-N}} \). The linkage through metal-halogen is confirmed by the appearance of a band in the region 320-275 cm⁻¹ assigned²³-²⁶ to \( \nu_{\text{M-X}} \) (X = Cl⁻, Br⁻ and I⁻). These assignments are confirmed by the low molar conductance of the complexes.

\[
\text{M(DIES)2 X2}
\]

M = Co(II), Ni(II); X = Cl⁻, Br⁻, I⁻ and NO₃⁻;
M = Cu(II); X = Cl⁻, Br⁻ and NO₃⁻;
R = Ethyl

Fig. 1.
Table 1: Analytical and physicochemical measurements of ligand DIES and its metal complexes

<table>
<thead>
<tr>
<th>Compounds electronic (Colour)</th>
<th>Mol. mass</th>
<th>Yield %</th>
<th>% Analysis found (calculated)</th>
<th>µ_eff</th>
<th>Ω_m</th>
<th>DT</th>
<th>λ_max</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metals C</td>
<td>N</td>
<td>H</td>
<td>B.M.</td>
<td>ohm</td>
<td>°C</td>
<td>cm⁻¹ cm² mol⁻¹</td>
</tr>
<tr>
<td>DIES (Colourless)</td>
<td>259</td>
<td>60</td>
<td>64.74 (64.86)</td>
<td>21.49</td>
<td>7.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co(DIES)₂Cl₂] (Brown)</td>
<td>647.93</td>
<td>62</td>
<td>8.93 (9.09)</td>
<td>52.01 (52.17)</td>
<td>17.28 (17.39)</td>
<td>5.82 (5.90)</td>
<td>4.84 (4.85)</td>
</tr>
<tr>
<td>[Co(DIES)₂Br₂] (Brown)</td>
<td>736.748</td>
<td>64</td>
<td>7.91 (7.99)</td>
<td>45.48 (45.60)</td>
<td>15.11 (15.20)</td>
<td>5.10 (5.15)</td>
<td>4.86 (4.86)</td>
</tr>
<tr>
<td>[Co(DIES)₂I₂] (Brownish red)</td>
<td>830.73</td>
<td>63</td>
<td>6.95 (7.09)</td>
<td>40.31 (40.44)</td>
<td>13.37 (13.48)</td>
<td>4.48 (4.57)</td>
<td>4.89 (4.90)</td>
</tr>
<tr>
<td>[Co(DIES)₂(NO₃)₂] (Brownish red)</td>
<td>700.93</td>
<td>61</td>
<td>8.31 (8.40)</td>
<td>47.84 (47.93)</td>
<td>15.88 (15.97)</td>
<td>5.06 (5.13)</td>
<td>4.99 (4.99)</td>
</tr>
<tr>
<td>[Ni(DIES)₂Cl₂] (Green)</td>
<td>647.71</td>
<td>60</td>
<td>8.96 (9.06)</td>
<td>51.74 (51.87)</td>
<td>17.18 (17.29)</td>
<td>5.80 (5.86)</td>
<td>3.04 (3.06)</td>
</tr>
<tr>
<td>[Ni(DIES)₂Br₂] (Green)</td>
<td>736.528</td>
<td>62</td>
<td>7.90 (7.97)</td>
<td>45.50 (45.61)</td>
<td>15.09 (15.20)</td>
<td>4.79 (4.86)</td>
<td>3.08 (3.08)</td>
</tr>
<tr>
<td>[Ni(DIES)₂I₂] (Green)</td>
<td>830.52</td>
<td>61</td>
<td>6.93 (7.06)</td>
<td>40.33 (40.45)</td>
<td>13.39 (13.48)</td>
<td>5.79 (5.86)</td>
<td>3.1 (3.2)</td>
</tr>
<tr>
<td>[Ni(DIES)₂(NO₃)₂] (Green)</td>
<td>700.71</td>
<td>62</td>
<td>8.29 (8.37)</td>
<td>47.80 (47.95)</td>
<td>15.89 (15.98)</td>
<td>5.09 (5.13)</td>
<td>3.06 (3.06)</td>
</tr>
<tr>
<td>[Cu(DIES)₂Cl₂] (Blue)</td>
<td>652.54</td>
<td>61</td>
<td>9.64 (9.73)</td>
<td>51.33 (51.49)</td>
<td>17.08 (17.16)</td>
<td>5.74 (5.82)</td>
<td>1.88 (1.88)</td>
</tr>
<tr>
<td>[Cu(DIES)₂Br₂] (Blue)</td>
<td>741.348</td>
<td>60</td>
<td>8.48 (8.57)</td>
<td>45.26 (45.38)</td>
<td>15.02 (15.10)</td>
<td>5.04 (5.12)</td>
<td>1.92 (1.92)</td>
</tr>
<tr>
<td>[Cu(DIES)₂(NO₃)₂] (Deep blue)</td>
<td>705.54</td>
<td>60</td>
<td>8.91 (9.00)</td>
<td>47.53 (47.64)</td>
<td>15.78 (15.87)</td>
<td>5.30 (5.38)</td>
<td>1.94 (1.94)</td>
</tr>
</tbody>
</table>

DT = Decomposition Temperature
The significant band at 1520 cm\(^{-1}\) and 1420 cm\(^{-1}\) with a separation of 120 cm\(^{-1}\) indicates monocordinate nature of nitrate group. The electronic spectral and magnetic susceptibility measurements suggest octahedral geometry for the complexes which is justified by other physico-chemical as well as IR spectral data. Conductivity measurement

Molar conductance values of the complexes of Co(II), Ni(II) and Cu(II) were found to be in the range 2.8-6.4 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\). The molar conductance values also supported the structure assigned on the basis of physicochemical and spectroscopic measurements.

