CHAPTER - III

Synthesis of Co(II), Ni(II) and Cu(II) Complexes of Schiff Bases Derived from 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazoles and 8-Formyl-7-Hydroxy-4-Methylcoumarin

Section-A

IR, $^1$H NMR, FAB-Mass and Fluorescence Spectra of Schiff Bases

Section-B

IR, Magnetic, Uv-Vis, ESR, FAB-Mass, CV, Fluorescence and Thermal Studies of Cobalt(II), Nickel(II) and Copper(II) Complexes of 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazole Schiff Bases
INTRODUCTION

Synthesis of 1,2,4-triazole derivatives has attracted widespread attention due to their diverse biological activities. Moreover, 1,2,4-triazoles are a new class of antimicrobial agents. For instance, fluconazole and itraconazole are used as antimicrobial drugs in medicine [19, 20]. Beside these, some biheterocyclic compounds incorporating 1,2,4-triazole moiety have been reported as antimicrobial agents [21-24]. In addition to 1,2,4-triazole derivatives coumarin derivatives display an additional significant biological [25-29] and pharmacological [30, 31] properties. Many of these compounds possess antibacterial [30], antifungal [31] and insecticidal [28] activities and the hydroxycoumarins are the typical phenolic compounds and therefore, act as potent metal chelators and free radical scavengers. They are powerful chain-breaking antioxidants [32]. Metal complexes of 1,2,4-triazole derivatives have been extensively investigated and reported from our laboratory [33-36].

Recently, a number of attempts have been made to obtain Co(II), Ni(II), Cu(II) and Zn(II) complexes with the Schiff bases derived from cinnamaldehyde and 4-amino-3-ethyl-5-mercapto-s-triazole/4-amino-5-mercapto-3-n-propyl-s-triazole [37] and cobalt(II), Nickel(II) and copper(II) complexes with Schiff base derived from furfuraldehyde and 3-substituted-4-amino-5-mercapto-s-triazole have been isolated and characterized by elemental analyses, magnetic, spectral (IR, Uv-Vs, EPR) and thermal studies [38].

The survey of the literature reveals that, no work has been carried out on the synthesis of metal complexes with these Schiff bases. These ligands have donor sites with the ONNO sequence and varied coordination abilities. Because of importance of triazole and coumarin compounds in biological and medicinal fields; it attracted our attention and aroused our interest in elucidating the structure of Co(II), Ni(II) and Cu(II) complexes with these bioactive Schiff bases (Figure-1). The Schiff bases are characterized by spectral, thermal and molar conductivity studies, and these are evaluated for their antibacterial and antifungal properties against various pathogenic bacterial strains using the minimum inhibitory concentration (MIC) method.
Section-A

IR, $^1$H NMR, FAB-Mass and Fluorescence Spectra of Schiff Bases

Results and Discussion

The purity of ligands has been verified by analyzing them for C, H and N contents. The analytical data is listed in Table-1.

Infrared Spectra of Schiff Bases I-IV

The typical infrared spectrum of the Schiff base (II) has been reproduced in Figure-2. The important infrared frequencies along with their assignments are listed in Table-2.

It is well established that, the Schiff bases having O-hydroxy group either on aldehyde or on aniline residue can form intramolecular hydrogen bonding [39, 40]. This has direct impact on the $\nu$(OH) vibration and shifts to the lower frequency with broadening. The extent of shift depends on the strength of hydrogen bonding [41].

In the Schiff bases, the intramolecular H-bonded-OH was observed as a broad weak band with fine structure in the region 2758-2750 cm$^{-1}$ [42]. The medium intensity broad band is observed in the spectra of Schiff bases from

![Figure-1](image.png)

Figure-1

R=H, CH$_3$, C$_2$H$_5$ and C$_3$H$_7$
3130 -3058 cm\(^{-1}\) is attributed to the \(v(\text{NH})\). The medium to high intensity band at 1630-1615 cm\(^{-1}\), is assigned to \(v(\text{C}≡\text{N})\), that confirms the presence of the 8-formyl-7-hydroxy-4-methylcoumarin moiety. Medium intensity bands in the 1600-1590 cm\(^{-1}\) region are regarded as a combination of \(\text{C}=\text{N}\) of the triazole ring and aromatic \(\text{C}≡\text{C}\) stretching vibrations. A high intensity band in the 1295-1279 cm\(^{-1}\) region with an additional band around 1600-1590 cm\(^{-1}\) is assigned to the phenolic \(v(\text{C-O})\) vibration. The band located at 1710-1700 cm\(^{-1}\) in all these Schiff bases attributed to \(v(\text{C}=\text{O})\) [43].

NMR Spectral Studies

The NMR spectra of Schiff bases have been studied by \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR assignments. Spectra of \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR of representative Schiff base (II) have been reproduced in Figures 3 & 4 respectively.

\(^1\text{H}\) NMR Spectrum

The ligands exhibit signals at 13.58 ppm due to NH protons. These protons are D\(_2\)O exchangeable and confirming the assignment. The ligands also exhibit resonance due to phenolic-OH protons around 10.21 ppm. The other characteristic resonance due to azomethine proton in ligands appears at 8.62 ppm. In addition to above all observed signals in the region 6.29-7.880 ppm due to aromatic protons. A signal in the region 2.50 ppm is assigned to methyl protons. All these observations support the infrared conclusions.

\(^{13}\text{C}\) NMR Spectrum

The \(^{13}\text{C}\) NMR spectrum of Schiff base (II) (Figure-4) exhibits the signals at 118.2, 119.5, 121.6, 128.1, 134.8 and 148.5 ppm are corresponding to aromatic carbons. The resonance at 11.6 ppm is due to aliphatic (-CH\(_3\)) carbon and the azomethine (-HC≡N) carbon shows peak at 158.6 ppm.
**FAB-Mass Spectrum**

The FAB-mass spectrum of Schiff base (II) has been depicted in Figure-5. The spectrum showed a molecular ion peak at m/z 500 which is equivalent to its molecular weight \([L+H]^+\).

**Fluorescence Studies**

The emission spectrum of Schiff base (II) was investigated in various solvents viz., DMF, DMSO, MeCN and 1,4-Dioxan.

The Schiff bases (II) were characterized by an emission band around 503, 504, 494.8 and 468 nm in DMSO, DMF, MeCN and Dioxan respectively (Figure-6) is due to the formation of phenoxide anion and cleavage of the imine bond is observed in the Schiff bases. Upon addition of aqueous alkali (2% NaOH) to all the above prepared solutions, we observed the band at 472, 480.4, 464 and 471.4 nm in DMSO, DMF (Figure-7), MeCN and Dioxan solutions respectively. The changes clearly indicate that, proton transferred (H-bonded ion pair) species exist in equilibrium [44] and also we observed the \(\lambda_{\text{max}}\) of the Schiff bases undergoes red shift in DMSO, DMF, and MeCN and blue shift in Dioxan solutions is due to hydrogen bond formation [45].
Table-1. Analytical Data of 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazole Schiff Bases

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Empirical Formula</th>
<th>C% Obsd.</th>
<th>C% Calcd</th>
<th>H% Obsd.</th>
<th>H% Calcd</th>
<th>N% Obsd.</th>
<th>N% Calcd</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C_{24}H_{18}N_{6}O_{6}</td>
<td>59.20</td>
<td>59.25</td>
<td>3.67</td>
<td>3.70</td>
<td>17.21</td>
<td>17.28</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>C_{25}H_{20}N_{6}O_{6}</td>
<td>59.95</td>
<td>60.00</td>
<td>3.96</td>
<td>4.00</td>
<td>16.75</td>
<td>16.80</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>C_{26}H_{22}N_{6}O_{6}</td>
<td>59.97</td>
<td>60.70</td>
<td>4.24</td>
<td>4.28</td>
<td>16.30</td>
<td>16.34</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>C_{27}H_{24}N_{6}O_{6}</td>
<td>61.31</td>
<td>61.36</td>
<td>4.51</td>
<td>4.54</td>
<td>15.87</td>
<td>15.90</td>
<td>72</td>
</tr>
</tbody>
</table>

Table-2. The Important Infrared Frequencies (in cm\(^{-1}\)) of 3-Substituted-4-Amino (8-Formyl-7-Hydroxy-4-Methylcoumarin)-5-Hydrazino-1,2,4-Triazole Schiff Bases.

<table>
<thead>
<tr>
<th>Ligand No.</th>
<th>v (NH)</th>
<th>Lactone v (C=O)</th>
<th>H-bonded -OH Stretching v (C-O)</th>
<th>Phenolic v (C=O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3130 brm 3071 m</td>
<td>1700</td>
<td>1625</td>
<td>2758</td>
</tr>
<tr>
<td>II</td>
<td>3125 brm 3068 m</td>
<td>1707</td>
<td>1630</td>
<td>2750</td>
</tr>
<tr>
<td>III</td>
<td>3115 brm 3058 m</td>
<td>1705</td>
<td>1615</td>
<td>2755</td>
</tr>
<tr>
<td>IV</td>
<td>3120 brm 3065 m</td>
<td>1710</td>
<td>1620</td>
<td>2752</td>
</tr>
</tbody>
</table>
Figure-2. IR Spectrum of Schiff Base (II)

Figure-3. $^1$H NMR Spectrum of Schiff Base (II)
Figure-4. $^{13}$C NMR Spectrum of Schiff Base (II)

Figure-5. FAB-Mass Spectrum of Schiff Base (II)
Figure-6. Emission Spectrum of Schiff Base(II) in DMF (a), DMSO (b), MeCN (c) and Dioxan (d).

Figure-7. (a) Emission Spectrum of Schiff Base in DMF. (b) Emission Spectrum (redshift) of Schiff Base in DMF with 2% NaOH.
Section-B

IR, Uv-Vis, Magnetic, ESR, FAB-Mass, Electrochemical, Fluorescence and Thermal Studies of Cobalt(II), Nickel(II) and Copper(II) Complexes of Schiff Bases I-IV

Nature and Stoichiometry

All the cobalt(II), nickel(II) and copper(II) complexes are colored, stable in air and non-hygroscopic solids. Complexes are sparingly soluble in common organic solvents (EtOH, CHCl₃, acetone, benzene, etc.); however, they are soluble in DMF and DMSO. The elemental analyses show that, the cobalt(II), nickel(II) and copper(II) complexes have 1:1 stoichiometry of the type M.L.2H₂O where L stands for a doubly deprotonated ligand. The molar conductance values are too low to account for any dissociation of the complexes in DMF. Hence, these complexes can be regarded as non-electrolytes in DMF.

To know whether the water molecules were coordinated to the metal ion, a weighed complex was dried over P₂O₅ in vacuum for about an hour and weighed again. There was no loss in the weight of the complex. Then, the same complex was heated for about 2 h at 105°C could indicate no loss in weight of the complex. These observations suggest that, the water molecules present in the complexes are coordinated to the metal ion. The analytical, magnetic and molar conductance data of all the complexes are listed in Table-3.

Infrared Spectra

The important infrared frequencies of the complexes are listed in Table-4. The typical infrared spectra of the complexes are reproduced in Figures 8-10.

All the complexes exhibited a broad medium intensity band at 3010-2990 cm⁻¹, which is ascribed to the v(NH) vibration. A broad weak band with fine structure in the 2758-2750 cm⁻¹ region, assigned to the H-bonded -OH in the Schiff bases is disappeared in the complexes. The high intensity band due
to phenolic C-O appeared in the region 1295-1279 cm$^{-1}$ in the Schiff bases, appeared as a medium to high intensity band in the 1380-1370 cm$^{-1}$ region in the complexes. These observations support the formation of M-O bonds via deprotonation. It mean that H-atoms of –OH groups have been replaced by the metal ion. The bands at 1505-1500 cm$^{-1}$ in the Schiff bases are appeared in the 1520-1515 cm$^{-1}$ region in the complexes this suggests the phenolic oxygen atoms are monodentate. The medium intensity band appeared around 1630-1615 cm$^{-1}$, due to v(C=N) in Schiff bases, showed a lower shift by 10-20 cm$^{-1}$ in these complexes. The low shift indicating that, the (C=N) groups of ligand are coordinated to the metal ion through nitrogen atoms. The band located at 1715-1700 cm$^{-1}$ due to v(C=O) in the Schiff bases are unaffected in the complexes indicating that, the lactone oxygen atoms are not involved in the coordination. All these complexes exhibit a broad through band in the region 3440-3427 cm$^{-1}$ with the additional two weaker bands in the region 800-750 and 720-700 cm$^{-1}$ due to v(-OH) rocking and wagging mode of vibrations, respectively [46] indicates the presence of coordinated water molecule [47].

Thus, the IR spectral data provide strong evidences for the complexation of the potentially tetradentate ligands to the metal ions.

v(M-N)

The v(M-N) vibrations assigned in the region 500-400 cm$^{-1}$ by the previous workers have been shown to be inert to the metal ion [48-50]. The metal sensitive vibrations are reported to occur in the lower region [51, 52]. For nickel(II) and copper(II) glycine complexes, these bands have been located in the region 483-443 cm$^{-1}$. These assignments are based on $^{14}$N-$^{15}$N isotopic studies [51, 52]. For nickel(II) complexes of tetradeinate Schiff bases, the partially isotope sensitive bands at 533 and 448 cm$^{-1}$ have been ascribed to the v(Ni-N), associated with the ligand vibrations [53]. The isotope sensitive bands are reported to appear at 432 and 365 cm$^{-1}$. Recently [54] the v(M-N) bands have been assigned to the region around 380 cm$^{-1}$. Based on these reports, we
have assigned the bands in the 540-460 cm\(^{-1}\) region to the \(v(M-N)\) vibration coupled with new ligand vibrations.

\(v(M-O)\)

Nakamoto, [55] have observed the pure \(v(M-O)\) vibrations in the region 444-405 cm\(^{-1}\) for various metal acetylacetonates and these are metal sensitive. The recent studies on these \(v(M-O)\) vibrations using \(^{18}\text{O}\) isotope have fixed the region 400-200 cm\(^{-1}\) for \(v(M-O)\) [56]. Taking into consideration of these assignments we have assigned the bands in the region 385-375 cm\(^{-1}\) to \(v(M-O)\) vibration in Co(II), Ni(II) and Cu(II) complexes.

**Magnetic Data**

The magnetic moments obtained for these complexes at room temperature are listed in Table-3.

**Cobalt(II) Complexes**

The ground state in octahedral cobalt(II) complexes is \(^{4}\text{T}_{1g}\) and a large orbital contribution to the magnetic moment is expected. The value in excess of 5.00 BM is expected even though the mixing of singlet states lowers the magnetic moment. Several workers have reported the magnetic moment in the range of 4.61 to 5.03 BM for octahedral cobalt(II) complexes [57, 58].