Antifungal activity

Fungicidal activity of the ligand DIES and their metal complexes of Co(II), Ni(II) and Cu(II) were done by disc plate method on Pencillium expansum and Aspergillus flavus. On comparison with reference to fungicide, the complexes were found to be more effective than free ligand due to chelation theory.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\nu_{\text{N-H}})</th>
<th>(\nu_{\text{C = O}})</th>
<th>(\nu_{\text{C = N}})</th>
<th>(\nu_{\text{M-O}})</th>
<th>(\nu_{\text{M-N}})</th>
<th>(\nu_{\text{M-X}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIES</td>
<td>3260 s,b</td>
<td>1700 s,b</td>
<td>1480 s,b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co(DIES)(_2)]^+(\text{Cl}^-)</td>
<td>3260 s,b</td>
<td>1675 m,b</td>
<td>1455 m,b</td>
<td>540 m</td>
<td>445 m</td>
<td>300 m</td>
</tr>
<tr>
<td>[Co(DIES)(_2)]^+(\text{Br}^-)</td>
<td>3260 s,b</td>
<td>1675 s,b</td>
<td>1455 m,b</td>
<td>525 m</td>
<td>445 m</td>
<td>320 m</td>
</tr>
<tr>
<td>[Co(DIES)(_2)]^+(\text{I}^-)</td>
<td>3260 s,b</td>
<td>1670 s,b</td>
<td>1450 s,b</td>
<td>520 m</td>
<td>440 m</td>
<td>310 m</td>
</tr>
<tr>
<td>[Co(DIES)(_2)]^+(\text{NO}_3^-)</td>
<td>3260 s,b</td>
<td>1695 s,b</td>
<td>1455 s,b</td>
<td>515 m</td>
<td>445 m</td>
<td></td>
</tr>
<tr>
<td>[Ni(DIES)(_2)]^+(\text{Cl}^-)</td>
<td>3260 s,b</td>
<td>1670 s,b</td>
<td>1450 m,b</td>
<td>540 m</td>
<td>420 m</td>
<td>280 m</td>
</tr>
<tr>
<td>[Ni(DIES)(_2)]^+(\text{Br}^-)</td>
<td>3260 s,b</td>
<td>1670 s,b</td>
<td>1455 m,b</td>
<td>540 m</td>
<td>430 m</td>
<td>275 m</td>
</tr>
<tr>
<td>[Ni(DIES)(_2)]^+(\text{I}^-)</td>
<td>3260 s,b</td>
<td>1675 s,b</td>
<td>1450 m,b</td>
<td>535 m</td>
<td>435 m</td>
<td></td>
</tr>
<tr>
<td>[Ni(DIES)(_2)]^+(\text{NO}_3^-)</td>
<td>3260 s,b</td>
<td>1670 s,b</td>
<td>1455 s,b</td>
<td>520 m</td>
<td>440 m</td>
<td></td>
</tr>
<tr>
<td>[Cu(DIES)(_2)]^+(\text{Cl}^-)</td>
<td>3260 s,b</td>
<td>1670 s,b</td>
<td>1455 m,b</td>
<td>535 m</td>
<td>445 m</td>
<td>280 m</td>
</tr>
<tr>
<td>[Cu(DIES)(_2)]^+(\text{Br}^-)</td>
<td>3260 s,b</td>
<td>1670 s,b</td>
<td>1460 m,b</td>
<td>535 m</td>
<td>440 m</td>
<td>305 m</td>
</tr>
<tr>
<td>[Cu(DIES)(_2)]^+(\text{NO}_3^-)</td>
<td>3260 s,b</td>
<td>1670 s,b</td>
<td>1460 m,b</td>
<td>530 m</td>
<td>470 m</td>
<td></td>
</tr>
</tbody>
</table>

\(m = \text{medium}, \ s = \text{strong}, \ b = \text{broad}\)

Thus on the basis of above studies it is concluded that the ligand DIES acts in a bidentate manner and coordination is proposed through azomethine N and thione S of thiosemicarbazone moiety. The remaining center of metal ions are satisfied by negative ions such as Cl\(^-\), Br\(^-\), I\(^-\) or NO\(_3^-\). On the basis of physicochemical and spectroscopic observations it is proposed that the geometry of the complexes of the type [M(DIES)\(_2\)]\(^2+\)\(X^-\) are monomeric octahedral in geometry as shown in Fig.1.

**CONCLUSION**

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**ACKNOWLEDGEMENTS**

Table 2: IR spectral data of ligand DIES and Co(II), Ni(II) and Cu(II) metal complexes
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