The present cobalt(II) complexes under study show magnetic moments in the range of 4.90 to 4.52 BM, these values are well within the range [59,60] for octahedral complexes. The observed values are higher than spin only value of (3.87 BM) three unpaired electrons, this is because of large orbital contribution in distorted octahedral environment due to the three-fold orbital degeneracy of the \(^{4}\text{T}_{1g}\) ground state.

**Nickel(II) Complexes**

It is reported that, the octahedral nickel(II) complexes exhibit magnetic moments in the range of 2.5 to 3.5 BM [60, 61]. All the nickel(II) complexes show magnetic moment in the range of 3.35 to 3.22 BM. These values are
slightly higher than the spin only value of 2.83 BM. This is because of slight
distortion from Oh to $D_{4h}$ symmetry. Thus leading to orbital contribution to the
spin only values in the $T_{2g}$ state.

**Copper(II) Complexes**

The observed magnetic moments of copper(II) complexes fall in the
range of 1.65 to 1.80 BM, which correspond to one unpaired electron. The
magnetic moment of the regular octahedral copper(II) complexes are expected
to follow the relationship.

$$\mu_{\text{eff}} = \mu_{\text{spin only}} \left(1 - \frac{2\lambda'}{10Dq}\right)$$

Where $\lambda'$ = spin orbital coupling constant.

Then $\mu_{\text{spin only}}$ and $2\lambda'$ values for free copper(II) ion are 1.73 BM and
830 cm$^{-1}$ respectively. The calculated $\mu_{\text{eff}}$ values are in the range of 1.62 to 1.92
BM for the copper(II) complexes. The tetragonally distorted octahedral
copper(II) complexes are normally expected to have lower magnetic moment as
compared to the octahedral ones due to larger separation in interaction terms.

The observed $\mu_{\text{eff}}$ values are in the range of 1.80 to 1.75 BM. Thus, the
copper(II) complexes under investigation may be considered to have
tetragonally distorted octahedral structure with planer arrangement of Schiff
base around copper(II) and two water molecules at an axial positions. This is
further proved by electronic spectral data.
Table-3. Elemental Analysis of Co(II), Ni(II) and Cu(II) Complexes and their Magnetic and Molar Conductance Data of 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazolo Schiff Bases.

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Empirical Formula</th>
<th>M%</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>Molar Conductance Ohm(^{-1}) cm(^2) mole(^{-1})</th>
<th>Mag. Moments ((\mu_{eff}) BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co(C(<em>{24})H(</em>{16})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>10.16</td>
<td>49.72</td>
<td>2.73</td>
<td>14.48</td>
<td>14.51</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>Co(C(<em>{25})H(</em>{18})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>09.91</td>
<td>50.57</td>
<td>3.02</td>
<td>14.15</td>
<td>14.17</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>Co(C(<em>{26})H(</em>{20})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>09.69</td>
<td>51.38</td>
<td>3.27</td>
<td>13.81</td>
<td>13.84</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Co(C(<em>{27})H(</em>{22})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>09.45</td>
<td>52.15</td>
<td>3.53</td>
<td>13.51</td>
<td>13.53</td>
<td>27</td>
</tr>
<tr>
<td>5</td>
<td>Ni(C(<em>{24})H(</em>{16})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>10.11</td>
<td>49.75</td>
<td>2.75</td>
<td>14.50</td>
<td>14.52</td>
<td>23</td>
</tr>
<tr>
<td>6</td>
<td>Ni(C(<em>{25})H(</em>{18})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>09.88</td>
<td>50.61</td>
<td>3.01</td>
<td>14.14</td>
<td>14.17</td>
<td>27</td>
</tr>
<tr>
<td>7</td>
<td>Ni(C(<em>{26})H(</em>{20})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>09.65</td>
<td>51.41</td>
<td>3.27</td>
<td>13.82</td>
<td>13.85</td>
<td>26</td>
</tr>
<tr>
<td>8</td>
<td>Ni(C(<em>{27})H(</em>{22})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>09.42</td>
<td>52.16</td>
<td>3.51</td>
<td>13.50</td>
<td>13.53</td>
<td>23</td>
</tr>
<tr>
<td>9</td>
<td>Cu(C(<em>{24})H(</em>{16})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>10.87</td>
<td>49.33</td>
<td>2.71</td>
<td>14.37</td>
<td>14.39</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>Cu(C(<em>{25})H(</em>{18})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>10.61</td>
<td>50.19</td>
<td>3.00</td>
<td>14.03</td>
<td>14.06</td>
<td>18</td>
</tr>
<tr>
<td>11</td>
<td>Cu(C(<em>{26})H(</em>{20})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>10.37</td>
<td>51.01</td>
<td>3.26</td>
<td>13.71</td>
<td>13.74</td>
<td>26</td>
</tr>
<tr>
<td>12</td>
<td>Cu(C(<em>{27})H(</em>{22})N(<em>{6})O(</em>{6})).2H(_2)O</td>
<td>10.14</td>
<td>51.78</td>
<td>3.50</td>
<td>13.41</td>
<td>13.43</td>
<td>19</td>
</tr>
</tbody>
</table>
Table-4. The Important Infrared Frequencies (in cm⁻¹) of Co(II), Ni(II) and Cu(II) Complexes of 3-Substituted-4-Amino(8-Formyl-7-Hydroxy-4-Methylcoumarin)-5-Hydrazino-1,2,4-Triazole Schiff Bases.

<table>
<thead>
<tr>
<th>Complex No.</th>
<th>v (OH)</th>
<th>v (C=O)</th>
<th>v(C=N)</th>
<th>Phenolic v (C-O)</th>
<th>v(NH)</th>
<th>v (M-N)</th>
<th>v (M-O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3440</td>
<td>1704</td>
<td>1615</td>
<td>1380</td>
<td>3010</td>
<td>535</td>
<td>376</td>
</tr>
<tr>
<td>2</td>
<td>3435</td>
<td>1707</td>
<td>1620</td>
<td>1377</td>
<td>3003</td>
<td>540</td>
<td>378</td>
</tr>
<tr>
<td>3</td>
<td>3430</td>
<td>1700</td>
<td>1605</td>
<td>1372</td>
<td>3006</td>
<td>475</td>
<td>375</td>
</tr>
<tr>
<td>4</td>
<td>3434</td>
<td>1705</td>
<td>1610</td>
<td>1379</td>
<td>2995</td>
<td>480</td>
<td>379</td>
</tr>
<tr>
<td>5</td>
<td>3429</td>
<td>1700</td>
<td>1614</td>
<td>1375</td>
<td>2998</td>
<td>520</td>
<td>380</td>
</tr>
<tr>
<td>6</td>
<td>3431</td>
<td>1707</td>
<td>1624</td>
<td>1374</td>
<td>3001</td>
<td>510</td>
<td>381</td>
</tr>
<tr>
<td>7</td>
<td>3430</td>
<td>1705</td>
<td>1607</td>
<td>1377</td>
<td>3000</td>
<td>495</td>
<td>379</td>
</tr>
<tr>
<td>8</td>
<td>3429</td>
<td>1710</td>
<td>1609</td>
<td>1373</td>
<td>3005</td>
<td>485</td>
<td>384</td>
</tr>
<tr>
<td>9</td>
<td>3427</td>
<td>1712</td>
<td>1613</td>
<td>1371</td>
<td>2995</td>
<td>532</td>
<td>382</td>
</tr>
<tr>
<td>10</td>
<td>3437</td>
<td>1707</td>
<td>1619</td>
<td>1370</td>
<td>2990</td>
<td>515</td>
<td>385</td>
</tr>
<tr>
<td>11</td>
<td>3432</td>
<td>1705</td>
<td>1604</td>
<td>1376</td>
<td>3008</td>
<td>474</td>
<td>381</td>
</tr>
<tr>
<td>12</td>
<td>3438</td>
<td>1704</td>
<td>1602</td>
<td>1372</td>
<td>3007</td>
<td>460</td>
<td>378</td>
</tr>
</tbody>
</table>
Figure-8. IR Spectrum of Co(II) Complex (2)

Figure-9. IR Spectrum of Ni (II) Complex (6)
Electronic Spectra

The observed band maxima for cobalt(II), nickel(II) and copper(II) complexes are listed in Tables 5, 6 & 7. Typical electronic spectra of the complexes are reproduced in Figures 11, 12 & 13 respectively.

In the electronic spectra of transition metal complexes, basically the bands correspond to the following three kinds of electronic transitions

1) Bands due to d-d transitions.

2) Charge transfer bands.

3) Bands due to electronic transfer within the ligand.

In case of d-d transition, the electron is transferred by excitation from one d-orbital to another in the transition $\text{eg} \leftarrow \text{t}_{2g}$. Actually, this transition is forbidden and occurs only as a result of the perturbation effects brought about by the ligands.
In general, electronic spectra of transition metal complexes, disregarding the absorption band of the ligand, reveals that, the charge transfer band is found in the ultraviolet region, while the much less intense band due to d-d transition appears in the visible region. If the energy of charge transfer electronic transition is small, this may shift to visible region and it may obscure the bands due to d-d transition.

**Cobalt(II) Complexes**

The electronic spectra of cobalt(II) complexes exhibit two distinct bands in the region 9636-8950 and 19047-20195 cm\(^{-1}\), which may be assigned to \( ^4T_{1g} (F) \rightarrow ^4T_{2g}(F) \) (\( \nu_1 \)) and \( ^4T_{1g} (F) \rightarrow ^4T_{1g} (P) \) (\( \nu_2 \)) \([62, 63]\). These bands are characteristic of high spin octahedral cobalt(II) complexes. However, \( \nu_2 \) band is not observed because of its proximity to strong \( \nu_3 \) transition. However, the position of \( \nu_2 \) band can be calculated by using the relation \( \nu_2 = \nu_1 + 10 \ Dq \) \([64-65]\) which is very close to the \( \nu_3 \) transition. In some cases, the \( \nu_2 \) and \( \nu_3 \) transitions are predicted to lie almost at the same position, with perhaps \( \nu_2 \) with a few wave numbers higher than the \( \nu_3 \). Lever \([66]\) has suggested that, the shoulder on the principal band in order to be assigned to the \( \nu_2 \) transition in an octahedral cobalt(II) complexes. This must have an energy approximately twice but not greater than 2.2 times that of the \( \nu_1 \) transition \([67]\).

The ligand field parameters \( Dq \) and \( B^1 \) have been calculated by using the following equation \([68]\) derived from secular determinants as follows:

\[
\begin{vmatrix}
-6 \ Dq - E & 4 \ Dq \\
4 \ Dq & 15B^1 - E \\
\end{vmatrix}
= 0
\]

\[
Dq = \frac{\left[ (2\nu_1 - \nu_3) + (\nu_3^2 + \nu_1 \nu_3 - \nu_1^2)^{1/2} \right]}{20}
\]
The ligand field stabilization energy (LFSE) calculated for the relation [69].

\[ \text{LFSE} = \frac{6 \times Dq}{350 \text{ K.Cal/mol}} \]

which is well within the range reported [70-72] for octahedral Co(II) complexes.

These calculated LFSE, Dq, B¹, β, β°% and v₂/ v₁ ratio values for these Co(II) complexes (Table-5) agree well with other reported [73-77] values for octahedral Co(II) complexes.

**Nickel(II) Complexes**

The electronic spectra of these complexes show three bands in the region 9000-27000 cm⁻¹. The spectra of all these complexes are similar to each other suggesting that, all nickel(II) complexes maintain the same coordination number and geometry.

The octahedral nickel(II) complexes display a simple spectra consisting of three transitions viz., \( ^3A_{2g} \rightarrow ^5T_{2g} \), \( ^3A_{2g} \rightarrow ^3T_{1g} (F) \) and \( ^3A_{2g} \rightarrow ^3T_{1g} (P) \). These are reported to occur in the following regions 7000-13000, 11000-20000 and 19000-27000 cm⁻¹ respectively. These bands show shifts to the higher wavelength in the weaker field. In the light of these assignments, the observed bands for these complexes in the region 9812-9785, 15840-15775 and 26355-262207 cm⁻¹. These are assigned [62] to the transitions \( ^3A_{2g}(F) \rightarrow ^3T_{2g}(F) (v₁) \); \( ^3A_{2g}(F) \rightarrow ^3T_{1g}(F) (v₂) \) and \( ^3A_{2g}(F) \rightarrow ^3T_{1g}(P) (v₃) \) respectively, consistent with their well defined octahedral configuration [62, 63].

The values of Dq, B¹ (Racah parameter), B (nephlauxetic ratio), LFSE, \( \mu_{\text{eff}} \) and \( v₂/ v₁ \) were calculated as described in the literature [78]. The \( v₂/ v₁ \) ratio fall in the range of 1.611-1.616 which occurs well within the range expected for octahedral Ni(II) complexes [79]. Since, the configuration interaction between high spin \( T_{1g} (P) \) and \( T_{1g} (F) \) excited states in octahedral symmetry lowers the ratio \( v₂/ v₁ \) from the usual range [80]. This renders the proof for
octahedral symmetry. Further, this is supported by the yellowish green color of
diaquo nickel(II) complexes. The reduction of the Racah parameter from the
free ion value (1056 cm\(^{-1}\)) and the B\(^{\circ}\) values are indicative of the presence of
strong covalent bonds in the complexes.

Calculation of Ligand Field Parameters of Nickel(II) Complexes

For Ni(II) in an octahedral field the energies of the states relative to
the spherical field are given in the following equations.

For \(^3\!T_{2g}\ (F)\) state,  \(E = -2\ Dq\)  \(\text{(1)}\)

For \(^3\!A_{2g}(F)\) state,  \(E = -12\ Dq\)  \(\text{(2)}\)

and for \(^3\!T_{1g}\ (F)\) and \(^3\!T_{1g}(P)\) states

\[6\ Dq\ p - 16 (Dq)^2\] + (-6Dq - p) \(E + E^2 = 0\)  \(\text{(3)}\)

Where P = energy of \(^3\!P\) state.

The quantity P = 15\(\beta\) for nickel (II) ion in the complex [p = 15\(\beta\) for free
Ni(II) ion] where \(\beta\) is a Racah parameter.

The \(\beta\) indicates the magnitude of inter-electronic repulsion between the
various levels in the gaseous ion and it is expressed as the energy difference
between the levels of highest spin multiplicity \(^3\!F\) and \(^3\!P\). The \(\beta\) can be
computed according to the method of Drago [78]. For a ligand which produces
a spin free octahedral Ni(II) complexes the energy difference between \(^3\!A_{2g}\) and
\(^3\!T_{2g}\ (F)\) states is 10Dq i.e., \(v_1 = 10Dq\).

The absorption bands observed (Table-6) for a complex No. 6 is
employed to illustrate the calculation of \(\beta\) and to verify the \(v_2\) band observed.
The absorption bands observed for the complex No.6 corresponding to the
transitions and \(v_1\), \(v_2\) and \(v_3\) are at 9792, 15820 and 26270 cm\(^{-1}\) respectively.
\(v_1 = 10Dq = 979.20\ cm^{-1}\).
\[\cdot.\ Dq = 979.20\ cm^{-1}\]

and \(v_3 = 26270\ cm^{-1}\)

The energy of \(^3\!T_{1g}\ (P)\) state is given as \(E\) (observed transition)=\(E\) \(^3\!T_{1g}(P)\)-\(^3\!A_{2g}\)
\[\cdot.\ E \: ^3\!T_{1g}(P) = E\ \text{obs} - E \: ^3\!A_{2g}\]  \(\text{(4)}\)

but E(obs) = 26270 cm\(^{-1}\) and \(^3\!A_{2g} = -12\ Dq\) from equation  \(\text{(2)}\)
By substituting $E$ observed and $Dq$ in equation (4)

$$E^{3T_{1g}}(P) = 26270 - 12 \times 979.20$$

$$= 14519.6 \text{ cm}^{-1}$$

:. $E = 14519.6 \text{ cm}^{-1}$

By substituting the values of $Dq$ and $E$ (calcd) in equation (3) the value of $P$ is obtained as:

$$\left[\frac{6 \times (979.20)P - 16 \times (979.20)^2}{-6 \times (979.20) - P} \right] 14519.6 + (14519.6)^2 = 0$$

i.e.,

$$P = 12744.59 \text{ cm}^{-1}$$

But $P = 15 \beta = \beta = 12744.59 \text{ cm}^{-1}$

:. $\beta = 12744.59 / 15 = 849.6 \text{ cm}^{-1}$

To calculate the energies for the $3^{3}T_{1g}$ (F) and $3^{3}T_{1g}$ (P) states $P$ and $Dq$ values must be substituted in the equation (3) and it is solved for $E$ values. Thus, the energy of $3^{3}T_{1g}$ (F) i.e., $\nu_2$ band is calculated as

$$\left[\frac{6 \times (978.0) \times 12748.78 - 16 \times (978.0)^2}{-6 \times (978.0) - 12748.78} \times E + E^2 = 0\right]$$

:. $E = 4099.96 \text{ cm}^{-1}$ for $3^{3}T_{1g}$ (F) state

Hence $\nu_2$ (calcd) = $4099.96 - (-12Dq)$

$$= 4099.96 + 11750.4$$

$$= 15850 \text{ cm}^{-1}$$

The observed $\nu_2$ band in the spectrum of the complex is at 15820 cm$^{-1}$.

The agreement of these two values has been proposed as confirmatory evidence for the existence of an octahedral complex. But, the experimentally observed values are mostly lower than the calculated values. The deviation may be attributed to the covalence in the bonding. The effect of covalence is to delocalize the metal ion electron density onto the ligand and thus to reduce electron-electron repulsions of the d-electrons in the complexed metal ion compared to the repulsions in the gaseous state. This reduces the energy difference between $3p$ & $3F$ states in the complex relative to that of gaseous ion. The lowering of $3P$ state is expressed as percentage lowering of energy $\beta^o$ in the complex i.e. calculated from the equation as
Lowering of 3P state or % distortion

\[ \% \text{ Distortion} = \frac{v_2(\text{Calcd.}) - v_2(\text{Obsd.})}{v_2(\text{Calcd.})} \times 100 \]

\[ 15850 - 15820 \]

\[ = \frac{15850}{15850} \times 100 \]

\[ = 0.189 \% \]

In most of the cases \( \beta \) (measure of covalence character in bonding) is used instead of \( \beta^0 \)

\[ \beta = \frac{B'}{B} \]

it is also termed as nephelauxetic ratio.

The \( \beta \) for the above complex = \( \frac{847.6}{1056} \times 0.805 \)

When all the d-d transitions are observed in the spectrum of the complex the calculation of \( D_q \) and \( B' \) can be done by using secular - equation (diagonal sum rule).

\[ B' = \frac{v_2 + v_3 - 3 v_1}{15} \]

Hence the value of \( B' \) of the above complex is

\[ 15820 + 26270 - 3 \times 9792 \]

\[ B' = \frac{15820 + 26270 - 3 \times 9792}{15} \]

\[ = 847.65 \text{ cm}^{-1} \]

This is in close agreement with the value computed from Drago's method. This treatment can be verified as a numerical fit for experimental data and it is an interesting check on the accuracy of the method.

The values of Racah parameter, \( B' \) listed in Table-6, which lies in the range of 843.82 - 857.37 cm\(^{-1}\). These values are less than the free ion value (1056 cm\(^{-1}\)), suggesting the considerable orbital overlap and delocalization of electron in the metal ion. There is a reduction to about 71-94\% of the free ion
value upon incorporation of metal ion into the complex formation that shows the extent of covalent character in the metal-ligand bond.

The $v_2/v_1$ ratio for the octahedral Ni(II) complexes showed around 1.8; whereas, for tetrahedral complexes these are nearly 2.2. For the present Ni(II) complexes this ratio lies in the range of 1.616 to 1.611. This is very close to the rejected one. The interaction between and $^3T_{1g}(P)$ and $^3T_{1g}(F)$ states gradually lowers the $v_2/v_1$ ratio from the theoretical values of 1.8 to 1.5-1.7 and values in the range of 1.602 to 1.621 are common in the pseudo-octahedral structure.

The ligand field stabilization energies (LFSE) have been calculated for all the Ni(II) complexes. These lie in the range of 33.64 to 33.54 K. Cal/mole and agree well with the reported values. In an attempt to seek correlation between the electronic spectral and magnetic properties, the $\mu_{\text{eff}}$ calculated by using the relation suggested by Figgis. The calculated values are in good agreement with the experimental values.

**Copper(II) Complexes**

The copper(II) ion (3d$^9$) in the complexes can have either tetrahedral or a distorted octahedral environment. The cubic octahedrally coordinated copper(II) ion has the ground state $^2E_g$ and the excited state is $^2T_{2g}$. The $^2E_g$ ground state is highly susceptible to a Jahn-Teller distortion and then no regular octahedral Cu(II) complexes should exist. The doubly degenerate ground state $^2E_g$ splits into two other components. Thus, three principle bands are expected due to the transitions $^2B_{1g} \rightarrow ^2A_{1g}, ^2B_{2g}$ and $^2E_g$ in the order of increasing energy for Cu(II) ion in tetragonal environment. These three bands can be located in the region 10000 to 14000 cm$^{-1}$ [81]. Campbell et al [82] have assigned these bands in the region 13000 to 19000 cm$^{-1}$ for tetragonally distorted octahedral Cu(II) complexes. Eilbeck et al [83], have contributed to the literature that, the octahedral Cu(II) complex show d-d transition at 14390 cm$^{-1}$. Many workers [84-86] have reported the d-d transitions in the region 13000-16000 cm$^{-1}$ for distorted octahedral Cu(II) complexes. Waters et al; [87] have reported the
green color Cu(II) complexes exhibit absorption band in the vicinity of 14300 cm\(^{-1}\) is an indication of five or six coordinated Cu(II). Similarly, Duff et al; [88] have assigned the absorption band in the region 13000-14000 cm\(^{-1}\) for tetragonally distorted octahedral Cu(II) complexes.

The recent studies [89-94] show that, the absorption spectra of octahedral Cu(II) complexes exhibit three transitions, viz., \(^2B_{1g} \rightarrow ^2A_{1g}(v_1)\), \(^2B_{2g}(v_2)\), and \(^2E_g(v_3)\), are of similar energy and often give rise to a single broad absorption band. Because of low intensity of \(^2B_{1g} \rightarrow ^2B_{2g}(v_2)\) which is usually not observed as spectral band in tetragonal Cu(II) complexes [95]. Hence, the main broad band is assigned to \(v_3\) as the \(v_2\) merges with the \(v_3\) (~ 10 Dq). These observations suggest that, the present copper(II) complexes are tetragonally distorted octahedral species. The copper(II) complexes under investigation exhibit a single broad absorption band in the region 14540-14780 cm\(^{-1}\) in the visible region assigned to \(^2E_g \rightarrow ^2T_{2g}\). The broadness of the band due to Jahn-Teller effect, which is characteristic of distorted octahedral environment. This data suggests that, no gross deviation in stereochemistry of these complexes occurs in solid and solution phases. The \(B^1\) and \(\beta\) values could not be determined as there is no interelectronic repulsion in a d\(^9\) system.
Table 5. Ligand Field Parameters of Co(II) Complexes of 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazole Schiff Bases

<table>
<thead>
<tr>
<th>Complex No.</th>
<th>$v_1$ (cm$^{-1}$)</th>
<th>$v_2$ (Calcd.) (cm$^{-1}$)</th>
<th>$v_3$ (cm$^{-1}$)</th>
<th>$Dq$ (cm$^{-1}$)</th>
<th>$B^1$ (cm$^{-1}$)</th>
<th>$v_2/v_1$</th>
<th>LFSE</th>
<th>$\beta$</th>
<th>$\beta^\circ$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9636</td>
<td>19986</td>
<td>20195</td>
<td>1071.01</td>
<td>794.64</td>
<td>2.125</td>
<td>19.45</td>
<td>0.818</td>
<td>24.02</td>
</tr>
<tr>
<td>2</td>
<td>9452</td>
<td>19780</td>
<td>19965</td>
<td>1061.89</td>
<td>779.45</td>
<td>2.127</td>
<td>20.30</td>
<td>0.796</td>
<td>23.81</td>
</tr>
<tr>
<td>3</td>
<td>8950</td>
<td>18929</td>
<td>19047</td>
<td>997.94</td>
<td>751.76</td>
<td>2.125</td>
<td>23.29</td>
<td>0.784</td>
<td>22.76</td>
</tr>
<tr>
<td>4</td>
<td>9250</td>
<td>19657</td>
<td>19685</td>
<td>1040.77</td>
<td>772.85</td>
<td>2.125</td>
<td>20.17</td>
<td>0.799</td>
<td>23.78</td>
</tr>
</tbody>
</table>

Table 6. Ligand Field Parameters of Ni(II) Complexes of 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazole Schiff Bases

<table>
<thead>
<tr>
<th>Complex No.</th>
<th>Transitions (cm$^{-1}$)</th>
<th>$v_2$ Calcd. (cm$^{-1}$)</th>
<th>$Dq$ (cm$^{-1}$)</th>
<th>$B^1$ (cm$^{-1}$)</th>
<th>Distortion</th>
<th>$v_2/v_1$</th>
<th>LFSE</th>
<th>$\mu_{\text{eff}}$</th>
<th>BM</th>
<th>Calcd.</th>
<th>$\beta$</th>
<th>$\beta^\circ$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>9785</td>
<td>15775</td>
<td>26355</td>
<td>15860</td>
<td>978.50</td>
<td>857.37</td>
<td>0.540</td>
<td>1.612</td>
<td>33.54</td>
<td>3.194</td>
<td>0.812</td>
<td>18.80</td>
</tr>
<tr>
<td>6</td>
<td>9792</td>
<td>15820</td>
<td>26270</td>
<td>15850</td>
<td>979.20</td>
<td>847.65</td>
<td>0.189</td>
<td>1.616</td>
<td>33.57</td>
<td>3.194</td>
<td>0.805</td>
<td>19.54</td>
</tr>
<tr>
<td>7</td>
<td>9812</td>
<td>15840</td>
<td>26245</td>
<td>15866</td>
<td>981.20</td>
<td>845.06</td>
<td>0.170</td>
<td>1.614</td>
<td>33.64</td>
<td>3.193</td>
<td>0.800</td>
<td>19.97</td>
</tr>
<tr>
<td>8</td>
<td>9806</td>
<td>15795</td>
<td>26220</td>
<td>15855</td>
<td>980.60</td>
<td>843.82</td>
<td>0.381</td>
<td>1.611</td>
<td>33.62</td>
<td>3.194</td>
<td>0.799</td>
<td>20.02</td>
</tr>
</tbody>
</table>
Table 7. Electronic Transitions of Cu(II) Complexes of 3-Substituted-4-Amino-5-Hydrazino-1,2,4-Triazole Schiff Bases

<table>
<thead>
<tr>
<th>Complex No.</th>
<th>Electronic Transitions (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>14540 14656 14624 14780</td>
</tr>
<tr>
<td>10</td>
<td>14656 14624 14780</td>
</tr>
<tr>
<td>11</td>
<td>14624 14780</td>
</tr>
<tr>
<td>12</td>
<td>14780</td>
</tr>
</tbody>
</table>
Figure-11. Electronic Spectrum of Co(II) Complex (2)

Figure-12. Electronic Spectrum of Ni(II) Complex (6)

Figure-13. Electronic Spectrum of Cu(II) Complex (10)
**ESR Spectra**

The ESR spectral studies are useful method to determine the arrangement of metal ions in the structure of the metal complexes and to determine the ground state of electrons in metal ions. The fundamental principles of ESR are same as those of NMR. In ESR a transition between two different electron spin energy states occurs upon absorption of quantum radiation in the microwave region. The energy of the transition is given by the relation, $\Delta E = h \nu = g\beta H$.

Where $h = $ Plank's constant

$\nu = $ Frequency of radiation

$g = $ Spectroscopic splitting factor

$\beta = $ Bohr magneton

$H = $ Magnetic field

The ESR spectra of a few copper (II) complexes in polycrystalline state were recorded at LNT using Varian E-4 x-band ESR spectrometer with cylindrical quartz sample tube operating at microwave frequency ~9.1GHz with corresponding field intensity ~3000 Gauss. Field calibration was checked using tetracyanoethylene (TCNE) free radical for which $g=2.00277$.

The value of ‘$g$’ in any arbitrary direction can be expressed as the resultant of the tensor component $g_X, g_Y$ and $g_Z$ corresponding to the direction of the X, Y and Z-axis. The average value ($g_{av}$) is given by the relation.

$$g_{av} = \frac{1}{3} (g_x^2 + g_y^2 + g_z^2)$$

The $g_{\parallel}$ and $g_{\perp}$ values are observed in the case of copper(II) complexes under study.

The $g_{\parallel}$ and $g_{\perp}$ values are compared with resonance position of tetracyano ethylene (TCNE) radical. The $g_{\parallel}$ and $g_{\perp}$ values are calculated by the following relations.

$g_{\parallel}$ or $g_{\perp} = g_{TCNE} \times H_{TCNE}/H$

$g_{av} = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$

$G = (g_{\parallel}-2)/(g_{\perp}-2)$

**CHAPTER-III**

70
The ESR spectrum of copper (II) complex (10) was recorded at LNT. The spectrum has been depicted in Figure-14 and it displays the following features.

The $g_\parallel$ and $g_\perp$ values have been found to be 2.0404 and 2.15887 respectively. The $g_{av}$ was calculated to be 2.1194. The Cu(II) complex shows reversed axial (compressed octahedral) with $g_\parallel < g_\perp$. The trend $g_\parallel < g_\perp$ showed that, the electron is delocalised in $d_z^2$ orbital of the ground state of Cu(II). In this case, ($g_\parallel < g_\perp$) distortion occur by compression [96]. The parameter $G$, determined as $G = (g_\parallel-2)/(g_\perp-2)$ is found to be much less than 4 suggesting the considerable interaction in the solid state [97].

**Thermal Studies**

Thermograms obtained for one representative cobolt(II) (2), Ni(II) (6) and copper(II) (10) complexes at room temperature have been reproduced in Figures 15, 16 & 17. The percentage weight loss, nature of decomposed chemical change with the temperature range and percentage of metal oxide obtained is given in the Table-8.

These complexes decompose gradually with the formation of respective metal oxide above 500°C. The thermal decomposition of one respective Co(II) (2), Ni(II) (6) and Cu(II) (10) complexes takes place in three steps as indicated by DTG peaks around 105-135, 330-365 and 440-480°C of Co(II) and Ni(II) and around 220-230, 300-330 and 455-473°C of Cu(II) complexes corresponding to the mass loss of two coordinated water molecules, one triazole moiety and two coumarin moieties respectively.

**Kinetic Studies**

The Freeman and Carroll procedure [98] was used to evaluate the kinetic parameters (Table-9) such as order of reaction and energy of activation from a single experimental curve (Figure-18) from the plot of

$$\Delta \log \frac{dw/dt}{\Delta \log Wr} \text{ versus } \frac{\Delta T}{\Delta \log Wr} \times 10^3 K^{-1}.$$ 

The Freeman and Corrol procedure and A log Wr AiogWr equations have been deployed to evaluate the order of reaction and energy of
activation from a single experimental curve. Consider the reaction in the liquid or solid state where one of the products "B" is volatile, all the other substances being in the condensed state.

\[ aA = bB (g) + cC \]

The rate expression for the disappearance of reactant 'A' from the mixture is

\[ \frac{-dx}{dt} = kX^x \quad \cdots \quad (1) \]

Where, \( X \) = concentration, mole fraction or amount of reactant "A".

\( k \) = specific rate

\( x \) = order of reaction with respect to 'A'

It is assumed that, the specific rate may be expressed as

\[ k = Ze^{-E*/RT} \quad \cdots \quad (2) \]

Solving for \( k \) in (1) and substituting (2) for \( k \), gives

\[ Ze^{-E*/RT} = \frac{-(dx / dt)}{x^x} \quad \cdots \quad (3) \]

Where \( Z \) = frequency factor

\( E^* \) = energy of activation

\( R \) = gas constant

\( T \) = absolute temperature

The logarithmic form of equation (3) is differentiated with respect to, \( dX/dt \), \( x \) and \( T \), resulting in equation (4)

\[ \frac{E^*}{RT^2} \frac{dt}{dt} = d \ln (-dX/dt) = -x \frac{d \ln X}{d \ln X} \quad \cdots \quad (4) \]

Integrating the above reaction,

\[ \frac{-E^*}{R} \frac{\Delta (1/T)}{dt} = \Delta \ln \left( \frac{-dX}{dt} \right) - x \Delta \ln X \quad \cdots \quad (5) \]

Dividing (4) and (5) by \( d \ln X \) and \( \Delta \ln X \), respectively, one obtains equations (6) and (7).

\[ \frac{E^*dT}{RT^2d \ln X} = \frac{d \ln(-dX/dt)}{d \ln X} - x \quad \cdots \quad (6) \]

\[ \frac{E^*}{\Delta (1/T)} \frac{d \ln(-dX/dt)}{d \ln X} \]

CHAPTER-III 72
\[
\frac{R}{\Delta \ln X} = -x \quad \ldots \ldots \ldots (7)
\]

From the equation (6) and (7) it is apparent that, the plots of
\[
\frac{dT}{d \log(-\frac{dX}{dt})} \quad \text{VS} \quad \frac{T^2 \log X}{d \log X}
\]
and
\[
\frac{\Delta (1/T)}{\Delta \log(-\frac{dX}{dt})} \quad \text{VS} \quad \frac{T^2 \log X}{\Delta \log X}
\]
Should result in straight lines with slopes of \( \pm \frac{E^*}{2.3R} \) and intercepts of \(-x\).

Let us consider the cases where \( X \) refers to the amount of reactant \( X = na \)
where, ‘na’ is number of moles of the reactant at time \( t \).

\[
\ln K = -x \ln na + \ln(-\frac{dn_a}{dt}) \quad \ldots \ldots \ldots (8)
\]
and
\[
\frac{- (E^*/R) \Delta (1/T)}{\Delta \ln(-\frac{dn_a}{dt})} = -x + \ldots \ldots \ldots \ldots (9)
\]

The following relationship may be used to correlate the number of moles
of reactant to weight.

\[
\frac{-dn_a}{dt} = \frac{no}{wc} \cdot \frac{dw}{dt} \quad \ldots \ldots \ldots (10)
\]
and
\[
W_r = wc - w \quad \ldots \ldots \ldots (11)
\]
where

\( no \) = initial number of moles of A
\( wc \) = weight loss at completion of reaction
\( w \) = total weight loss upto time \( t \)

Combining equations (10 and 11) with (9)

\[
\frac{-E^*}{2.3R} \frac{\Delta (1/T)}{\Delta \log dw/dt} = -x + \frac{\Delta \log W_r}{\Delta \log W_r} \quad \ldots \ldots \ldots (12)
\]

The plot of
The dw and Wr for the purpose of plot can be directly determined from the thermograms.

The determined order of reaction and energy of activation are listed in the Table-9.

**FAB-Mass**

The FAB mass spectrum of Ni(II) complex (6) showed a molecular ion peak $M^+$ at $m/z$ 593, which is equivalent to its molecular weight of the Ni(II) complex (6) shown in Figure-19. The molecular ion peak fragmentation with the loss of two water molecules, gave a peak $A_1$ at $m/z$ 557 due to the fragment ion $[\text{Ni}(\text{C}_{25}\text{H}_{18}\text{N}_6\text{O}_6)]^+$. Further, the fragment ion $A_1$ by the loss of $\text{C}_{11}\text{H}_7\text{O}_3$ species gave a fragment ion $A_2$, at $m/z$ 370. The fragment ion $A_2$ gave a fragment ion $A_3$, at $m/z$ 183 by the elimination of another $\text{C}_{11}\text{H}_7\text{O}_3$. All these fragments leading to the formation of the species $[\text{Ni}(\text{L})]^+$ which undergoes demetallation to form the species $[\text{L}+\text{H}]^+$ gave a fragment ion at $m/z$ 498. All these fragmentation patterns are well observed in the FAB mass spectrum.
CHAPTER-III

Figure-14. ESR Spectrum of Cu(II) Complex (10)

Figure-15. Thermogravimetric (TG/DTG) Curves of Co(II) Complex (2)
Figure-16. Thermogravimetric (TG/DTG) Curves of Ni(II) Complex (6)

Figure-17. Thermogravimetric (TG/DTG) Curves of Cu(II) Complex (10)
Figure-18. Kinetics of Thermal Decomposition Study of Co(II), Ni(II) and Cu(II) Complexes

Figure-19. FAB-Mass Spectrum of Ni(II) Complex (6) of Schiff Base (II)
Table-8. Thermogravimetric Data of Co(II) (2), Ni(II) (6) and Cu(II) (10) Complexes of 3-Substituted-4-Amino(8-Formyl-7-Hydroxy-4-Methylcoumarin)-5-Hydrazino-1,2,4-Triazole Schiff Base(II)

<table>
<thead>
<tr>
<th>Empirical Formula</th>
<th>Decomposition temperature °C</th>
<th>% Weight loss Obsd.</th>
<th>% Weight loss Calcd.</th>
<th>Metal Oxide % Obsd.</th>
<th>Metal Oxide % Calcd.</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co($C_{25}H_{18}N_{6}O_{6}$).2H$_2$O</td>
<td>105-135</td>
<td>6.05</td>
<td>6.07</td>
<td>12.62</td>
<td>12.64</td>
<td>Loss of coordinated water molecules</td>
</tr>
<tr>
<td></td>
<td>330-365</td>
<td>20.90</td>
<td>20.91</td>
<td></td>
<td></td>
<td>Loss of triazole moiety</td>
</tr>
<tr>
<td></td>
<td>440-480</td>
<td>63.05</td>
<td>63.08</td>
<td></td>
<td></td>
<td>Loss of coumarin moieties</td>
</tr>
<tr>
<td>Ni($C_{25}H_{18}N_{6}O_{6}$).2H$_2$O</td>
<td>110-140</td>
<td>6.04</td>
<td>6.07</td>
<td>12.57</td>
<td>12.60</td>
<td>Loss of coordinated water molecules</td>
</tr>
<tr>
<td></td>
<td>325-355</td>
<td>20.89</td>
<td>20.92</td>
<td></td>
<td></td>
<td>Loss of triazole moiety</td>
</tr>
<tr>
<td></td>
<td>435-472</td>
<td>63.09</td>
<td>63.10</td>
<td></td>
<td></td>
<td>Loss of coumarin moieties</td>
</tr>
<tr>
<td>Cu($C_{25}H_{18}N_{6}O_{6}$).2H$_2$O</td>
<td>220-230</td>
<td>6.00</td>
<td>6.02</td>
<td>13.30</td>
<td>13.31</td>
<td>Loss of coordinated water molecules</td>
</tr>
<tr>
<td></td>
<td>300-330</td>
<td>20.73</td>
<td>20.75</td>
<td></td>
<td></td>
<td>Loss of triazole moiety</td>
</tr>
<tr>
<td></td>
<td>455-473</td>
<td>62.57</td>
<td>62.59</td>
<td></td>
<td></td>
<td>Loss of coumarin moieties</td>
</tr>
</tbody>
</table>
### Table 9. Kinetics of Thermal Decomposition Data of Co(II), Ni(II) and Cu(II) Complexes

<table>
<thead>
<tr>
<th>Complex No.</th>
<th>Empirical Formula</th>
<th>$\frac{\Delta \text{log} dw/dt}{\Delta \text{log} wr}$</th>
<th>$\frac{\Delta T}{\Delta \text{log} Wr} \times 10^3 \text{ K}^{-1}$</th>
<th>Order of reaction</th>
<th>Energy of Activation $E_a$ (Kcal mol$^{-1}$)</th>
</tr>
</thead>
</table>
| 2           | Co(C$_{25}$H$_{18}$N$_6$O$_6$).2H$_2$O | -4.413  
-2.98  
-0.801  
0.320  
0.601 | 2.331  
1.839  
1.091  
0.702  
0.632 | 0.82  | 13.46 |
| 6           | Ni(C$_{25}$H$_{18}$N$_6$O$_6$).2H$_2$O | -2.15  
-1.53  
-0.902  
0.860  
1.58 | 2.086  
1.859  
1.571  
0.827  
0.498 | 1.18  | 10.76 |
| 10          | Cu(C$_{25}$H$_{18}$N$_6$O$_6$).2H$_2$O | -2.504  
-1.330  
-0.34  
1.230  
0.320 | 1.516  
1.291  
1.087  
0.761  
0.955 | 1.01  | 22.77 |
Cyclic Voltammetry

Electrochemical properties of the complexes were studied on a CHI1110A-Electrochemical analyzer in N,N-dimethyl formamide (DMF) containing 0.05 M n-Bu₄NC104 as the supporting electrolyte. A cyclic voltammogram of Cu(II) (10) (Figure-20) radical displays a reduction peak at $E_{pc} = 0.1792\text{V}$ and again it reduced to Cu(I) displays a reduction peak at $E_{pc} = -0.3248\text{V}$ respectively, with a corresponding oxidation peak (Cu(I) radical) at $E_{pa} = -0.2254\text{V}$ and $E_{pa} = 0.5451\text{V}$ for Cu(II) respectively. The peak separation ($\Delta E_p$) of this couple is 0.33V and 0.191V respectively at scan rate 0.05V and increases with scan rate. The most significant feature of the Cu(II) complex is the Cu(II)/Cu(I) couple. The difference between forward and backward peak potentials can provide a rough evaluation of the degree of the reversibility of one electron transfer reaction. The analyses of cyclic voltammetric responses with the scan rate varying 50 to 250 mV/s gives the evidence for quasi-reversible one electron oxidation state. The ratio of cathodic to anodic peak height was less than one. However, the peak current increases with the increase of the square root of the scan rates. This establishes the electrode process as diffusion controlled [99].

The separation in peak potentials increases at higher scan rates. These characteristic features are consistent with the quasi-reversibility of Cu(II)/Cu(I) couple.

The Co(II) (2) complex (Figure-21) exhibits a reduction peak at $E_{pc} = 0.1592\text{V}$ with a direct re-oxidation peak at $E_{pa} = 0.5704\text{V}$ corresponding to the formation of Co(II)/Co(I) couple. The peak separation of this couple ($\Delta E_p$) is 0.41V. The Ni(II) (6) complex exhibits a reduction peak at $E_{pc} = -0.7895\text{V}$ with a direct re-oxidation peak at $E_{pa} = -0.6507\text{V}$ corresponding to the formation of Ni(II)/Ni(I) couple. This Co(II) and Ni(II) complex also have a quasi-reversible character as the separation in peak potential are higher than 59 mV and the peak
currents rise with increasing $v^{1/2}$. The difference between forward and backward peak potentials can provide a rough evaluation of the degree of the reversibility.

**Fluorescence Studies**

Emission spectra of Co(II) (2), Ni(II) (6) and Cu(II) (10) complexes were investigated in various solvents such as DMF, DMSO, MeCN and Dioxan.

The emission spectra of the Cu(II) in DMSO and Co(II), Ni(II) and Cu(II) complexes of Dioxan solution is reproduced in Figures 22 & 23 respectively. In case of DMF solution the Co(II), Ni(II) and Cu(II) complexes were characterized by the emission band around 470.8, 487.6 and 440.2 nm respectively. It is observed that, the emission band of Schiff bases around 504.0 nm disappeared because of the interaction of the phenolic oxygen with the metal ion. There was decrease in intensity of fluorescence of Co(II), Ni(II) and Cu(II) complexes in all prepared solutions. In all other previous studies, it has been reported that, transition metal ions decrease the fluorescence quite effectively [100, 101]. Magnetic perturbation, redox activity, etc., has been invoked [101] in the past to rationalize fluorescence quenching by transition metal ions. But, in case of Ni(II) complexes, we could observed the enhancement of fluorescence in MeCN solution.
Figure-20. Cyclicvoltammogram of Cu(II) (10) complex

Figure-21. Cyclicvoltammogram of Co(II) (2) complex
Figure-22. (a) Emission Spectrum of Schiff Base in DMSO. (b) Emission Spectrum of Cu(II) complex in DMSO.

Figure-23. Emission Spectra of Cu(II) (a), Co(II) (b) and Ni(II) (c) Complexes in Dioxan.
Conclusion

Analytical, magnetic, spectral and thermal data taken together suggest the following structure for Co(II), Ni(II) and Cu(II) complexes.

M= Co(II), Ni(II) and Cu(II)
R=H, CH₃, C₂H₅ and C₃H₇